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FACULTAD DE QUIMICA

Estudio Técnico y Económico para la Producción de Alcohol Polivinílico en México

TESIS
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A mi Padre con el recuerdo del
filial cariño y agradecimiento
que vivirá en mi eternamente.

A mi Madre con
todo mi cariño.

Un sincero agradecimiento a mi
hermano Ernesto por su gran
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A mis hermanos todos
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Introducción

El alcohol polivinílico pertenece a la rama petroquímica, conocida bajo el nombre de Resinas Sintéticas, que es la rama de la industria petroquímica que muestra después de las fibras artificiales y sintéticas, un mayor dinamismo.

Las resinas sintéticas constituyen propiamente la materia prima para la industria manufacturera de artículos de plástico, así como para pinturas y adhesivos la gran variedad de tipos de resinas sintéticas, así como sus propiedades físicas y químicas permita un amplio campo de aplicaciones.

Las aplicaciones se llevan a cabo en la gran variedad de formas: película, lámina, tubo flexible y rígido, perfiles y en la multitud de formas obtenidas en el moldeado por inyección, por extrusión por soplado y rotacional, etc. Sus aplicaciones han ido en aumento, pues sus propiedades han permitido sustituir a materiales tradicionales como: papel, metales, vidrio, telas, madera y cuero, para citar las principales.

Prácticamente todas las resinas sintéticas tienen origen petroquímico. Aunque existen varias maneras de clasificar las resinas, en este estudio se han hecho por tipos y de éstos se consideran dos grupos poliolefinas, cuya elaboración está reservada a Petróleos Mexicanos y las demás resinas, cuya elaboración pertenece al sector secundario.

Existen otros tipos de resinas, cuyo origen no es petroquímico: breas esterificadas y los resinatos de sodio, calcio y zinc.

Clasificación de las Resinas Sintéticas por tipos.

Poliolefinas

Poliétileno de baja densidad (alta presión)

Polietileno de alta densidad (baja presión)

Polipropileno.

Las demás

- Acrílicas
- Alcídicas
- Alcohol polivinílico
- SAN
- ABS
- Celulósicas
- Epoxícas
- Fenólicas
- Fumáricas
- Intercambiadoras de Iones
- Maléicas
- Melamina - Formaldehído
- Poli (Acetato de vinilo)
- Poli acrilamida
- Poli (Cloruro de vinilo)
- Poliamidas
- Poliester
- Poliestireno
- Poliformaldehido
- Poliuretanos
- Polivinil butiral
- Polivinil formal

Urea fenol forfurílico

Urea formaldehido

La producción de resinas sintéticas se inició en nuestra país en 1947, con la elaboración de resinas fenólicas por la empresa Bakelita de México,- S.A. Cuatro años más tarde en 1951 se inició la producción de poliestireno. Para 1960 ya se elaboraban nuevos tipos de resinas. En 1971 se elaboraron - ventiún de los veintiocho tipos de resinas consideradas en este estudio. Queda aún sin fabricarse entre otras el alcohol polivinílico y las resinas polivinil butiral.

La inversión del Sector Industrial en la rama de Resinas sintéticas y artificiales ascendió en 1975 a 8,0602 millones con respecto a 1974, que - equivale a un crecimiento de 34.2%. De continuar presentándose las tendencias tradicionales de crecimiento de mercado, se estima un incremento anual promedio del orden del 15% en las inversiones de esta industria, para poder satisfacer tanto el mercado nacional como el de exportación.

Para 1976 la inversión programada era del orden de 1,000 millones de - pesos incluyendo tanto las obras en construcción como la iniciación de nuevos proyectos.

A Diciembre de 1975 la capacidad instalada era del orden de 278,322 - toneladas anuales, correspondiendo 232, 177 toneladas (83.5%) a las fibras sintéticas y 46,145 toneladas (16.5%) a las artificiales. Estas cifras representan un incremento de 24.1% con respecto a 1974. Este crecimiento fué logrado básicamente por las fibras sintéticas.

Para 1976 existen expansiones previstas que aumentarán la capacidad total instalada en 60,000 toneladas ó sea 21.6% sobre 1975.

En 1975 la fuerza de trabajo ascendió a 20,911 personas, lo que representa un incremento de 16.5 sobre 1974.

Los sueldos, salarios y prestaciones erogados por el sector en 1975 - fueron de $ 2,086 millones, lo que equivale a un aumento de 120.3% sobre - 1974. Esto se traduce en un ingreso promedio anual por capital de $99,566.00 y una inversión de $ 411,362.00 por persona empleada.

La importación de resinas se redujo en 1975 considerablemente, volviendo al nivel de 1973.

I.- ESTUDIO PRELIMINAR DE MERCADO

I Estudio Preliminar de Mercado

El estudio preliminar de mercado comprende.

1 Consumo Nacional

- a) Producción Interna
- b) Importación en Volumen y Valor
- c) Empleos del producto y sustitutos
- d) Datos históricos

2 Consumo Internacional

- a) Precios en Estados Unidos
- b) Principales Consumidores en el Mundo
- c) Compañías Productoras Mundiales

3 Proyección de la Demanda

1 Consumo Nacional

a) Hasta el presente, el alcohol polivinílico no ha sido fabricado en México y la totalidad de la demanda es satisfecha mediante importaciones, aunque han sido pedidos los siguientes permisos petroquímicos.

Permisos Petroquímicos Otorgados

Fecha Diario Oficial	Nombre de la Empresa	Nombre del Producto	Capacidad Ton/año
28/IV/66	Alco - Pol, S. A.	Alcohol Polivinílico	365
18/VIII/75	Polivin,S.A.de C.V.	Alcohol Polivinílico	3000

Inversión en:

Millones de pesos	Localización	Materias Primas Principales
1.0	Edo. de México	Acetato de Polivinilo Metanol
7.1	Santiago Tianquistenco Edo. de México	Acetato de Polivinilo Metanol

El primero de dichos permisos petroquímicos no se ejerció, el segundo de los permisos petroquímicos hasta la fecha no se inicia, aunque existe - la posibilidad de realizarlo y posteriormente efectuar una ampliación del- mismo a 6,000t/A.

b) Importaciones en Volumen y Valor

Origen de las Importaciones

Año 1970

País	Unidad y Cantidad K g.legal	Valor en Pesos
Alem. Rep. Fed.	168 206	1 713 944
España	7 006	55 098
E.U.A.	136 130	1 340 867
Japón	766 124	6 317 208
Noruega	500	7 000
Paises Bajos	75	1 547
	1 078 041	9 435 664
1971		
Alem. Rep. Fed.	145 281	1 405.560
Canada	734	37 391

1971	146 015	1 442,951
Costa Rica	1 756	25 172
España	40	325
E.U. A.	201 059	2 012 302
Japón	694 713	5 515 620
Total	043 583	8 996 370
1972		
Alem. Rep. Fed.	156 646	1 848 270
Costa Rica	1 760	20 550
España	7 000	50 750
E.U. A.	643 626	4 543 407
Japón	942 144	7 735 238
Países Bajos	125	2 841
Imp. al Interior	1 753 301	14 201 056
Perímetros Libres	2 800	10 000
Total	1 756 101	14 211 056
1973		
Alem. Rep. Fed.	286 536	4 053 636
Bélgica Luxemburgo	20 000	217 500
Canada	43 080	383 295
E.U.A.	512 273	4 866 602
Italia	50	1 134
Japón	740 847	6 693 386

1973

Paises Bajos	120	2 651
Imp. al Interior	1 602 908	16 218 20
Perímetros Libres Total	4 351	3 159
	1 607 259	16 249 795

1974

Alem. Rep. Fed.	272 231	5 810 317
Canada	122	8 755
E.U.A.	723 382	9 717 619
Japón	906 435	17 850 129
Países Bajos	350	8 289
Imp. al Interior	1 902 720	33 395 109
Perímetro Libres	4 815	36 000
Total	1 907 535	3 431 109

Distribuidores en muestro País.

Química Mexibras, S. A.

Corporaciones Industriales, S. A.

Productos de Maíz, S. A.

Empresas Consumidoras en nuestro país.

Se presenta a continuación un desglose de las principales compañías consumidoras de Alcohol Polivinílico que obtienen el producto mediante importaciones, en el año de 1976.

1982

Nombre	Kg	Importe en pesos.
Industrias Resistol, S. A.	220 550	7 035 050
Química Henkel, S. A.	30 000	450 000
Química Hoechst de México,S.A.	142 000	5 015 195
Comercial Mexicana de Pinturas,S.A.	100 000	1 700 000
Nylon de México, S.A.	36 000	600 000
Textiles Morelos , S. A.	32 000	1 395 000
Namex , S. A.	40 000	1 040 000
Pegamentos Garantizados, S.A.	40 000	1 088 210
Stoffel y Cía., S. A.	30 000	545 000
Policyd , S. A.	4 060	205 400
Optigraph , S. A.	15 000	274 500
Ind. Químicas Synres , S. A.	20 000	440 000
Cía., Papelera el Fenix , S. A.	10 000	240 750
Hexaquimia , S. A.	5 000	31 250
Servistol, S. A.	20 000	398 000
Polímeros y Produc. Químicos , S. A.	5 000	110 000
Mon Química , S. A.	100 000	2 280 000
Cía. Ind. Atzcapotzalco , S. A.	15 000	450 000

Cartonajes Estrella, S.A.	20 625	484 250
Industriales Ebro-Quimex, S.A.	1 908	103 892 50
Avon Cosmetics, S.A. de C.V.	1 800	45 000
Max Factor & Co., Suc. en México	50	1 150
Estee Lauder Cosmeticos, S.A.	50	1 414
Perfumes Importados, S.A.	2.5	222
Juama, S.A.	1 000	32 480
Helio Sensimex, S.A.	250	8 873
Capacitrón, S.A.	100	4 000
Corporación Industriales, S.A.	40 000	1 210 000
R.O Hule de México, S.A.	91	3 489
Hull de México, S.A.	136	2 563
Allegran, S.A.	300	15 000
Probst, S.A.	250	8 125
Barnes Hind de México, S.A. DE C.V.	100	14 375
Electrónica ABC, S.A.	280	13 720
Janet, S.A.	500	15 000
Química Mexibras, S.A.	160 000	3 012 600
Instituto Mexicano de Rehabilitación	323	29 300
Proveedor Científico, S.A.	2	200
TOTAL	109 627.5	28 311 812

Como materia prima en la elaboración de polivinil butiral el cual es empleado e la fabricación de cristales de seguridad encuentra también un alto grado de empleo.

d) Datos Históricos.

La demanda en México de alcohol polivinílico es satisfecha únicamente mediante importaciones la cual se puede compendiar en la siguiente tabla.

Alcohol Polivinílico

(1962 - 1976)

1975 - 1962

x y

	Año	Importación (toneladas)	Importación (Miles de Pesos)	Producción Toneladas	Consumo Aparente Toneladas
	1962	---	---	---	---
	1963	---	---	---	---
1	1964	187	2,753	---	187
2	1965	358	5,089	---	358
3	1966	518	6,314	---	518
4	1967	480	5,686	---	480
5	1968	724	7,738	---	724
6	1969	822	7,886	---	822
7	1970	1,079	9,460	---	1,079
8	1971	1,044	8,999	---	1,044
9	1972	1,757	14,211	---	1,757
10	1973	1,608	16,250	---	1,608
11	1974	1,908	33,396	---	1,908
12	1975	518	8,038	---	518
13	1976	1,540	27,229	---	1,540
	77	1247			
	78	1404			
	79	2102			
	80	1972			
	81	2716			
	82	936			

Datos obtenidos S I C Dirección General de Estadísticas Anuarios Estadísticas de Comercio Exterior con fraccione~~s~~ arancelaria~~s~~ 39 02B 007 de 1970 a 1974 y 39 02B 005 para 1975.

Tasa de crecimiento del Consumo Aparente

Años	Tasa
1965 - 1974	20.4%
1967 - 1974	21.8%
1969 - 1974	18.3%
1971 - 1974	22.2%
1973 - 1976	15.64%

2.- Consumo Internacional

Los precios históricos de Importación de este producto son en E.U.A.-.

Año	Precio de Importación ($/Ton)	Precio de Venta en E.U.A. ($/Ton.)
1965	14,220	13,750
1966	12,188	13,750
1967	11,835	12,375
1968	10,694	9,350
1969	9,591	9,350
1970	8,753	8,800
1971	8,621	8,800
1972	8,092	8,800
1973	10,110	8,800
1974	17,551	13,475

Año	Precio de Importación ($/Ton.)	Precio de Venta en E.U.A. ($/Ton.)
1975	--------	15,675
1976	--------	------

Régimen de Importación

Fracción arancelaria	39 02B 007
Cuota ad valoren	20% del precio unitario
Precio oficial	8.50 $/Kg.

b) Principales consumidores mundiales

La producción anual mundial de alcohol polivinílico alcanzó en 1967, 173,000 Toneladas y cerca de 200,000 toneladas se produjeron en el Japón solamente en 1973, que es el principal productor y consumidor en el mundo.

Entre otros países consumidores encontramos a E.U.A. Francia, Paises Bajos, República Federal Alemana, Noruega y el Canadá.

c) Principales productores mundiales

Nombre Comercial	Fabricante	País
Gohsenol	Nippon Gohsei Co., (Nippon Synthetic Chemical Industry Co., Ltd.)	Japón
Kuyashiki Poval	Kuraray Co., Ltd	Japón
Denka Poval	Denki Kagaku Kogyo KK.	Japón
Shinetsu Poval	Shin-Etsu Chemical Ind.Co.,Ltd.	Japón

Nombre	Fabricante	País
El Vanol	EI du Pont de Nemours and Co Inc.	E.U.A.
Gelvatol	Shawinigan Resins Ltd. (Monsato)	E.U.A.
Lemol	Borden Inc.	E.U.A.
Vinol	Airco Chemical Co., (Air - - Reduction Co. Inc.)	E.U.A.
Moviol	Farbwerke Hoechst A.G.	Alemania Federal
Polyviol	Wacker-Chemie Gm. b.H	Alemania Federal
Rhodoviol	Rhone - Pulenc, S.A.	Francia
Alcotex	Revertex Ltd.	Gran Bretaña
Polivinol	Rhodiatoce, S.p.A.	Italia

3.- Proyección de la Demanda

Para la proyección de la demanda fueron probados 7 tipos de ecuaciones que en cada caso los coeficientes se ajustaron por mínimos cuadrados a los - datos históricos estos tipos de ecuaciones probadas fueron:

Polinomio grado 1 $y= a + bx$

Polinomio grado 2 $y= a + bx+cx^2$

Polinomio grado 3 $y= a + bx + cx^2 + dx^3$

Hiperbólica compuesta $y= \frac{1}{a + bx}$

Exponencial compuesto	$y= ae^{bx} + ce^{dx}$
Hiperbólico	$y= ax^{b}$
Logarítmico	$y= ab^{x}$

Donde

y= Consumo proyectado

x= Número de año (1,2,3.....) 1965=1

a,b,c, y d = Coeficientes

e= 2.3025

De estas proyecciones, se escogió la que cumplía con los siguientes requisitos:

a) Mayor ajuste a los datos históricos (desviación estándar)

b) Tendencia parecida a la tendencia del producto

Los resultados obtenidos de la proyección de la demanda con base a los datos históricos son:

Año	Consumo Aparente
1975	2,223
1976	2,521
1977	2,839
1978	3,178
1979	3,537
1980	3,916
1981	4,316
1982	4,736
1983	5,176
1984	5,636
1985	6,117

Las tasas probables de crecimiento del consumo aparente son:

Años	Tasa de
1975 - 77	13.01%
1977 - 79	11.02%
1979 - 81	10.46%
1981 - 83	9.51%
1983 - 85	8.71%

Demanda de alcohol polivinílico que puede ser obtenido por la técnica desarrollada.

Año	Oferta	Demanda (Ton/año)
1976	—	1185
1977	—	1335
1978	—	1494
1979	—	1623
1980	—	1840
1981	—	2028
1982	—	2221

Precio de Venta en México.

El precio de venta actual en México es de 50 a 65 pesos / Kg.

L.A.B. Ciudad de México.

Datos obtenidos de los distribuidores Químicos Mexicanos, S.A. y Corporaciones Industriales, S.A.

II.- CAPACIDAD DE LA PLANTA

Capacidad de la Planta

Debido a que la técnica desarrollada está destinada principalmente a la producción de alcohol polivinílico de baja viscocidad y no hay producción en la República Mexicana de este producto, se estimó de acuerdo con la proyección de la demanda obtenido en el estudio de mercado, el poder elaborar 2221 Ton/año de las 4,736 Ton/año consideradas para el año de 1982 para una producción - diaria de 6.73 Ton. considerando 330 días hábiles por año.

III.- PROPIEDADES FISICAS Y QUIMICAS

III.- Propiedades Físicas y Químicas del Acetato de Polivinilo y Alcohol Polivinílico.

El acetato de vinilo se ha polimerizado industrialmente en masa, solución, suspensión y en emulsión. La mayor parte, tal vez un 90%, del material indentificado como acetato de polivinilo o sus copolímeros constituidos predominantemente de acetato de vinilo son fabricados mediante técnicas de emulsión.

Las emulsiones son líquidos de color blanco lechoso conteniendo cerca de 55% de acetato de polivinilo y el resto estando formado por agua, pequeñas cantidades de agentes humectantes y coloidos protectores, eliminándose de esta manera la necesidad del uso de solventes que pueden resultar tóxicos, inflamables y caros y los requerimientos de recuperación de dichos solventes.

Las emulsiones también ofrecen la ventaja de un gran contenido de sólidos que presenta gran facilidad para fluir, ya que la viscocidad de las emulsiones es independiente del peso molecular de la resina.

Una formulación de emulsión, deberá contener, monómero, agua coloido protector, surfactante, iniciador, buffer y puede llevar también un regulador de peso molecular.

Los iniciadores o catalizadores usados en polimerizaciones de acetato de vinilo son del tipo de radicales libres, tales como el peróxido de hidrógeno, peroxifulfatos, peróxido de benzoilo y combinaciones redox. Las polimerizaciones en emulsión son conducidas con catalizadores solubles en agua.

Los buffers son añadidos a las formulaciones debido a que las velocidades de descomposición de algunos iniciadores son afectados por el pH, por lo cual muchas veces es deseable minimizar la hidrólisis del monómero ya que produce ácido acético (que afecta al catalizador) y Acetaldehido (que produce al peso molecular del polímero). En las formulaciones el pH es controlado en el lado ácido a un pH de 4-5 con fosfatos ó acetatos pero añadiendo a pH neutro como buffer bicarbonatos se obtienen resultados excelentes el pH de las emulsiones comerciales varia de 4 a 6.

En cuanto a surfactantes y coloide protector se refiere existen gran variedad de combinaciones y de ellas dependen las propiedades de la emulsión y la película formada de ella.

Las emulsiones de acetato de polivinilo pueden contener surfactante ó coloido protector en forma aislada pero la práctica commn es usar ambas en general, entre mayor es la cantidad de emulsificantes, menor será el tamaño de partícula de la emulsión.

A niveles bajos de emulsificante (ejem. 0.1% el polímero no forma una dispersión cremosa que permanece suspendida indefinidamente en la fase acuosa, sino que forma pequeñas perlas que se sedimentan y pueden separarse fácilmente por filtración.

Por lo regular todos los procesos de polimerización son operados a presión atmosférica y en reactores convencionales vidriados ó de acero inoxidable.

PROPIEDADES.

Los acetatos de polivinilo varían al aumentar los valores de peso molecular, de líquidos viscosos, sólidos de bajo punto de fusión a materiales sumamente duros. Son productos neutros, de color que varía del color del agua al color de la paja, sin sabor, sin olor y no tóxicos. Las resinas no tienen un punto de fusión definido pero son más suaves conforme la temperatura se aumenta. Son solubles en solventes orgánicos, tales como ésteres, cetonas, arómaticos, hidrocarburos halogenados, ácidos carboxílicos, etc, pero insolubles en alcoholes (excluyendo el metanol que es un solvente), glicoles, agua y líquidos no polares tales como el eter, disulfuro de carbono, hidrocarburos alifáticos, aceites y grasas. A Alcoholes tales como el etílico propílico y butílico conteniendo 5-10% de agua disolverán el acetato de polivinilo.

PROPIEDADES FISICAS.

Propiedad	Valor
Densidad g/cm^3 a 20° C	1.19
Indice de refracción $n_D 20$	1.467
Absorción de agua, % en 24 Hr.	2-3
Temperatura de transición, segundo orden °C	30-34
Coeficiente térmico de expansión linear	8.6×10^7
Conductividad Térmica cal/seg) (cm^2) (°C/cm)	38×10^{-5}
Calor Específico cal/gm	0.389
Constante Dieléctrica ε'	

!!!!!

a	$30^{\circ}C$, $60H_z$	3.3
	$60^{\circ}C$, $60H_z$	6.5
	$25^{\circ}C$, $1KH_z$	3.15
	$25^{\circ}C$, $100H_z$	3.09
	$25^{\circ}C$, $1MH_z$	3.06
	$25^{\circ}C$, $10MH_z$	3.02

Las propiedades eléctricas son fuertemente afectadas por la habilidad del acetato de polivinilo a absorber agua.

El acetato de polivinilo comercial, se encuentra en forma seca como perlas y granos, se clasifica según su viscosidad a 20 C de una solución de 86.1 gr, ó una mol, de resina disuelta en benceno para hacer 1L; los grados de viscocidad corresponden a los pesos molecualres descritos en la tabla que a continuación se presenta. En Europa, el valor "K" de Fikentsher, también derivado de medidas de viscocidad, es usado igualmente para caracterizar las resinas comerciales.

Relación de peso molecular y viscocidad del Acetato de Polivinilo.

VISCOCIDAD	FIKENTSHER VALOR "K"	PESO MOLECULAR PROMEDIO
1.5	13	11,000
2.5	19	18,000
7	32	45,000
15	42	90,000
25	48	140,000
60	58	300,000
100	62	500,000
800	79	1 500,000

Cuando se calienta arriba de la temperatura ambiente, el acetato de polivinilo se transforma en un sólido muy flexible y a 50°C se blando. Puede permanecer por muchas horas a 125°C sin cambio, pero a 150°C, gradualmente se obsurece y sobre 225°C se liberará ácido acético formando una resina café insoluble, se carbonizará a temperaturas mucho mayores. Al disminuir la temperatura por debajo de la temperatura ambiente el acetato de polivinilo se hace quebradizo.

Las cualidades de envejecimiento son excelentes debido a su resistencia a la oxidación y que son inertes a los efectos de la luz ultravioleta.

PROPIEDADES QUIMICAS

Las propiedades químicas del acetato de polivinilo son las mismas que las de un ester alifático. De esta manera por medio de una hidrólisis ácida ó básica se produce alcohol polivinílico y ácido acético ó el acetato del cation básico. Industrialmente el alcohol polivinílico se produce por intercambio de ester con metanol con un catalizador básico, que, en adición al producto polimérico, se forma acetato de metilo.

Muchas propiedades de las emulsiones de acetato de polivinilo se determinan, no por las características del polímero puro que contienen, sino propiedades de la fase acuosa y su contenido. La gravedad específica a 20°C para todas las emulsiones es de 1.1 aproximadamente.

En general poseen un ligero olor del monómero residual. Las trazas de ácido acético que se presentan pueden ser neutralizadas con bases tales como el bicarbonato de sodio, y cuando el monómero residual es removido, el pH de la emulsión resultante se puede ajustar a 7. Por medio de la selección juiciosa de la concentración del monómero, coloide protector y agentes emulsificantes y humectantes, método de polimerización y tratamiento posterior, las propiedades pueden variarse para llenar las especificaciones de su uso. Tales propiedades incluyen, tamaño, promedio de partícula y rango de tamaño de partícula, peso molecular del polímero, pH, viscocidad de la emulsión, carga de la partícula, tolerancia a los solventes, características de la película y resistencia al agua.

ESPECIFICACIONES Y ESTANDARDS.

Las especificaciones de las emulsiones comerciales más comunes son las siguientes:

Propiedad	Rango
Solidos %	54-56
Viscocidad cP	40-4500
pH	4-6
Monómero residual	< 1.0-0.3
Tamaño de partícula µ	0:2-3.0

Carga de partícula	neutra ó negativa
Densidad al 25° C, lb/gal	9.2
Estabilidad de Borax	estable ó inestable
Estabilidad mecánica	buenas ó excelentes

USOS

Los productos de acetato de polivinilo son usados principalmente como adhesivos y en la fabricación de pinturas, en la fabricación de alcohol polivinílico, como copolímero con cloruro de vinilo, etileno acrilonitrilo.

ALCOHOL POLIVINILICO.

El alcohol polivinílico, se cree que fué preparado por el químico, Willie Hermann. Su primera aplicación comercial fué llevada a cabo en la decada de los veintes en Alemania y fué introducido comercialmente en los Estados Unidos en 1939. Químicamente hablando, el alcohol polivinílico puede ser clasificado burdamente como un alcohol polihédrico con grupos hidroxilos secundarios en átomos de carbono alternado. Aunque el alcohol polivinílico puede ser visto como el polímero del alcohol vinílico, recordando que el monómero teórico, $CH_2 = CHOH$, no existe ya que se re arregla a acetaldehido, $CH_3 - CHO$.

El alcohol polivinílico, solo puede ser obtenido mediante la hidrólisis de algún otro polímero vinílico. Comercialmente, el termino alcohol polivinílico incluye todas las resinas derivadas de la hidrólisis del acetato de polivinilo.

La variación de dos factores principales, durante el proceso afectan marcadamente las propiedades del producto final. Las propiedades varían de acuerdo al peso molecular del acetato de polivinilo original y el grado de hidrólisis. La estructura del alcohol polivinílico obtenido por la hidrólisis completa puede ser representado por $CH_3 - CHOH(CH_2 - CHOH)n$, donde n está relacionado al peso molecular de la resina original.

Aunque la fórmula ordinaria del alcohol polivinílico se escribe normalmente de esta forma, debe recordarse que ésta es una estructura ideal, y en la práctica ocurre alguna polimerización del tipo de cabeza con cabeza, resultando una estructura de 1.2 Glicol, $- CH_2 - CHOH\ CH_2CHOH - CHOH\ CH_2\ CHOH\ CH_2$.

En hidrólisis parciales, cantidades proporcionales de residuos de grupos CH_3 - COO- se encuentran distribuidos a lo largo de la cadena en lugar de OH, y la cantidad de tales grupos de acetato se pueden expresar como porcentaje de contenido de acetato, así en un alcohol polivinílico de 70% de contenido de acetato, 30% de los grupos acetato del polímero original se hidrolizaron a grupos hidroxilo y 70% permanecieron como grupos de acetato. El contenido de grupos hidroxilo del alcohol polivinílico está en relación directa a su aplicación comercial y en las muestras en las cuales el 87-89% de los grupos acetoxi presentes han sido convertidas a grupos hidroxilo, se llama parcialmente acetilados; en los grados completamente hidrolizados un mínimo de 98% de los grupos acetoxi es sustituido por los grupos alcohol y en los grados super hidrolizados, más del 99.7% del polimero se hidroliza a alcohol polivinílico.

El alcohol polivinílico se distribuye comercialmente en forma de polvo ó granos. Una variedad de grados, que difieren en peso molecular contenido de acetato elaborados por los fabricantes.

PROPIEDADES.

El alcohol polivinílico es estable en cuanto a color hasta los 140°C. Con calentamiento prolongado a 160-170°C se obscurece y se hace insoluble en el agua. Arriba de los 170°C ocurre la formación de eter sobre los 200°C, se funde y a temperaturas todavía mayores se descompone con carbonización. Bajo altas presiones a 200° - 250°C, se obtiene una resina moldeable, con una solubilidad ligeramente alterada.

Su calor de combustión es de 5902 cal/gr. Las densidades e índices de refracción de resinas conteniendo diversos contenidos de acetato están dados en la siguiente tabla.

Acetato en la resina %	d_{20}^{20}	N_{D}^{20}
0	1.329	1.557
5	1.322	1.553
10	1.316	1.545
20	1.301	1.539
30	1.288	1.530
40	1.274	1.521
50	1.260	1.512
60	1.246	1.503
70	1.232	1.494

El coeficiente de expansión linear del alcohol polivinílico es de 7-12x10^{-5} El agua es realmente el único solvente práctico para el alcohol polivinílico. - Soluciones acuosas de alcohol polivinílico toleran cantidades sustanciales de - alcoholes tales como, metanol, etanol, 2 propanol, creciendo la proporción conforme decrece el porcentaje de hidrólisis.

Si permanecen constantes las demás propiedades, las diferencias en el grado de hidrólisis gobernarán la facilidad con que el alcohol polivinílico se disolverá en agua. Por otro lado entre menor es el grado de polimerización, mayor será la solubilidad. Para cualquier peso molecular específico, la solubilidad - es máxima en rango de hidrólisis de 92-94%.

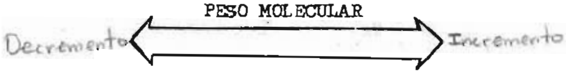
El alcohol polivinílico no se disuelve en agua fría, pero cuando se obtiene una solución en agua caliente con agitación, la resina no precipita al enfriar.- En un período de tiempo las soluciones de alcohol polivinílico de bajo contenido de acetato incrementan su viscocidad y pueden aún gelarse, el fenómeno es dependiente de la concentración y peso molcular.

Propiedades del Alcohol Polivinílico

Incremento en flexibilidad
Incremento en sensibilidad al agua
Incremento en facilidad de solvatación

Incremento en viscocidad
Incremento en resistencia de bloqueo
Incremento en resistencia de la tensión
Incremento en resistencia al agua
Incremento en resistencia adhesiva
Incremento en resistencia a solventes
Incremento en potencia a la dispersión

PESO MOLECULAR



% de Hidrólisis

Incremento en flexibilidad
Incremento en sensibilidad al agua
Mayor adhesión a superficies hidrofóbicas

Incremento en resistencia al agua
Incremento en resistencia a la tensión
Incremento en resistencia de bloqueo
Incremento en resistencia de solventes
Mayor adhesión a superficies hidrofílicas

La figura superior muestra la variación en propiedades que ocurre con cambios en el peso molecular cuando se mantiene constante el porciento de hidrólisis y en la parte inferior cuando se varía el porciento de hidrólisis y permanece constante el peso molecular.

Generalmente hablando, las variaciones son las mismas en ambos casos, con algunas excepciones.

La viscocidad del alcohol polivinílico en solución es determinado principalmente por el peso molecular conforme aumenta el pesos molecular, aumenta también la viscocidad.

Los alcoholes polivinílicos de bajo contenido de acetato son insolubles y casi no son afectados a temperaturas ordinarias por la gasolina, propano, dióxido de azufre, kerosono, benceno, xileno dicloruro de metileno, tricloro etileno tetracloruro de carbono, clorofluoro carbonos, monocloro benceno, metanos, alcohol etílico, etilen glicol, acetona, furfural, acetato de metilo, dioxano formamida, dietilen glicol, acido cresílico,monoetanol amina, trietanolamina, quinolina, morfolina, piridina, nitrobenceno, eter y anilina.

Solo hay pocos tipos de compuestos orgánicos que tiene acción solvente en los grados completamente hidrolizados de alcohol polivinílico. Estos compuestos son usados como plastificantes y en la mayoría de los casos, también funcionan humectantes. La presencia de uno ó más grupos hidroxilo aumentan su actividad.- Ejemplos incluyen, glicerol etilenglicol y algunos polietilenglicoles. También son útiles las aminas tales como las etanolaminas, sus sales y aminas incluyendo la formamida, N (-2Hidroxietil) fordamida y la N (-2- Hidroxietil) acetamida. La Mayoria, si no todos los solventes requieren calor para disolver aún pequeñas cantidades de alcohol polivinílico. Compuestos con bajo poder solvente, pero aún útiles como plastificantes son el sorbitol y la urea.

La presión osmótica de una solución de alcohol polivinílico de 1.2g/100 ml de agua. (Bajo contenido de acetato, bajo peso molecular) es de 0.008 atm. La viscocidades en poises de alcohol polivinílico con varios contenidos de acetato en solución al 4, 8 y 12% en agua a 20°C están dados en la siguiente tabla.

Viscocidad de Soluciones de alcohol polivinílico en relación a su peso molecular.

Peso molecular del acetato de polivinilo original	Contenido de acetato	Sol 4%	Sol 8%	Sol 12%
		μ	μ	μ
10,000	20	0.0165	0.026	0.045
15,000	20	0.024	0.054	0.125
33,000	5	0.048	0.18	0.65
33,000	20	0.045	0.16	0.52
135,000	5	0.20	5.5	28
135,000	30	0.30	—	—
400,000	1	0.50	16	40
400,000	40	0.70	—	—

La resistencia a la abrasión es 10 veces aquella del hule, y su dureza medida en durómetro "Shore" es de 10-100 plastificada. La resistencia a la tensión y elongación al rompimiento en materiales de bajo contenido de acetato, está dado por la tabla.

	Extruido		Prensado	
Temperatura °C	Resistencia a la tensión psi	Elongación %	Resistencia a la tensión	Elongación %
-32	7650	30	7400	40
-18	6770	85	6760	85
0	6760	99	3640	267
25	5200	225	2110	445
46	3530	255	1610	520
66	3040	300	1490	540
80	2110	340	1250	620

La conductividad térmica del alcohol polivinílico en cal/(seg) (cm^2) (°C/cm) es de 5 x 10^{-4} para la resina estruida y 18 x 10^{-4} para la resina moldeada. El calor específico del alcohol polivinílico varía de 0.005 Cal/(°C) (g) a 10 K a 0.256 cal/(°C) (g) a 245 C. A esta temperatura la entropía es de 0.2655 cal/(C) (g) y la entalpia es de 32.45 cal/g.

PROPIEDADES QUIMICAS.

El monómero del alcohol polivinílico CH_2=CHOH es el enol del acetaldehido y es desconocido en estado libre, aunque algunos de sus derivados tales como compuestos de mercurio son bastante estables.

El alcohol polivinílico fué mencionado en primer lugar por Herrmann y Haehnel en 1927; haciéndolo mediante la saponificación de ésteres polivinílicos.

El alcohol polivinílico reacciona en forma muy similar a los alcoholes alifáticos de bajo peso molecular. Por ejemplo reacciona con cloruros de ácido o anhidridos para formar ésteres y con aldehidos y cetonas para formar acetales. En muchos casos es posible obtener una resina completamente nueva haciendo reaccionar todos los grupos hidroxilo, aún cuando el grado de la reacción sea pequeño, las propiedades pueden ser alteradas considerablemente, pudiéndose retener, si se desea, la solubilidad en agua.

Variaciones posteriores, que pueden resultar interesantes son alcanzadas al usar un alcohol polivinílico parcialmente hidrolizado, reteniendo así algunos de los grupos de acetato.

El alcohol polivinílico, reacciona con trióxido de azufre, resultando - OH + SO_3 $-OSO_3H$ que es altamente soluble en agua. Cloruros de sulfonilo de Alcanos ó Arenos al reaccionar con el alcohol polivinílico, dan como resultado sulfonatos -OH + R SO_3H - OSO_3 R.

Los copolímeros del alcohol polivinílico con etileno preparados por hidrólisis completa del copolímero con acetato de vinilo se han hecho reaccionar con fosfito de fenil deneopentil $(C_5H_{11}O)_2POC_6H_5$ para dar esteres de fosfito retardadores de flama por desplazamiento del fenol. Acidos poliméricos tales como el ácido poliacrílico reaccionan con el alcohol polivinílico dando como resultado ésteres con características de una gel insoluble y que tienen propiedades mécanicas que varian reversiblemente con el pH y la temperatura.

Se puede obtener una gelación controlada de alcohol polivinílico con la adición de compuestos trivalentes de titanio y agentes oxidantes. El alcohol polivinílico puede ser eterificado usando reactivos que incluyen haluros de alquilo y anilo dando como resultado películas con una permeabilidad ~ 50% de eterificación de un décimo de la del alcohol polivinílico.

La reacción de alcohol polivinílico con aldehidos da como resultado acetales. El butiral es muy conocido en vidrios de seguridad.

El alcohol polivinílico no es atacado por oxígeno comprimido a temperaturas bajo 70°C. El permanganato de potasio oxida solo ligeramente al alcohol polivinílico. Con Acido crómico da una masa insolublre de color café que contiene algo de los materiales iniciales. Esto es usado en imprentas usando el ácido como tinta y posteriormente se lava el área no tratada. Con ácido nítrico concentrado forma nitrato polivinílico en frío, pero se oxida en caliente con la evolución de óxido nítirico y la formación de ácido oxálico. El ácido periódico no oxida al alcohol polivinílico pero rompe la estructura 1·2 glicol.

A causa de su resistencia a la oxidación, el alcohol polivinílico con contenido bajo y medio de acetato es practicamente inmune al deterioro con el tiempo.

Un estudio detallado de las propiedades físicas y Químicas del Alcohol polivinílico se puede encontrar en los capítulos 2 y 9 de l Polyvinyl alcohol - Proparties and Applications C.A. Finch 1973.

TOXCICIDAD.

Estudios realizados en el metabolismo en ratones nos muestran efectos dañinos. Los humanos no muestran efectos en su salud cuando se usa película de alcohol polivinílico en cirujía y en contacto con medicamentos. A causa de su toxicidad oral mínima, han sido aprobada componente de adhesivos en el empaque de alimentos ó en recubrimientos que ésten en realción directa con alimentos. Aunque debe tomarse en cuenta, que el alcohol polivinílico no es asimilado por el organismo y por lo cual, se debe tener en cuenta no inhalar el polvo en los pulmones.

El alcohol polivinílico ha sido también aprobado en la industria de los cosmeticos. El uso del alcohol polivinílico para usos de consumo interno en el organismo como por ejemplo en alimentos, debe ser autorizado por la dependencia gubernamental correspondiente.

APLICACIONES.

La mayoría de los usos del alcohol polivinílico involucran la extrusión de la resina o su aplicación en recubrimientos de superficies. A causa de su carácter intratable, la resina se debe plastificar, para poderla extruir sin descomponerse. Se producen por estos medios, mangueras de alcohol polivinílico. La mayor aplicación del alcohol polivinílico involucra las soluciones acuosas usadas en procedimientos de recubrimientos de Vaciado y Sumergido. El vaciado de la película acuosa se complica debido al límite de solubilidad del alcohol polivinílico, aún en agua caliente siendo 50% de concentración el límite util máximo y aún este debe ser trabajado cercano a los 100°C. Operaciones bajo presión se llevan a cabo arriba de los 100°C.

Los procesos de disolución dependen del grado de acetilación. Para el alcohol polivinílico parcialmente acetilado en altas concentraciones se usa agua fría preferentemente bajo 75°F, que es agitada vigorosamente y el polvo añadido en forma lenta. Este procedimiento evita que se formen masas.

Para disminuir el tiempo de solución, la dispersión se calienta a una temperatura entre 100° y 190°F. A esta temperatura se completa la solución entre 20 y 30 mins. Este procedimiento se emplea satisfactoriamente para los grados completa y mediamente hidrolizados. Aunque algunos grados requieren la adición de alcohol ó acetona para ayudar a la disolución.

El alcohol polivinílico ha encontrado aplicación en el campo de la fotografía como base de soporte ó recubrimiento. Un tratamiento químico especial en el alcohol polivinílico permite recubrimientos endurecidos.

La combinación en el alcohol polivinílico de la alta tensión superficial y la fácil disolución en agua, lo han hecho útil en el empaque de blanqueadores y detergentes para uso doméstico.

Para propósitos de empaque de comida el alcohol polivinílico usado en los recubrimientos, se mejora usando otras resinas como el copolímero de cloruro de vinildeno - cloruro de vinilo ó el de cloruro de vinilideno - acrilonitrilo.

El alcohol polivinílico se ha usado como homopolímero ó copolímero para la preparación de la recubierta de embutidos y salchichas.

Se han realizado estudios de la permeabilidad de películas de alcohol polivinílico a la humedad y al vapor de agua, siendo esto de interés en el campo alimenticio, además está información ha sido útil en el desarrollo de membranas para la diálisis artificial de Riñon.

Película.- Se ha hecho películas de alcohol polivinílico capaces de servir como membranas en la desalinización del agua. Copolímeros del alcohol Polivinílico con ácido estirensulfónico dan como resultado membranas selectivas de cationes. Derivados son 1,2 epoxi -3- dietilamina propano, tiourea, éter clorometílico y trietanolamina ó piridina aniónicas ó cationicas.

Adehisivos.- El alcohol polivinílico se ha usado como un adehiso superior - en aplicaciones en donde el almidón y otros materiales de costo bajo eran empleados. Aplicaciones en papel y cartón commmente emplean una formulación que comprende la adición de agentes ramificantes disolventes inertes y sales inorgánicas Variaciones con los aditivos empleados en las mezclas permiten al alcohol polivinílico ser usado para cubrir muros con cuero, tela, corcho y espuma de poliestireno.

El alcohol polivinílico ha encontrado aplicación como intermediario en la - fabricación de polivinil butiral usado en cristales de seguridad.

Electricidad.- El alcohol polivinílico ha sido usado en una gran variedad - de aplicaciones eléctricas en donde se puede sacar ventaja de sus propiedades - dieléctricas.

El uso del alcohol polivinílico en baños electrolíticos, ha reportado mejoras en el recubrimiento con metales especialmente con el cadmio ó zinc berilio y cromo.

TEXTILES.

El alcohol polivinílico es usado como sustituto del almidón y otras resinas naturales en la industria textil del algodón de mezclas de algodón y fibras sintéticas.

Han favorecido su uso no obstante su costo más elevado el que el producto- sea de mayor calidad y que las concentraciones usadas sean mucho más bajas.

Los textiles conocidos como de "lavar y usar" necesitan tratamiento químico para obtener resistencia a las arrugas. Soluciones acuosas ó dispersiones del - alcohol polivinílico han resultados adecuadas para este propósito.

TRATAMIENTOS DE PAPEL.

El alcohol polivinílico muestra una excelente adhesión y compatibilidad - con materiales celulósicos y ha encontrado un uso considerable en formulaciones adhesivas en papel, en construcción de bolsas, en el encuadernado de libros, en la fabricación de tubo enrollado etc.

Como adehsivo en papel, el alcohol polivinílico comparado con los adehsivos naturales tales como el almidón. gomas, dextrinas, gomas animales y caseina, tiene las siguientes ventajas, uniones más fuertes y en muchos casos, mayor resistencia al agua, mayor compatibilidad con otras resinas adhesivas, alto grado de resistencia al ataque por bacterias y menor costo debido a cantidades menores de material empleado.

El alcohol polivinílico es útil para darle el apresto al papel, ya que es de fácil aplicación, es soluble en agua, y da gran resistencia a las grasas, aceites y solventes, facilidad para hacer película y gran resistencia a la abrasión. Los recubrimientos pueden mezclarse con sólidos, inertes, extendedores, otras resinas y/o pigmentos.

El pretratado de la superficie del papel con agentes gelantes ó ramificantes reduce la cantidad de alcohol polivinílico necesario y provee recubrimientos superiores. Los materiales de papel cubiertos de esta manera son útiles en el empacado de alimentos, productos grasosos y productos químicos. Alternativamente el alcohol polivinílico se usa a menudo en aplicaciones de papel, por mezcla directa con la pulpa del papel la cual se convierte a papel en la forma normal ó presionando las fibras extruidas mezcladas.

FIBRAS.- Las fibras preparadas de alcohol polivinílico tienen aplicación debido a su gran fuerza tensil, habilidad de absorver humedad y atractivas al tacto. La fibra se prepara extruyendo una solución acuosa del polimero en un baño coagulante, que usualmente contiene sales inorgánicas. La fibra se trata entonces con otros productos químicos orgánicos, incluyendo aldehidos y cetonas para impartir propiedades adicionales tales como resistencia al fuego, insolubilidad en agua, y resistencias químicas adicionales, el desarrollo comercial de la fibra del alcohol polivinílico, en los E.U. ha sido llevada a cabo pero hay fibras competititivamente más atractivas particularmente en el costo, sin embargo en Japón la fibra es ampliamente usada en muchas aplicaciones textiles, particularmente en la del vestido. Aunque en los últimos años, las fibras de poliester han arrasado algunos mercados, la economía química peculiar del Japón y la carencia de materiales crudos naturales explican la producción en volúmen del alcohol polivinílico en Japón y no en otro país.

Es posible preparar fibras de alcohol polivinílico que sean fácilmente solubles en agua. Se ha sacado ventaja de sus propiedades especiales al tejer patrones especiales en textiles cuando la tela se lava despues de que el tejido ha sido terminado, resulta una tela de estructura abierta y alta porosidad.

El alcohol polivinílico se ha recomendado, debido a que da mejor dispersión de pigmento en pinturas de base acuosa y en tales formulaciones a menudo sirve como agente emulsificante no iónico.

Las cremas limpiadoras para el cutis han sido formuladas usando alcohol polivinílico, la resina también a encontrado aplicación como ingrediente de un protector de la piel contra los solventes orgánicos.

IV.- ESTUDIO TECNICO

a) Estudio de Laboratorio

b) Cálculo del Equipo y Costos del Mismo

a) ESTUDIO DE LABORATORIO

Introducción

Desde el descubrimiento del alcohol polivinílico en 1924 por Hermann y Haehnel y por Staudinger, Frey y Stark éste se ha convertido en un polímero importante especialmente durante los últimos 15 años. La producción anual mundial de alcohol polivinílico alcanzó 173 000 ton. en 1967, y cerca de 200 000 ton. se produjeron en Japón solamente en 1970.

La elaboración de alcohol polivinílico fué estudiado extensivamente en los últimos años y principalmente en el pasado por Kainer en 1949.

Preparación de Acetato de Polivinilo

El alcohol vinílico, el monómero real del alcohol polivinílico no existe en estado libre, la manufactura industrial del alcohol polivinílico es llevada a cabo solamente a partir del acetato de vinilo, aunque hay otras rutas para producir alcohol polivinílico.

Monómero de Acetato de Vinilo

El acetileno es la materia prima para la manufactura del acetato de vinilo desde 1920. Recientemente se han desarrollado varios procesos que emplean la oxidación del etileno en presencia de ácido acético. El acetato de vinilo preparado por la vía del etileno parece ser más puro que el obtenido por el proceso de acetileno de acuerdo al espectro de luz ultravioleta. Por lo cual el monómero obtenido por los nuevos procesos es más adecuado para la polimerización que el monómero obtenido por el proceso de acetileno.

Mecanismo de polimerización del acetato de vinilo

El acetato de vinilo es un monómero vinilico típico no conjugado y puede ser fácilmente polimerizado por iniciadores catiónicos. El mejor indicador de la polimerización por radicales del acetato de vinilo está dado por los parámetros de copolimerización de Alfrey - Price Q, a y Kiz definidos por la ecuación.

$$K_{12} = P_1 \; Q_2 \; \exp\left(-e_{1,} e_2\right) \quad .$$

donde

k 12 = constante de velocidad de reacción del monómero 2 al radical 1

P, Q = Reactividades específicas del radical y el monómero

e = El caracter polar del radical aducido ó el monómero

Los valores del acetato de vinilo y otros monómeros están dados en la tabla siguiente, que muestra que el monómero de acetato de vinilo por si - mismo no reaccionaria fácilmente con otros radicales monoméricos, pero que el radical de acetato de vinilo reaccionaria rápidamente con otros monómeros en comparación con otros monómeros vinílicos.

Q, e y K_{11} para monómeros vinílicos

	Q	e	K_{11}[a] ($1\ mol^{-1} s^{-1}$)
Acetato de metilo	0.026	- 0.22	3700
Acrilato de metilo	0.42	+ 0.6	2100
Metacrilato de metilo	0.74	+ 0.4	367
Estireno	1.0	- 0.8	176

[a] A 60°C

En una polimerización en solución por radicales libres hay 4 reacciones principales que considerar: iniciación, propagación, transferencia y terminación - El esquema siguiente muestra los pasos de reacción.

Iniciación

$I \xrightarrow{kd} 2R.R. + Mi \xrightarrow{} Mi$ $\qquad Ri = 2\,K\,d\,f$ (1)

Transferencia al solvente

$Mn. + S \xrightarrow{Ktrs} M\,n\,t\,S$ $\qquad K\,trs\,(M)\,(S)$

Propagación

$Mn. + M \xrightarrow{kp} Mn + 1$ $\qquad R\,p = K\,p\,(M)\,(M)$

Transferencia al iniciador

$Mn. + I \xrightarrow{ktri} Mn + I$ $\qquad K\,tri\,(M)\,(I)$

Transferencia al monómero

$Mn. + M \xrightarrow{ktrm} Mn + M.$ $\qquad Ktrm\,(M.)\,(M)$

Transferencia al polímero

$$Mn. + P \xrightarrow{ktrp} Mn + P. \qquad Ktrp\ (M.)\ (P)$$

Terminación

$$Mr. + Mm. \xrightarrow{kt} K\,t \cdot (M.)^2$$

$$Mn. + S. \xrightarrow{kts} Kts\ (S.)\ (M.)$$

$$S. + S. \xrightarrow{ktss} Ktss\ (S.)^2$$

Han sido investigadas las energías de activación y velocidades de reacción Bagdasmryan ha mostrado que los valores más reales son los establecidos por Bengough y Melville.

$$Ep - \frac{1}{2}\,E\,T = 4200\ Cal/Mol$$

$$Kp/Kt^{\frac{1}{2}} = 0.306\ A\ (50°C)$$

$$Kp/Kt = 2.5 \times 10^{-5}\ a\ (15°C)$$

$$E\,t = 0$$

Así

$$Ep = 4700\ Cal/_{mol}$$

$$Kp/Kt^{\frac{1}{2}} = 202\ \exp^{(-4200/RT)}$$

$$Kp/Kt = 3.62 \times 10^{-2}\ \exp^{(-4200/RT)}$$

$$Kp = 1.13 \times 10^{6}\ \exp^{(-4200/RT)}$$

$$Kt = 3.12 \times 10^{7}$$

El paso de reacción más importante y que deberá ser considerada en relación a las propiedades del alcohol derivado es la reacción de transferencia ya que los radicales de acetato de polivinilo son muy activos y fácilmente se transfieren al material en el sistema de polimerización. El grado de polimerización de acetato de polivinilo se calcula de la ecuación.

$$\frac{1}{P_{AC}} = \frac{Kt}{K_p^{\,2}}\,\frac{Rp}{(M)^2} + cm + Cs\,\frac{(S)}{(M)} + Ci\,\frac{(I)}{(M)} + C\,p\,\frac{(P)}{(M)} + Ca\,\frac{(A)}{(M)}$$

Donde
P a c = Grado promedio de polimerización
R p = Velocidad de polimerización
K t = Constante de velocidad de terminación
K p = Constante de velocidad de propagación

Cm, Cs, Ci, Cp, y Ca = Constante de transferencia del monómero, solvente iniciador, polímero y agente de transferencia.

Métodos de polimerización de Acetato de vinilo.

Polimerizaciones en masa, emulsión, solución y en perla pueden emplearse para el acetato de vinilo de acuerdo a la reacción.

$$R. + n\ CH_2 = CHOA_c \longrightarrow RCCH_2 - CHO\ Ac\ nH + n\ 21.3\ K\ cal$$

Detalles de la polimerización han sido resumidas por Yoshioka y Lindemann. Características de los 4 métodos para la preparación de alcohol polivinílico se han resumido en la siguiente tabla.

Método de Polimerización	Control de Polimerización	Grado de Control de la Polimerización	Tratamiento para la Hidrólisis
Masa	Difícil	Adición por Transferencia	Secado y Disolución en Me OH
Solución	Fácil	Adición de Solvente	Inmediata
Emulsión	Fácil	Adición por Transferencia	Inmediata
Suspensión	Fácil	Adición por Transferencia	Secado y Disolución en Me OH

Método de Hidrólisis	Propiedades del Alcohol polivinílico
	Ramificaciones y alto contenido de grupos terminales carboxilo
Alcohólisis	Buenas
Alcohólisis	Buenas
Hidrólisis	Ramificaciones, color obscuro
Hidrólisis ó Alcohólisis	Ramificaciones y alto contenido de grupos terminales carboxilo

Iniciador

Un gran número de compuestos pueden iniciar la polimerización del Acetato de vinilo, entre estos encontramos: peróxidos, hidroperóxidos y - compuestos.

Estos se descomponen en solución, ya sea debido al calor ó foto químicamente, a cierta velocidad. De esta manera no todas los radicales libres-utilizados producen una reacción de polimerización, en el más favorable de los casos, no más del 50 ó 60% de los radicales generados comienzan una - reacción de polimerización.

Trabajo de laboratorio para desarrollar acetato de polivinilo para la producción de alcohol polivinílico de baja viscocidad y 88% de hidrólisis.

En base en los datos y técnica reportados en la literatura, se procedió primeramente a realizar experimentos para la elaboración de una técnica adecuada para polimerizar el acetato de vinilo en emulsión con el fin de - obtener posteriormente un alcohol polivinílico con características semejantes a las de un producto comercial.

Las características de dicho producto están dadas por la siguiente - tabla.

Tipo	Viscocidad CPS (1)	Hidrólisis (%)	Pureza %	Contenido de Volatiles %
Comercial	5 ± 1	88 ± 2	Sobre 94.0%	Bajo 5.0

P H 2	Contenido de Cenizas
5 - 8	Bajo 0.5

1 Viscocidad medida en una solución acuosa al 4% con un Viscocímetro Brookfield a 20° C.

2 pH medida en una solución acuosa al 4% a 20° C.

Reacción de Polimerización en Emulsión

Teniendo como base, la bibliografía que se adjunta en la presente tesis, fueron realizados un total de doce experimentos, relativos a la polimerización en emulsión de monómero de acetato de vinilo, buscando como meta la obtención de una técnica, que diera lugar a la obtención del polímero de acetato de polivinilo que reuniera las siguientes características:

a) Propiedad del acetato de polivinilo congruentes con las del alcohol polivinílico que se desea obtener.

b) Contenido en la emulsión de 55% de sólidos

c) Empleo de materias primas de fabricación nacional

d) Obtención de las características físicas adecuadas para el método

e) Repetitividad del método

f) Pureza del producto obtenido, adecuada

g) Facilidad para obtener el sólido seco de la emulsión

h) Sencillez en el método

Método obtenido

Reactivos

1)	Acetato de vinilo (monómero)	357 ml
2)	Iniciador (Sol al 3%)	33 ml
3)	Solución Buffer (Sol al 2%)	66.4 ml
4)	Emulsificante (Sol al 10%)	116.7 ml
5)	Antioxicante	0.6 gr.
6)	Emulsificante alcohol polivinílico	1.6 gr.
7)	Agua	166.6 gr.

Si

Material

a) Reactor de vidrio que comprende tapa y vaso con junta esmerilada de 2 de capacidad y 4 bocas 24/40.

b) Brida de metal con tornillos, y junta de teflón

c) Refrigerante 24/40

d) Motor para agitación de tres velocidades

e) Varilla de agitación de metal

f) Guía para varilla de agitación

g) Embudo de adición de 125 ml.

h) Embudo de adición de 250 ml.

i) Cilindro de Nitrógeno

j) Frascos lavadores

k) Termómetro 0-100°C

l) Vaso de precipitados de 2 L para Nujol

m) Resistencia eléctrica de Nicromel

n) Agitación magnética

ñ) Tapón de vidrio 24/40

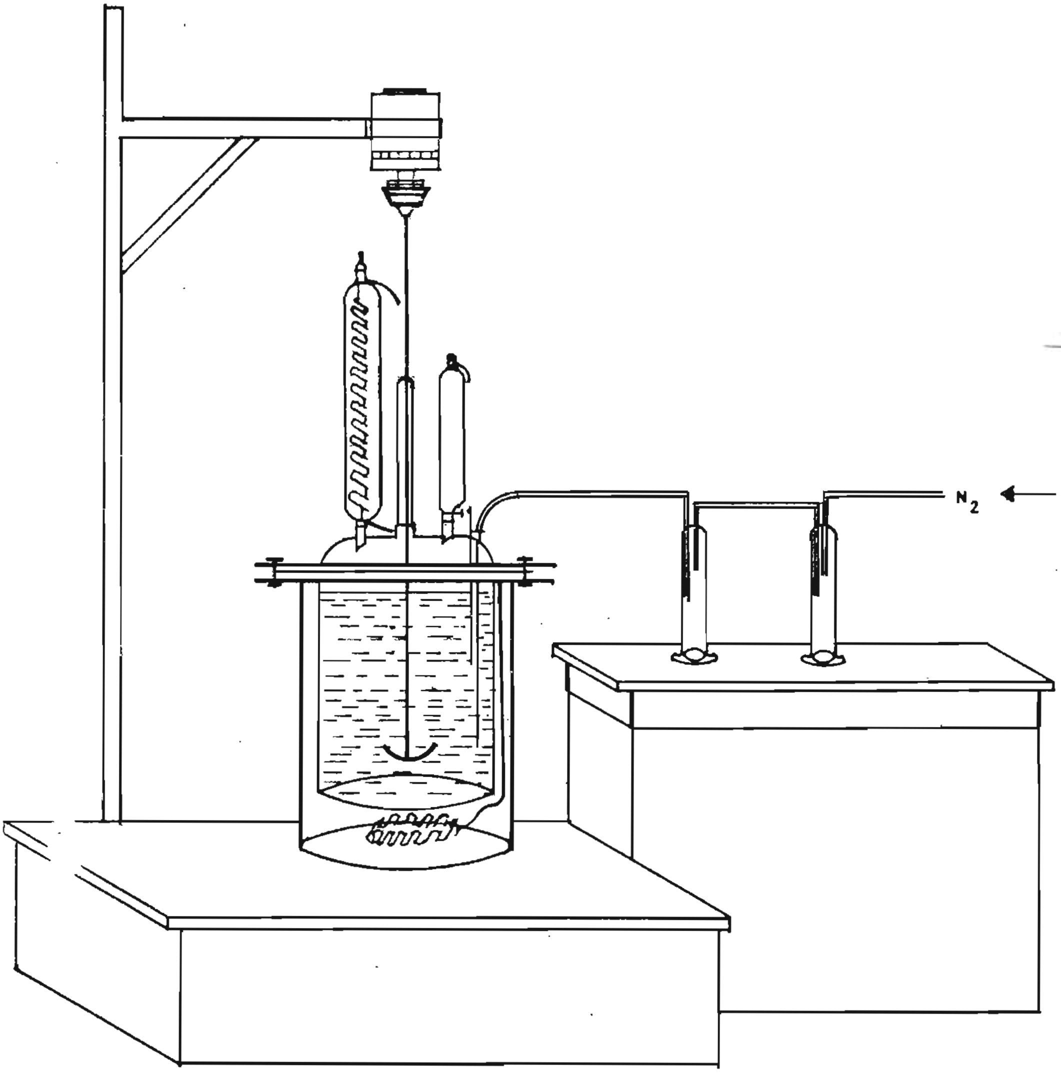
o) Pinzas de tres dedos

p) Soporte

Procedimiento.

Preparar las soluciones de Iniciador Buffer y Emulsificante con las concentraciones indicadas, ponga la solución de Iniciador en un embudo de adición y en el otro el monómero. Ponga en el reactor la solución de Emulsificante, Buffer y el agua.

Coloque el tubo de entrada del nitrógeno debajo de la superficie de la mezcla anterior y comiense a pasar N_2 por aproximadamente 15 minutos. Añada el antioxidante y el 10% de la cantidad total de monómero. Ajuste el tubo de entrada del Nitrógeno poniéndolo ahora sobre la superficie del líquido. Empiece la agitación (200 a 250 RPM.) y el calentamiento poco a poco hasta que la temperatura suba a 65°C. Agregue todo el Iniciador del embudo de adición aproximadamente en 5 minutos. La temperatura subirá a 75 - 80°C, después que la reacción exotérmica termine (Aproximadamente 35 minutos, se va adicionando el monómero a una velocidad tal que la adición dure unas 4 ó 5 horas y el reflujo no sea muy intenso. Durante este tiempo la temperatura se debe mantener entre 67 y 73°C al mismo tiempo que se efectua la adición de monómero deberán añadirse unos 40 ml. de la solución de Buffer con el objeto de regular el pH. La polimerización se continúa por 1 hora más. La emulsión se deja enfriar, se observa si no hay coágulos. Se evalua el color, el pH y la viscocidad en un aparato de Brookfield (Aguja # 3 a 50 RPM). El producto de la reacción de polimerización se vacía en una bolsa de plástico y se cierra herméticamente para evitar la formación de natas.


N_2

No

Conclusiones

A partir de la primera reacción de polimerización se presentó la formación de grumos una vez que la adición del monómero se concluía, por lo cual, la atención principal de los experimentos posteriores se dedicó a hacer variaciones en el método, con el fin de encontrar las condiciones tanto físicas como químicas, que determinaban que la técnica no pudiera concluir en forma adecuada, ya que el método se había diseñado para reunir las condiciones expresadas anteriormente. Estos cambios en el procedimiento se enuncian cronológicamente a continuación:

a) Cambio en el medio de calentamiento. Inicialmente el calentamiento era realizado mediante una canastilla de calentamiento, pero está mostró gran dificultad para regular la temperatura en ocaciones en que la reacción era muy exotérmica y debido a que la reacción es sumamente sensible a la temperatura, se decidió cambiarla por un baño, con el cual se tuvo la seguridad de un control adecuado, en cuanto a la temperatura se refiere.

b) Medio de agitación. Las reacciones de polimerización son dependientes tambien de una agitación adecuada para poder llevarse a cabo, por lo cual, el segundo paso fué el perfeccionamiento de la velocidad de agitación cambiándose en este caso el motor utilizado para la agitación por uno mayor potencia.

c) Emulsificantes. Otra de las condiciones, que podían afectar la realización del esperimento, era el emulsificante empleado y su concentración, debido a esto, fueron variándose los emulsificantes empleados, utilizando Natrosol y alcohol polivinílico, comprobándose que este último podía ser empleado sin problemas, con la ventaja de una producción menor de contaminantes en el producto final que se desea producir.

d) Tipo de agitador ya que la mayor formación de grumos se localizaba en las paletas del agitador, se decidió cambiar la forma del mismo, obteniendose óptimos resultados al efectuarse dicha operación.

e) p H - El propósito de regular el p H, fué factor determinante para evitar la formación de grumos durante la reacción y poder llevar a buen término la polimerización, esto fué realizado mediante la adición de una solución buffer mediante lo cual fué posible variar el PH de 4-5 a 6.9.

f) Tipo de recipiente - La variación realizada en cuanto al tipo de recipiente empleado, para realizar la reacción de polimerización buscó dos objetivos. Buscar la mayor semejanza posible con un reactor de tipo industrial y trabajar con cantidades menores de reactivos, ambos fines fueron alcanzados durante el desarrollo de la investigación

g) Repetitividad. La repetitividad del procedimiento fué comprobada, mediante cuatro experimentos los cuales mostraron una semejanza completa en todas sus condiciones.

Precipitación de la Emulsión de Acetato de Polivinilo

Durante la realización de los experimentos de polimerización, se encontró, que la emulsión de acetato de polivinilo se podrá romper facilmente, mediante la adición de una solución concentrada de sulfato de sodio en una proporción de 5 ml. por cada litro de emulsión, dando como resultado un sólido filtrable de color blanco, utilizando además una agitación moderada.

Lavado y Filtración del Acetato de Polivinilo

El sólido era filtrado en un embudo buckner y un kitasato y lavado varias veces con agua hasta que el emulsificante era eliminado en su totalidad, dejándose secar posteriormente.

Con miras a la realización industrial de la técnica, fué probado el secado, lavado y filtrado del sólido de acetato de polivinilo en una centrífuga de canasta a escala de laboratorio, obteniéndose un excelente resultado y determinándose la posibilidad de realizar 2 ciclos por hora en una centrífuga a escala industrial.

Propiedades del producto obtenido.

Emulsión

Densidad 20°C	Sólidos %	Viscocidad	pH	Pélicula *
1.08 Gr/cm^3	5 5	40 Brookfield	6.9	6-7

* Calificación de 0 a 10 el número 6 es con pocos grumos.

No

El monómero residual no se pudo checar ya que la emulsión se hace "Bolas" con el reactivo (Mezcla de Bromuro y Bromato de Potasio)

Aspecto: Líquido blanco lechoso

Olor : Ligero olor a mercaptano, no desagradable

Propiedades del sólido

Densidad 20°C	Color	%(Cenizas Centrífugas)
0.673 $^{gr}/_{cm^3}$	Blanco transparente	0.52

% Cenizas (filtración y lavado)

1.2

Hidrólisis de Acetato de Polivinilo para producir alcohol Polivinílico

Métodos de hidrólisis y sus características

a) Clasificación de los métodos de hidrólisis

Los métodos de hidrólisis del acetato de polivinilo generalmente se agrupan en hidrólisis alcalina, aminólisis, y acidólisis, de acuerdo al catalizador empleado. Las siguientes reacciones químicas tienen lugar.

$CH_3\overset{O}{\overset{\|}{C}}-H + Nu \xrightarrow{-80 \text{ a } -20°C} PV-OH$ Producto bajo P. Mol

Alcohólisis

$$PV\text{–}OAc + n\,ROH \xrightarrow[NaOH]{\text{ácido ó álcali}} PV\text{–}OH + nROAC \qquad 1$$

Hidrólisis

$$PV\text{–}OAc + n\,H_2O \xrightarrow{\text{ácido ó álcali}} PV\text{–}OH + nHOAC \qquad 2$$

Hidrólisis directa

$$PV\text{–}OAc + n\,NaOH \xrightarrow{H_2O} PV\text{–}OH + n\,NaOAc \qquad 3$$

Aminólisis

$$PV\text{–}OAC + nHNR,R_2 \xrightarrow{H_2O} PV\text{–}OH + nAc\,NR,R_2 \qquad 4$$

Amonólisis

$$PV\text{–}OAc + n\,NH_3 \xrightarrow{\text{NH4 CL ó NH4 OAC}} PV\text{–}OH + n\,Ac\,NH_2 \qquad 5$$

Al mismo tiempo, ocurren las siguientes reacciones secundarias

$$R\,O\,A_c + NaOH \xrightarrow{H_2\,O} ROH + Na\,OA_c$$

$$H\,O\,A_c + NaOH \xrightarrow{H_2O} + Na\,OA_c$$

Reacciones de Hidrólisis y sus características

Catalizador	Medio	Reacción Principal	Consumo de Catalizador	Subproductos	Control de Reacción	Comentarios de Aspectos Industriales	Tipo de Distribución Acetato Residual
Alcalino	MeOH	1	Muy Pequeño	MeOAc	Difícil	Economicamente bueno	Por bloques
	Agua	1			Velocidad muy rapida		
	MeOH	y 3	Pequeño	MeOAc			
				NaOAc	Difícil	Blancura y forma del alcohol polivinílico	Por bloques
	Agua ó Agua + Acetona	3	Equivalentes a la unidad de Acetato de Polivinilo	NaOAc Equivalente	Fácil	Proceso de recuperación NaOAc no es económico	Por bloques
Acido	MeOH	1	No	MeOAc	Fácil (reacción demasiada lenta)	Una pequeña proporción de uniones Acetal en la cadena del polímero	Al azar
	Agua	2	No	HOAc	Fácil (Reacción demasiada lenta)	Existe equilibrio químico: La recuperación del HOAc, no es económico.	Al azar

Hidrólisis Alcalina

Los catalizadores más importantes en la hidrólisis en escala industrial son el hidróxido de Sodio y el metóxido de Sodio.

Otros catalizadores alcalinos empleados en alcohólisis son el hidróxido de potasio, el metil carbonato de sodio, etóxido de sodio, carbonato de sodio, hidróxido de calcio é hidróxido de bario. El hidróxido de calcio se usa en la hidrólisis de dispersiones de acetato de polivinilo en presencia de metanol.

Al moler acetato de polivinilo sólido con Ba $(OH)_2$ $8H_2O$, la hidrólisis se lleva a cabo en ausencia de solvente o medio de suspensión. Sakaguchi y sus colaboradores investigaron el efecto de diferentes bases en la velocidad de hidrólisis del acetato de polivinilo en una mezcla de agua y acetona y encontraron que los valores de la constante inicial de velocidad Ko, de hidrólisis se encontraba en el siguiente orden(n-C4 H9) y NaOH > LiOH = NaOH = KOH ≥ CsOH.

Amonólisis

El amoniaco es usado como catalizador en la hidrólisis del Acetato de polivinilico para dar alcohol polivinílico de buena blancura, aunque la actividad catalítica es menor que la del hidróxido de sodio. El efecto del amoniaco en las propiedades del alcohol polivinílico usando cantidades catalíticas de hidróxido de sodio en la hidrólisis ha sido reportado en la literatura. Otras aminas usadas con metanol incluyen el $KNH_2 - NH_3$, monoetanol amina, metilamina y dimetilamina.

En estos sistemas se recuperan subproductos tales como acetamida, B-hidroxietil acetamida, metil acetamida etc., Okamura y Kamashita encontraron que la energía cinética de la amonólisis de acetato de polivinilo es de cerca de 7 Kcal mol y que el alcohol polivinílico se prepara principalmente por alcohólisis en presencia de amoniaco.

El acetato de metilo producido reacciona posteriormente como amoniaco, formado aceramido y metanol.

$$MeOAc + NH_3 \longrightarrow MeOH + AcNH_3$$

Hidrólisis Acida

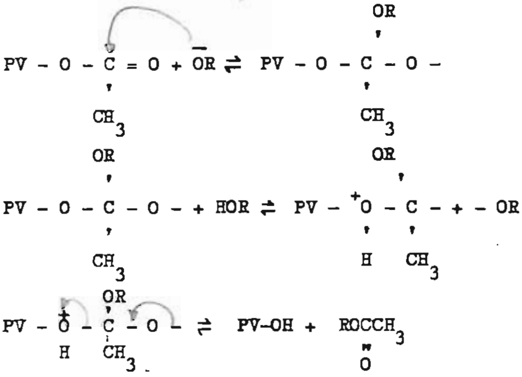
La alcohólisis acida del acetato de polivinilo con ácidos minerales en metanol ó etanol puede llevarse a cabo en un reactor estandard ó en un masticador a temperatura de ebullición a una velocidad mucho menor que la hidrólisis alcalina. En forma típica la reacción a escala industrial se completa en 48 ó 60 hr. a la temperatura de ebullición. Otros catalizadores empleados son ácido sulfúrico, ácido clorhídrico, ácido minerales con pequeñas proporciones de $HClO_4$ y cationes conteniendo SO_4.

Mecanismo de Reacción de la Alcohólisis.

En forma análoga el mecanismo de alcohólisis de ésteres orgánicos de bajo peso molecular, el primer paso en la reacción es un ataque en el átomo de carbono carbonilo del grupo acetato por el amión de alcohol (RO). La energía de activación puede considerarse como la energía requerida para atraer elanión al grupo carbonilo.

Los siguientes mecanismos están de acuerdo con los hechos conocidos.

Alcohólisis Alcalina

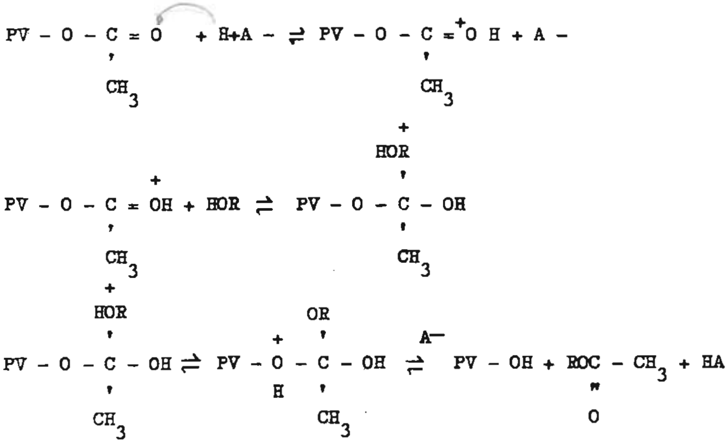


$$PV-O-\underset{CH_3}{C}=O+\overline{OR}\rightleftharpoons PV-O-\overset{OR}{\underset{CH_3}{C}}-O-$$

$$PV-O-\overset{OR}{\underset{CH_3}{C}}-O-+HOR\rightleftharpoons PV-\underset{H}{\overset{+}{O}}-\overset{OR}{\underset{CH_3}{C}}-+-OR$$

$$PV-\underset{H}{\overset{+}{O}}-\overset{OR}{\underset{CH_3}{C}}-O-\rightleftharpoons PV\text{-}OH+RO\underset{O}{\underset{\|}{C}}CH_3$$

Alcohólisis Acida.



$$PV-O-\underset{CH_3}{C}=O+H\text{+}A-\rightleftharpoons PV-O-\underset{CH_3}{C}={}^{+}O\,H+A-$$

$$PV-O-\underset{CH_3}{C}=\overset{+}{O}H+HOR\rightleftharpoons PV-O-\overset{\overset{+}{HOR}}{\underset{CH_3}{C}}-OH$$

$$PV-O-\overset{\overset{+}{HOR}}{\underset{CH_3}{C}}-OH\rightleftharpoons PV-\underset{H}{\overset{+}{O}}-\overset{OR}{\underset{CH_3}{C}}-OH\overset{A-}{\rightleftharpoons}PV-OH+RO\underset{O}{\underset{\|}{C}}-CH_3+HA$$

Sacaguchi, Nishino y Nita encontraron que, la adición de una pequeña cantidad de agua no afecta la velocidad de reacción al usar catalizadores alcalinos, pero con catalizadores ácidos la velocidad disminuye. Explicaron este fenómeno tomando el mecanismo de reacción encunta. La adición del proton, en el primer paso de la alcohólisis ácida parece ser afectada por la adición de agua, que posee una afinidad mayor por el protón.

La alcohólisis e hidrólisis de ésteres orgánicos no involucra grandes cambios de energía y similarmente la alcohólisis ó hidrólisis del acetato de polivinilo es solo ligeramente exotérmico.

Velocidad de reacción de la hidrólisis.

Sakurada y sus colaboradores encontraron que la velocidad de la reacción se eleva conforme se desarrolla la hidrólisis, dependiendo de la absorción del catalizador alcalino en los grupos OH adyacentes a los grupos de acetato. La velocidad de reacción se puede escribir.

$$dx/_{dt} = Ko \quad (1 + mX) \quad (1 - x)$$

donde x es el grado de hidrólisis en fracción mol Ko es la velocidad inicial de reacción y m es el orden del efecto auto catalítico de la hidrólisis de la ecuación anterior.

$$dx/_{dt} \quad (1/1 - x) = ko + Ko \; m^{x}$$

De acuerdo a esta ecuación, si se obtiene X a un tiempo t, Ko y m se pueden calcular de la ecuación. Los valores de Ko y m en las reacciones de hidrolisis, mostradas en la tabla siguiente, fueron calculadas asumiendo que $Ko \propto$ (catalizador)

Catalizador	Solvente	Ester	Método de Reacción	T OC
NaOH	M e O H 100	Acetato de Polivinilo	1	30
		Acetato de Polivinilo	2	30
	Acetona (73) + Agua (25)	Iso - PrO Ac	2	30
		C_2H_5 O Ac	2	30
	MeOH(90)+H_2O(10)	Acetato de Polivinilo	1	30
		Acetato de Polivinilo	2	30
		CH_3 O Ac	2	30
	E+OH(90)+H_2O(10)	Acetato de Polivinilo	1	30
		Acetato de Polivinilo	2	30
		CH_3 OAc	2	30

Ko L/mol min	K85 L/mol min	m	E Kcal/mol
0.347	4.71	13.7	12.5
0.366	13.4	41.9	11.8
0.572			
3.48			11.2
0.508	5.86	12.4	12.2
0.009	0.104	12.4	18.8
0.046			
			18.7
0.852	9.61	12.1	12.6
0.149	1.68	12.1	15.2
0.471			14.9

En catálisis Acida

Catalizador	Solvente	Esteres	Metodo de Reacción	T O C	Ko L/mol min	K85 L/mol min	m	E Kcal/mol
HCL	MeOH(100)	Acetado de Polivinilo	1	50	7.02×10^{-3}	49.4×10^{-3}	7.1	13.2
HCL	MeOH90+H$_2$(10)	Acetato de Polivinilo	1 + 2	50	1.57×10^{-3}	11.05×10^{-3}	9.7	13.8

Método de Reacción 1 = alcohólisis, 2 hidrólisis directa

K$_{85}$ Constante de velocidad a 85% de conversión

Influencia de las condiciones de hidrólisis en las propiedades del alcohol polivinílico.

Catalizadores

Alcalinos

Sakaguchi y sus colaboradores investigaron la influencia de la naturaleza del catalizado en la distribución de los grupos acetato residuales en el alcohol polivinílico parcialmente hidrolizado encontrando que este es por bloques y depende del catalizador en el siguiente orden (10h) KOH (n-C$_4$H$_9$NaOH).

Acidos

La secuencia de la distribución en la cadena del alcohol polivinílico parcialmente hidrolizado obtenido por hidrólisis ácida es a diferencia del obtenido por hidrólisis alcalina al azar.

Solvente

El acetato de metilo es mejor solvente del acetato de polivinilo que el metanol; por lo cual fué usado como medio para la hidrólisis del acetato de polivinilo, junto con el metanol en las primeras técnicas de producción de alcohol polivinílico.

Más recientemente, se encontró que el contenido de acetato de metilo en la mezcla de acetato de metilo y metanol afecta considerablemente la distribución en la cadena de los grupos acetato, haciendo que esta sea en forma más marcada por bloques.

Trabajo de laboratorio para la obtención de Alcohol Polivinílico

Con el propósito de obtener un alcohol polivinílico con características semejantes a las encontradas en productos comerciales y una vez realizada la reacción de polimerización del acetato de polivinilo para la elaboración de la materia prima requerida, fueron probadas diversas técnicas reportadas en la literatura y que se pueden encontrar en la sección bibliográfica de la presente tesis, que incluyen tanto métodos de hidrólisis ácida como alcalina encontrandose finalmente un procedimiento adecuado para este fin.

Métodos Experimentados

Entre los métodos experimentados, encontramos los reportados en el Chemical Abstracts y son los siguientes:

(C A Vol 63, 15007, 1965)

(C A Vol 50, 13505, 1956)

(C A Vol 53, 1845, 1959)

(C A Vol 55, 6934, 1961)

El método empleado se originó a partir del reportado bajo los siguientes caracteres: (Vol 50, 17531, 1956) al cual le fueron realizadas las modificaciones que se encontraron pertinentes.

Método. Selecccionado para la obtención de alcohol polivinílico

Reactivos:

Metanol	147.5 ml
Acetato de Polivinilo	50 gr
Hidróxido de Sodio (Sol Metanólica 50%)	8.5 ml

Material de Laboratorio

Reactor de vidrio

Agitación mecánica o magnética

Perilla de calentamiento

Kitasato

Embudo

Procedimiento

Disuelva 60 gr. de acetato de polivinilo obtenido mediante la polimerización en emulsión, en 147.5 ml de metanol mediante el uso de agitación y calentamiento a una temperatura de 40-50°C Una vez realizado la disolución y manteniendo la temperatura de 40°C, adicionar la solución metanólica de hidróxido de sodio al 50%, continuando con la agitación, después de 10 minutos aproximadamente comenzar´a precipitar un sólido blanco de alcohol polivinílico, el cual se deja reaccionando por 15 minutos más, el producto es filtrado y lavado varias veces con metanol, y finalmente se deja secar en un Kitasato y un embudo Buckner mediante el uso de vacío. El producto obtenido será un polvo blanco y fino con 88+2% de hidrólisis.

Conclusiones

El producto obtenido en la serie de experimentos realizados utilizando el método anteriormente descrito es un sólido, con las características físicas y químicas requeridas, a diferencia de una gel producida al utilizar los demás procedimientos, lo cual constituye una ventaja evidente, en cuanto a la facilidad conque se produce el producto final y la posibilidad de aplicar los métodos analíticos tendientes a la comprobación de sus propiedades y la repetitividad de la reacción.

Métodos Analíticos Empleados.

Una recopilación completa de los métodos analíticos estandardard oficiales empleados en el Japón (K 6726 - 1965) puede encontrarse en el Apéndice 3 del Polivinyl Alcohol, Proporties And Aplications. C.A. Finich John Wiley And Sons-1973 en lo concerniente a contenidos de volátiles, Hidrólisis, contenido de Acetato de Sodio, Grado promedio de polimerización contenido de cenizas, Pureza, tamaño de partícula, viscocidad, claridad y pHy que debido a su magnitud no pueden ser reproducidos en la siguiente tesis.

Además de los métodos anteriores, fueron empleados para la comprobación del % de alcohol polivinílico y % de acetato de polivinilo los métodos reportados en el Analitycal Chemistry of Polymers Parte 1 de Kliney que a continuación son detallados:

% en peso de alcohol polivinílico

Pasar 1.5 de la resina en un matraz de bola de 250 ml. Agregar mediante una pipeta 20 ml de una mezcla de 880 ml de piridina recién destilada y 120 ml de anhidrido acético, colocándole un refrigerante y un tubo de secador y mantenerlo en un baño a 98±2 °C por 4 horas. Remover el Aparato del baño y-dejarlo enfriar. Añadir 25 ml de metil isobutil cetona y 5 ml de agua y - colocarlo nuevamente en el baño por 30 minutos a 98±2 °C Añadir 35 ml de metil isobutil cetona y titular con una solución de hidróxido de potasio 0.5N añadiendo fenolftalaina como indicador.

Realizar el mismo procedimiento con una muestra testigo pero omitiendo la resina.

Cálculos

% en peso de alcohol polivinílico = $(B - A)\, N \times 2.933$

donde

A = ml de K O H 0.5 N gástados en la titulación de la muestra

B = ml de K O H 0.5 N gastados en la titulación del testigo

N = Normalidad de la solución de K O H.

% en peso de Acetato de Polivinilo

Colocar 2.15 g de muestra en un matraz de 500 ml y disolverla en una mezcla de 30 ml de piridina y 20 ml de metanol. Añadir unas gotas de Fenolftalaina y titular la mezcla con una solución 0.5 N de K O H a una coloración rosada permanente por 1 minuto. Llevar a cabo el mismo procedimiento con un testigo omitiendo la resina.

Añadir 25 ml de hidróxido de potasio 0.5 N mediante una bureta a ambas reacciones. Colocar un refrigerante y calentar en un baño a 98 ± 2°C durante 1 hora. Enjuagar el material empleado con una pequeña cantidad de agua destilada. Añadir una gotas de fenolftaleina y titular ambas reacciones con ácido clorhídrico 0.SN.

% en peso de acetato de polivinilo = $2\ (A - B)$

A = ml de ácido clorhídrico 0.5N empleados en el testigo

B = ml fr ácido clorhídrico 0.5N empleados en la muestra.

Método de Solución de Alcohol Polivinílico

Adicionar la resina a un recipiente conteniendo agua a temperatura ambiente, en pequeñas porciones, manteniendo una agitación que permita al material dispersarse uniformemente. Cuando la dispersión sea completa, calentar la mezcla a 65 - 100°C, obteniéndose una disolución completa en 30-60 minutos.

Resultados

Los resultados obtenidos mediante la aplicación de los métodos antes mencionados, han sido recopilados en la tabla siguiente:

Alcohol Polivinílico	Datos	Viscocidad	Hidrólisis % Mol	Pureza %	Contenido de volatiles
Comercial	Reportados en literatura	5 ± 1	88 ± 2	Sobre 94	Bajo 5
Comercial	Verificación de datos	10 - 13	88 ± 2	N.D.	Bajo 5
Obtenidos en Laboratorios	Obtenidos en Laboratorios	8	88 ± 2	N.D.	5.2

P^{H**}	Contenido de Cenizas %	Peso específico Aparente 8/cm^3	Apariencia	Solubilidad
5 - 8	Bajo 0.5	0.6	Polvo blanco con ligera tonalidad crema	Soluble en agua fría + Solubilidad en agua caliente
5 - 8	Bajo 0.5	0.6	Polvo blanco con ligera tonalidad crema	Soluble en agua fría + Soluble en agua caliente
6	Bajo 0.53	0.67	Polvo blanco con ligera tonalidad crema	Soluble en agua fría + Soluble en agua caliente

* Viscocidad medida en una solución acuosa al 4% y a 20°C con un viscocímetro Brookfield

** P H medida en una solución acuosa al 4% y a 20°C.

Estabilidad Térmica

Si el alcohol polivinílico obtenido en el laboratorio se calienta a 160°C por largo tiempo, aparece gradualmente una coloración amarilla. Por encima de los 200°C el material se colorea rápidamente en un tono café obscuro. Arriba de 300°C el material se descompone completamente.

Experimentos de Acetilación

Con el objeto de obtener el acetato de polivinilo original para las diferentes muestras de alcohol polivinílico, fué desarrollada la presente técnica, siendo realizadas con ella diversos experimentos.

Reactivos

a) 0.4_g de alcohol polivinílico

b) 50 ml de tetracloro etileno

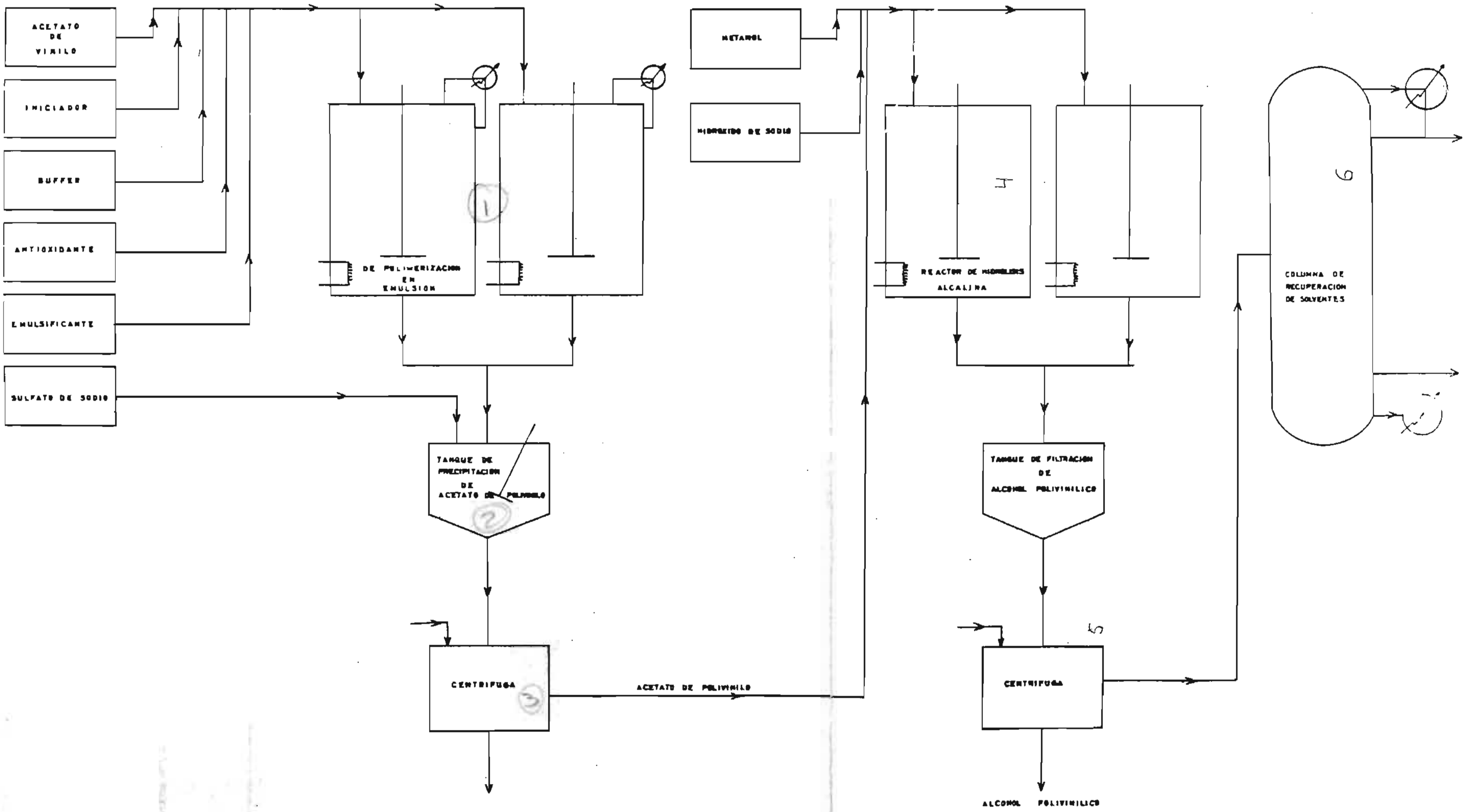
c) 0.1_g de $BF_3/E +_2O$

d) 1 ml de AC_2O

Desarrollo

Se colocan a, b, c y de en una bola de 250 ml previsto de un agitador magnético y un baño calibrado a 30°C durante 7 horas. El producto se vierte sobre eter de petróleo y se realizan varias lavadas usando Hexano.

diagrama de flujo



BALANCE DE MATERIA POR TONELADA DE ACETATO DE VINILO

EQUIPO	I C	II	III	IV	V	VI p	VII Q
ACETATO DE VINILO	1,000						
CATALIZADOR Y EMULSIFICANTES	40.8	40.8	40.8				
ACETATO DE POLIVINILO		1000	1000	1000			
SULFATO DE SODIO		5	5				
METANOL				2,334			
HIDROXIDO DE SODIO				170			
ALCOHOL POLIVINILICO					552.4	552.4	
ACETATO DE SODIO					124.6	124.6	
METANOL ACETATO DE METILO					2657		2657

b) CALCULO DEL EQUIPO Y COSTOS DEL MISMO

Diseño del reactor para polimerización

Los reactores usados para la polimerización de monómeros son relativamente simples en principio, pero su diseño requiere la consideración de numerosos factores.

La reacción de polimerización, puede ser llevada a cabo tanto en emulsión como en suspensión en estos reactores, tomando como base un sistema - intermitente.

El rango de variables consideradas en el desarrollo del sistema de reacción incluyen, el tamaño del reactor, los materiales de construcción, la relación agua-monómero usada. la cantidad y el tipo de iniciador, la cantidad- y tipo de surfactantes, y las temperaturas de los reactivos y los fluidos - usados como enfriamiento en la chaqueta.

Todos los factores antes mencionados tienen efecto significativo en los costos de operación. De especial importancia, es el hecho que ciertas combinaciones de las condiciones anteriores, pueden resultar en un sistema de reacción en el cual las temperaturas nos sean debidamente controladas.

Diseño básico del reactor. Antes de discutir las posibles condiciones de operación y del reactor, consideraremos el diseño básico del reactor.

Se requiere producir según los estudios económicos en 330 días hábiles- 6.73 Ton/días de alcohol polivinílico, para lo cual se necesita una produc - ción de 12.18 Ton/día, de acetato de polivinilo, que tomando en cuenta la - duración del proceso de 9 horas, resultan 2.66 ciclos por día, con una pro - ducción de 4.58 Ton. Ciclo, dando un 10% de margen por imprevistos, resulta- un requerimiento diario de 5.03 Ton. El resultado anterior representa un 55% en peso de la carga total que estará constituida por 9.16 Ton/ciclo.

La densidad de la emulsión a la temperatura de reacción es de 1.08 gr/ cm^3 y a 20°C es de 1.092 gr/cm^3 por lo cual:

$$9160 \text{ Kg. } \times \frac{1}{1.08 \text{ Kg/L}} = 8482 \text{ L}$$

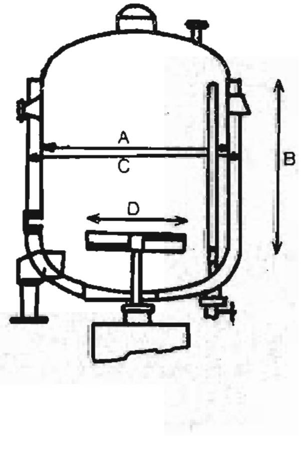
Sí

Además es requerido un 20% de espacios libres por lo cual el volumen total requerido es de 10,179 L.

Datos típicos reportados en la literatura para dimensiones de reactores de este tipo son los siguientes:

Volumen de 1	Potencia de 1	Dimensiones			
		A	B	C	D
1 Reactor L	Agitador en H.P.	Diámetro Interior m	Largo m	Diámetro exterior m	Diámetro del Agitador m
18 925	50	2.75	2.75	2.90	1.143
28 387.5	75	3.20	3.20	3.35	1.25
37 850	100	3.50	3.50	3.66	1.32
56 775	150*	3.66	4.88	3.81	1.30*
75 700	200*	3.66	6.40	3.81	1.37*

* Dos agitadores
The Brighton Co.



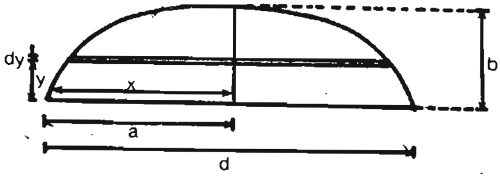
Según lo anteriormente establecido se procedió al cálculo del volumen y dimensiones del reactor, tomando la determinación de trabajar con dos reactores con la mitad de la capacidad cada uno, debido a la conveniencia de poder trabajar a la mitad de la capacidad en caso de desperfecto de alguno de ellos y evitar así el paro de la planta de alcohol polivinílico.

Los reactores seleccionados serán del tipo del diagrama anterior con las siguientes dimensiones en su sección cilíndrica.

A	B	C	$\frac{(A)^2}{2}$	V
1.71 m	1.71 m	1.86 m	.7310	$3.927 m^3$

Un recipiente cilíndrico cerrado a ambos lados por tapas elípticas tiene un volúmen igual al volumen de la sección cilíndrica más dos veces el volumen contenido en una de las tapas.

Las ecuaciones para el volumen de una tapa elíptica teniendo una relación 2:1 entre el eje mayor y el eje menor como es el seleccionado estan dadas por:



La ecuación de una elipse

$$\frac{x^2}{a^2} + \frac{4^2}{b^2} = 1$$

Para una tapa elíptica

$$a = 2b$$

Sustituyendo y rearreglando

$$\frac{x^2}{4b^2} + \frac{2}{b^2} = 1 \quad \text{ó} \quad x + 4\ y = 4b^2$$

Resolviendo para x^2

$$x^2 = 4b^2 - 4\ y^2 = 4\ (b^2 - y^2)$$

Diferenciando el volumen

$$d v = A\, d y = \pi x^2 \, d y$$

Integrando

$$V = \int_0^b \pi x^2 \, d y = 4 \pi \int_0^b (b^2 - y^2)\, d y = 4 \pi \int_0^b b^2\, d y - 4 \pi$$

$$\int_0^b (b^2 \quad y^2)\, d y \qquad V = 4 \pi \left[b^2 y - y^3 \right]_0^b = \frac{8}{3} \pi b^3 = \frac{\pi a^3}{3}$$

Sustituyendo por el valor de $a = 0.855$ m

$$V = \pi (0.855)^3 = 0.6945 \ m^3$$

Como son dos tapas $V = 1.309 \ m^3$ por las dos tapas

El volumen total está d

$V_T = 3.927 \ m^3 + 1.309 \ m^3 = 5.236 \ m^3$ que llena los requerimientos de volumen.

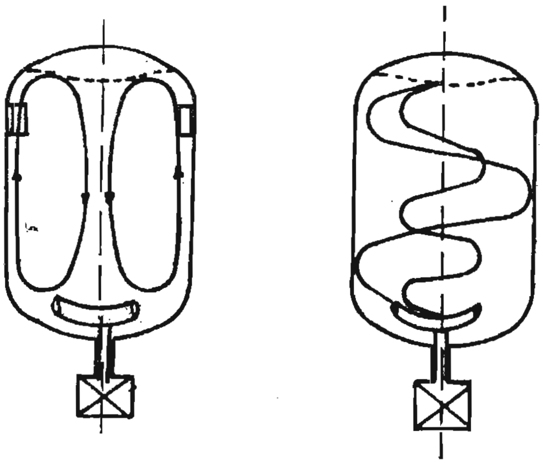
Agitación

Se provee de agitación para dispersar el monómero (y), posteriormente al polímero a traves de la fase acuosa. Ocacionando también una buena transferencia de calor.

En la construcción de los Agitadores, para este tipo de reactores hay dificultades inherentes que no deben ser pasadas por alto. Los agitadores no pueden colocarse, como es usual en la parte superior, debido a los problemas ocacionados por la flecha, demasiado larga y que permite la adhesión del polímero con todos los problemas ocacionados por este suceso. En la experiencia de laboratorio, se procurá tener un agitador, que presentara la menor área posible dando éste el mejor resultado.

Una posible solución a este problema, es que el agitador entre por el fondo. En este caso el elemento de agitación dentro del reactor y cercano al fondo del mismo es movido por una flecha corta relativamente delgada, con la unidad motriz localizada bajo el fondo del reactor. Agitadores del tipo de paleta son comunmente usados en este tipo de reactores.

La acción de mezclado de estos reactores, está basado en una circulación típica en el reactor, consistente en una corriente ascendente, una parte periférica y una corriente descendente. Claro, que además de la acción anteriormente descrita se observa un flujo rotacional que superimpone al anterior.



En un reactor con un buen mezclado, el tiempo requerido para el proceso de la corriente de subido, la periférica y la descendente debe ser corto.Los valores recomendados de intervalo de tiempo serán de 30 a 100 segundos.

Un punto crítico en la entrada del agitador por el fondo del reactor, es el sello de la flecha.Comunmente se usan dos sellos mecánicos, en diseños modernos, se provee de un sello adicional para emergencia. El sello de emergencia permite el reemplazo del sello mecánico, aun cuando el reactor este lleno.

En un número de polimerizaciones, particularmente en la polimerización de cloruro de vinilo y acetato de vinilo, el elemento rotatorio debe protegerse para evitar la difusión del monómero a la corriente de aceite del sello y se polimerise ahí, dejando el agitador fuera de servicio.

Si

Cálculo de la potencia por el agitador y sus dimensiones.

Los requerimientos de potencia están dadas por la ecuación dimensional de White y sus colaboradores.

$$hp = 1.29 \times 10^{4}\ D,^{1.1}\ L^{2.72}\ N'^{2.86}\ y^{0.3}{}_{2}{}^{0.6}\ \mu'^{0.14}\ \rho^{0.86}$$

donde y = al largo del agitador en pies

N' = velocidad rps

U' = viscocidad en lb/ft x S_{e_g}

Esta ecuación es útil para agitadores de paleta, localizados en el centro con una longitud >0.30; y una altura < L/G.

En nuestro caso, usando el mismo factor reportado en la literatura, en que L = 0.416 D;

$$L = 0.416 \times 171 cm \times \frac{1 \text{ pulgada}}{2.54 \text{ cm.}} \times \frac{1 \text{ pie}}{12 \text{ pulgadas}} = 2.33 \text{ pies ó } 71.065 \text{ cm.}$$

$$h < L/6 = \frac{71.065}{6} = 11.85 \text{ cm}$$

Cálculo de la potencia requerida

$$hp = 1.29 \times 10^{-4} (5.6102)^{1.1} (2.337)^{2.72} (4.16)^{2.86} (0.346)^{0.3} (3.92)^{0.6} (1.6093)^{0.14} (68.0316)^{0.86}$$

$$hp = 1.29 \times 10^{-4} (6.66) (10.063) (58.996) (0.7273) (2.27) (1.069) (37.68) = 34 \text{ hp}$$

Material de construcción para el reactor

La selección del material material utilizado, para la construcción de los reactores de polimerización es de la mayor importancia cuando se consideran los valores del coeficiente total de transferencia de calor (U) - obtenidos durante las polimerizaciones. Dentro de las informaciones reportadas por varias compañías industriales están las siguientes:

Reactor	U BTU $(nKf\text{-}1^2)$ (OF)
Vidriado	40-53
Vidriado	40-60
Acero inoxidable	50-110
Acero inoxidable	50-110

El material seleccionado para nuestros reactores será de acero inoxidable 316.

Cálculo del grosor de la placa de acero inoxidable para el reactor de - polimerización.

Para la presión atmosférica y siguiendo el método expuesto en el Brownell y utilizando la gráfica 15 para determinación del grosor de la sección cilíndrica construida de aceros austeníticos 18 cr- 8 Ni + Mo tipo 316 del código - ASME 1956. El grosor de la placa será de 5/16" ó 7.9375 mm.

Para las tapas elípticas se utilizó la figura 2.11 del Unfired Pressura - Vessels pag. 37 de Chose resultando tambien de 5/16" ó 7.93.75 mm.

Cálculo del Area de Enfriamiento

Sin importar el tamaño del reactor, la transferencia de calor es llevada a cabo principalmente a través de la pared del reactor. Se utiliza agua normalmente como fluido de transferencia de calor. Durante los primeros pasos del - proceso intermitente se vea agua caliente o vapor para calentar el monómero a la temperatura de reacción. Durante las etapas de polimerización el agua fría remueve el calor exotérmico de polimerización.

El control de la temperatura de la mezcla reaccionante es el factor principal en la operación de las polimerizaciones en suspensión ó en emulsión. Cada reactor debe ser diseñado de manera que el calor generado por la polimerización puede ser transferido al agua de la chaqueta con un máximo de transferencia de calor. Las velocidades de polimerización varian durante el proceso. De aquí que debemos considerar el periodo crítico cuando el calor de polimerización es más alto.

Consideramos primero, la velocidad de transferencia de calor del reactor.

$$q = UA\ (\Delta T) = UA\ (TM - TJ) \qquad (1)$$

La velocidad máxima de calor desprendido durante el proceso de polimerización puede ser calculada mediante:

$$q\ max = \frac{M\ (\Delta H\ r)\ FC}{t} \qquad (2)$$

El peso del monómero M en le ractor depende eh el volumen de la mezcla agua-monómero y en la relación de Agua a monómero utilizada.

$$M = \frac{V}{R/\rho\ agua + 1/\rho\ monómero} \qquad (3)$$

Combinando las ecuaciones 1, 2 y 3 y despejando el AT requerido para q max da como resultado.

$$AT = \frac{V}{R/\rho\ agua = L/\rho\ monómero} \quad \frac{\Delta Hr\ FC}{t\ U\ A.}$$

Nomenclatura

A	Superficie de transmisión de calor pies
C	Fracción del monómero polimerizado durante el proceso adimensional.
F	Relación entre la velocidad máxima de generación de calor al valor promedio adimensional
ΔHr	Calor de polimerización
M	Cantidad de monómero en el reactor
q	Velocidad de transferencia de calor BTU/lb
R	Relación en peso de agua a monómero
Ri	Resistencia a la transferencia de calor de la mezcla reaccionante a la pared interna del reactor.
Ro	Resistencia a la transferencia de calor de la pared externa al fluido en la chaqueta h (
R pared	Resistencia a la transferencia de calor a través de la pared del reactor.
Tj	Temperatura promedio del fluido en la chaqueta °F
Tm	Temperatura de la mezcla reaccionante °F
ΔT	Diferencia total de la temperatura Tm-Tj °F
t	Tiempo de polimerización en el proceso intermitente hr.
U	Coeficiente total de transferencia de calor BTU/
V	Volumen de trabajo del reactor gal
ρ monómero	Densidad del monómero a las condiciones de reacción lb/gal
ρ agua	Densidad del agua a las condiciones de reacción lb/gal

V = 1344.64 gal

$$R = \frac{W\ agua}{W\ Monómero} = 0.5$$

$$agua = 61.88\ lb/pie^3 \times \frac{pie^3}{7.481\ gal} = 8.27\ lb/gal$$

$$monómero = 0.885\ Kg/L \times \frac{1\ lb}{.454\ Kg} \times \frac{L}{.2642\ gal} \quad 7.37\ lb/gal$$

$$U = \frac{1}{1/ho \quad + \; 1/hi \quad + L/K}$$

L = grosor del metal
K = Conductividad térmica

$$U = \frac{\qquad}{1/500 \; + \; 1/150 \; + \; .3126/105} = 86.4$$

$$Hr \; = 21.3 \text{ K cal/g mol} \; \times \frac{1800 \text{ BTU/lb mol}}{\text{K cal/g mol}} \times \frac{1 \text{ lb mol}}{86.09 \text{ lb}} = 445.34 \text{ BTU}/_{\text{lb}}$$

Valores de C varian de 0.6 a 0.9 el valor de FC es de 1.8

$$\Delta T = \frac{1344.64}{.5/_{8.27} + 1/_{7.37}} \qquad \frac{445.34 \quad \times \quad 1.8}{7 \quad (\; 86.4 \;)}$$

$$T = \frac{9\ 085\ .69}{A}$$

Si se dispone de agua de enfriamiento a 20°c

$$AT = 82.6$$

$$A = \frac{9\ 085.69}{82.6} = 109.99 \text{ pie}^2 \text{ ó } 102184 \text{ cm}^2$$

Cáculo del área disponible en el reactor

A cilindro = π x D x L = 11 x 171 x 171 = 91863.31

Aréa de 1 tapa elíptica con una relación de ejemayor a eje menor de 2 : 1

Ecuación de la elipse

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$

$$a = 2b$$

Sustituyendo

$$\frac{x^2}{4b^2} + \frac{y^2}{b} = 1$$

de donde

$$x^2 = 4b^2 - 4\,y^2 = 4\,(b^2 - y^2), \quad y \quad x = 2\sqrt{b^2 - y^2}$$

$$d\,A = P\,d\,y$$

$$d\,A = 2\pi r d\,y$$

$$\int_0^b dA = \int_0^b 2\pi\, x\, d\,y = 4\,\pi \int_0^b \sqrt{b^2 - y^2}\, dy$$

$$\int_0^b d\,A = 4\pi\, \frac{b}{2}\sqrt{b^2 - b^2} + \frac{b^2}{2}\ \text{arc Sen}\ \frac{b}{b} + 4\pi\, \frac{0}{2}\, b^2 - 0 + 0$$

$$A = 2\,\pi\, b^2\ (1.57)$$

$$b = .42\,75\ \text{m} = 42.75\ \text{cm.}$$

$$A = 2\pi\,(\,42.75\ \text{cm}^2\,)\ (1.57) = 18028.17\ \text{cm}^2$$

Area total = 91 863.31 + 18 028.17 = 109,891.48 Sí

En la práctica es común utilizar equipo de enfriamiento adicional,que sirve además como equipo de seguridad. En la práctica de laboratorio se usé un condensador montado en la parte superior del reactor, lo cual es usual en reactores comerciales, debiéndose tomar las siguientes recomendaciones.

a) Gases inertes tales como el Nitrogéno interferirán ya que tenderán a formar un colchón gaseoso en el condensador.

b) El catalizador usado no deberá ser volatil, para evitar la polimerización en el condensador.

c) Si la reacción produce espuma, el enfriamiento solo puede ser utilizado en proporción limitada.

d) En cierta clase de polimerizaciones, la mezcla del material reflujada - con el reaccionante presente problemas.

Además del factor seguridad, la mezcla reaccionante está siempre reflujando por lo que es necesario el diseño de un condensador tomando en cuenta la - primera recomendación que es la que nos afectaría en este caso.

Cálculo de un condensador de Retorno "Rápido" de 20.32 cm. de diámetro - interno 1 paso por el envolvente, 1 paso por los tubos teniendo 37 tubos de - 1.905 cm. de diámetro externo 16 BWG de 152 cm. de largo en arreglo triangular de 2.54 cm. con una $U_d = 26.86$ una $U_c = 92$ Rd = .026.

Experimentalmente se encontró que la cantidad de monómero que refluja deba ser mínimo, pues el monómero debe ir polimerizándose conforme se esta agregando pero como medida de seguridad de optó diseñar el condensador para que en un - dado caso un 40% del acetato de vinilo se refluje.

Balance

Son agregados 2515 Kg. de monómero de acetato de vinilo durante 6 horas - por lo tanto se agregan 419 Kg. tomando el 40% descrito anteriormente habrá - que condensar 168 Kg/hr.

$$\frac{168\ \text{Kg/hr} \times \text{lb}}{.454\ \text{gr.}} = 370\ \text{lb/hr}$$

Datos indirectos

Acetato de vinilo punto de ebullición 63° (p = $88^{\text{cal}}/\text{gr.}$

$$88^{\text{Cal}}/_{\text{gr.}} \times 1.8\ \frac{\text{BTU/lb}}{\text{Cal}} = 158.4\ \text{BTU/lb}$$

1 Balance de calor

Q acetato = 370 lb/hr x 158.4 BTU/lb = 58 608 BTU/hr

QW = 1831.5 x 1 (100-68) = 58608 BTU/hr.

$$AT = LMTD = \frac{t2 - t1}{\ln\ T2/t1} = \frac{(T1 - t2) - (T2 - t1)}{\ln\ (T1 - t2)/ T2 - t1)}$$

Fluido Caliente			Fluido Frío	
T1	145.4°F	Temp.max.	120°F	t2
T2	145.4°F	Temp.min.	68°F	t1

2 $$T = \frac{25.4 - 77.4}{\ln\ 25.4/_{77.4}} = \underline{60.0}$$

3 Tc y Fc el uso de las temperaturas promedio será satisfactorio.

Fluido frío: Por el envolvente agua:

4 $as = 1D \times C' \ B/_{144\ pie}$ B = DI del envolvente mas.

$B\ min = \frac{\text{DI del envolvente ó 2"}}{5}$

$= 8 \times 0.25 \times 6/_{144 \times 1.0} = 0.083$

$GS = W/as = 1831.5\ 5/.083 = 22066$

a t a = 84

$= 0.84 \times 2.42 = 2.03\ ^{lb}/_{pie}\ (hr)$

$De = 0.73/12 = 0.0608$

$Res = De\ Gs/ = 0.0608 \times 22066/_{2.03} = 660$

JH= 14 Fig. 28

$k = 0.353\ BTU/hr\ pie^2\ (°F/pie)$

$C\mu/k)\ ^{1}/_{3} = 1 \times 2.03/.353 = 1.8$

$hO = jh \dfrac{K}{De} \left(\dfrac{C\mu}{K}\right)^{1/3}$

$ho = 14\ (0.353 \times (1.8)/.0.608) = 14$

$U_D = 26.86$

$A = Q/UD\ \Delta T$

$A = 58608/27(60) = 36.17$

$A = 0.1963 \times 5 = 0.9813 \times 37 = 36.32$

$h\,i\,o = 240$ asumiendo

$$t\,w = 84 + \frac{240\ (145.4}{240 + 14\ b} - 84)$$

$t\,w = 120.$

$$Tf = \frac{145.4 + 120}{2} = 133\ °F$$

kf = 33 x 10 calorías/(cm) (seg) (°C)/cm

$33 \times 10^{-5} \times 10^{-3} \times 100 \times 3600 = 01188$ K cal/m^2 hr °C/m y $\dfrac{\text{I BTU/hr pie}^2\,°\text{F/pi}}{1.49\ \text{Kcal}/m^2\text{hr}^{oC}/m}$

$\mu f = .3 \times 2.42 = 0.726$

$\rho f = .94 \times 62.5 = 58$

$D = 0.62/12 = 0.0517$ ft

$G' = 370/\pi \times 37 \times 0.0517 = 62\ ^{lb}/$hr pie lineal

$$Re\ f = 4(62)/_{.726} = 342$$

$$h\ i = .27\ \underline{(.08)^3 \times 58 \times 4.17 \times 10^8}\ ^1/_3 = 299.43$$
$$.726$$

$$300 \times 0.62/075 = 248$$

$$Uc = \frac{248\ (146)}{248 + 168} = \frac{36208}{394} = 92$$

$$Uc = 92$$

$$UD = 27$$

$$Rd = \frac{92-27}{27(92)} = \frac{65}{2482} = 0.026$$

Pérdidas por presión en los tubos.

$a'f = 0.302$ pulgadas^2

$a\ T = 37 \times 0.302/144 \times 1$

$G\ t = 370/0.78 = 4743.3$

$= 0.21$ lb/fthu

$D = 0.62/12 = 0.0517$ pie

$$Re = \frac{0.0517\ (\ 4743\ )}{1021} = 11677.0$$

$f = .00031$

$$= \frac{86.1}{359\ (605.4/_{492})} = 0.195\ \text{lb/pie}^3$$

$S = 0.195/62.5 = 0.00312$

$$\Delta PT = \frac{1}{2} \; \frac{.00031 \times 22287841 \times 2}{5.22 \times 10^{10} \times 0.0517 \times 0031}$$

$\Delta PT = .0016$ psi

Envolvente

Para Re = 660

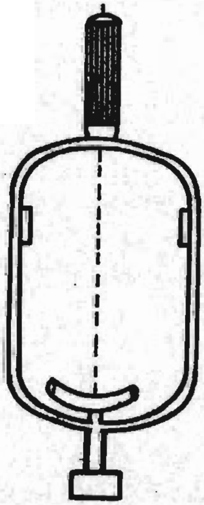
$f = 0.0044$

$N + 1 = 122/_{B} = 10$

$DS = 8/12 = .666$ ft

$$\underline{\Delta PS} = \frac{.0044 \times (22066)^2 \times .666 \times 10}{5.22 \times 10^{10} \times 0.0792 \times 1.0 \times 1.0}$$

$\underline{\Delta PS} = 3.45 \times 10^{3}$ psi.



Resumen

Limpieza del reactor

Con la gran mayoría de polimerizaciones, esto es de gran importancia. En reactores grandes, la limpieza manual de las paredes internas es menos económica que los métodos mecánicos y químicos. En la limpieza manual con herramientas raspadoras, es necesario eregir un andamio en el reactor ó introducir uno. Los operarios puedan pararse en el andamio y trabajar con agua que drene el reactor conforme se proceda con la operación de limpieza.

La limpieza mecánica, que pueda ser automotizada requiere agua a presión- Bombas de alta presión (50 a 300 atm.) son requeridas en este proceso junto con cabezales rociadores que son movidos hacia arriba y hacia abajo (similares a los empleados para la limpieza de tanques). La presión del agua romperá cualquier depósito de material dentro del reactor. De cualquier manera el reactor debe diseñarse previniendo la existencia de espacios muertos que puedan ser limpiados con el agua a presión. El agua a presión también puede contener aditivos al final del ciclo de limpieza para permitir cierto acondicionamiento del reactor para la siguiente polimerización.

Reciéntemente, se han desarrollado métodos para la limpieza de reactores de polimerización contaminados con depósitos en las paredes. Estos métodos tienden también a la automatización. Solventes calientes con la capacidad adecuada para disolver ó desprender el material adherido se están empleando. Las presiones utilizadas en este método son menores a las empleadas en la limpieza con agua.

Se usa el solvente, hasta que se vuelve viscoso debido al polímero disuelto. Después deberá ser tratado con equipo separado, es decir deberá ser liberado de los sólidos que contiene. Para este propósito metodos de destilación, precipitación y filtración pueden ser utilizados, dependiendo de la estabilidad térmica y la solubilidad. La toxicidad y inflamabilidad de algunos solventes presentan problemas, ya que se desea prevenir purgas con gases inertes que son costosos.

Las trazas de solvente deberán ser removidas antes del nuevo ciclo de polimerización, si el solvente interfiere o afecta la reacción de polimerización.

En nuestro caso se encontró útil el uso de agua a presión con lo que los residuos de monómero eran removidos fácilmente si se realizaba esta operación en forma inmediata a la terminación de la reacción y la descarga del mismo.

Seguridad

A causa de la gran cantidad de monómero manejado en un reactor, medidas especiales de seguridad se deben realizar para prevenir ó minimizar el riezgo de que la reacción se salga de control.

Obviamente un prerequisito para la operación segura de un reactor es el diseño liberal del sistema de enfriamiento y agitación. Pero se debe tomar - en cuenta, que durante condiciones anormales de operación, el sistema de enfriamiento ó de agitación ó ambos puedan fallar ó ser inadecuados. Por ejemplo, el agitador y la bomba de agua de enfriamiento puedan pararse durante - una falla de corriente. Similarmente, la flecha del agitador puede romperse- ó taparse la tubería de agua de enfriamiento. En tales casos se debe preveer que la agitación se salga de control ya que un alza en la temperatura y presión pueda ocasionar que el reactor se vomite ó explote.

Dos medidas pueden tomarse para obtener un grado adecuado de seguridad.

1.- Paro de emergencia. En una emergencia se puede agregar una sustancia química al reactor que detenga en forma rápida la reacción. Esta adición deberá hacerse de manera tal que el agente químico se mezcle inmediatamente c n el contenido del reactor aún con el agitador parado. Esto puede, realizarse usando como agente químico gaseoso, que es introducido al reactor por la parte inferior y se mezcle mediante el burbujeo.

2.- Venteo de Emergencia. El venteo de emergencia se utiliza cuando el sistema de enfriamiento falla. En el evento de una alza de temperatura que- no pueda ser controlada una válvula en el reactor se abra y se ventea el gas del reactor, a la atmósfera por lo cual deberá ser llevado a un tanque ó - condensador. El uso en estos casos de globos de gas ha sido tomado en consideración.

Es importante que la operación de venteo sea controlada para evitar que sólidos salgan del reactor.

Por esta razón es más adecuado el uso de una válvula de control que una válvula de descarga de mariposa.

La gran capacidad de producción e los reactores hace económico el uso de materia de seguridad costoso tales como válvulas de seguridad. Generalmente se puede decir que los grandes reactores deberán ser equipados con - más instrumentos y accesorios que un reactor pequeño.

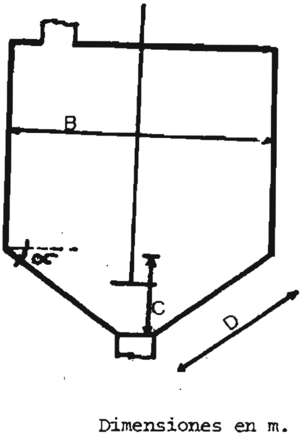
En nuestro caso el sistema de enfriamiento ha sido diseñado, con un - área de enfriamiento sobrado además de un condensador adicional.

Tanque de Precipitación para Emulsión de Acetado de Polivinilo

Aplicación en forma inmediata a la terminación de la reacción de polimerización, la emulsión de acetato de polivinilo, deberá depositarse en un tanque, con el propósito de efectuar la precipitación de la misma, como paso — previo al lavado, secado y filtrado que se efectuará en una centrifuga de canasta.

Requerimientos. Los parámetros para la selección de dicho tanque deberán ser tales que permitan contener el volumen de la carga de uno de los reactores de polimerización más el de la solución de sulfato de sodio utilizado para - precipitar la emulsión con un margen de seguridad, debido a la posibilidad de que el tanque no se encuentre vacio al término del siguiente ciclo en los - reactores, deberá poseer una agitación adecuada para la dispersión del sulfato de sodio en la emulsión y deberá ser cerrada para evitar la formación de - - "Natas", permitiendo al mismo tiempo ser desalojado fácilmente para poder - llevar al producto precipitado a la centrífuga.

Características del equipo seleccionado según el balance de materia - efectuado se requerirá un volumen de 5042 L la tapa superior del tanque será plana y el fondo será de forma cónico con las siguientes dimensiones.



Dimensiones en m.

A	B	C	D	α
1.5	2.0	0.5775	1.155	30°

Agitación

La agitación requerida será igual a la utilizada en el reactor de polimerización.

$$hp = 1.29 \times 10^{-4} (Dj)^{1.1} (L)^{2.72} N'^{2.86} y^{0.3} {}_{2}^{0.6} \mu^{10.14} \rho^{0.36}$$

$$hp = 1.29 \times 10^{-4} (6.66)\ (10.063)\ (58.996)\ (0.7273) \\ (2.27)\ (1.069)\ (37.68) = 34\ Hp.$$

Material de Construcción siguiendo el mismo procedimiento para el cálculo del reactor se obtuvo que el material seleccionado deberá ser Acero Inoxidable 304 de un gruesor de 1/4 de pulgadas.

Centrífuga de Canasta para filtrado, Lavado y Secado de Acetato de Polivinilo.

Aplicación: Con el fin de llevar a cabo la filtración, lavado y secado del acetato de polivinilo proveniente del tanque de precipitación y en vista de la experiencia obtenida en las pruebas de laboratorio, se seleccionó una centrífuga de canasta para la realización de este proceso.

Requerimientos: Según el balance de materia la producción en volumen de emulsión de acetato de polivinilo es de 4 209.5 e, por cada carga efectuada, tomando en cuenta que la duración del proceso es de nueve horas la producción en volumen será de 467.7 dm^3/hr. En cuando a producto seco se refiere se producen 2,515 Kg. cada nueve horas ó 280 Kg/hr, que ocupan el volumen con una densidad de 0.673 $Kg./dm^3$ de 416 dm^3/hr.

En base a estos datos se seleccionó una centrífuga de producción nacional capacidad para realizar dos ciclos por hora.

Características del equipo seleccionado:

Marca	Nacional
Tipo	Centrífuga extractora modelo SP. de operación semi-automática.

Distribuidor Mexicana de Maquinaria, S. A.

Diámetro de la canasta m.m.	1000
Capacidad máxima en Kg producto seco por ciclo	150
Capacidad Total dm^3 por ciclo	338
Capacidad útil dm^3 por ciclo	229
Velocidad de la canasta r.p.m	930
Profundidad de la canas m.m.	470
Diámetro de la boca de carga m.m.	724
Centro de la máquina al eje de la Columna m.m.	663
Centro de la máquina al eje del motor m.m.	812
Diámetro de la descarga de extracción m.m.	63(2)
Potencia del motor	S H p
Voltaje de operación	220/440
Ancho total m.m.	1581
Largo total m.m.	1480
Altura total m.m.	968
Peso aproximado Kgs.	1200
Espacio sobre piso m^2	2.34
Descarga	Manual

Cuerpo sólidamente construido en placa de acero inoxidable 304,totalmente soldado eléctricamente a prueba de fugas. El cuerpo puede ser fácilmente desmontado para un servicio de limpieza y mantenimiento.

Canasta. Consta esencialmente de tres partes, perfectamente ensambladas,- el cono central totalmente maquinado, para un ajuste preciso con el árbol de giro y el fondo de placa de acero al que va firmemente sujeto por tornillos, - del mismo material. El fondo así ensamblado, es forrado con lámina de acero - inoxidable. El envolvente, convenientemente perforado para obtener un máximo -

efeciencia en la extracción, se contruye con lámina de acero inoxidable de 3 m m con perforaciones de 3.9 m m y en un paso de 19 mm. Dichos envolventes van reforzados exteriormente con 4 aros de acero. Todo el conjunto así ensamblado es balanceado estáticamente, para un mínimo de vibraciones.

Baleros. El mecanismo de giro está diseñado para contener tres tipos de baleros, axial, radial - axial y radial lo que permite soportar fuertes - cargas.

Flecha de transmisión de acero, con alta resistencia a la torsión, la - cual garantiza, una máxima seguridad a los esfuerzos originados por cargas— desbalanceadas en el trabajo de extracción.

Freno. Tipo banda, opera a fricción sobre un tambor de freno, pauta integral de la polea motriz, al cual actua por medio de una palanca con resorte de torsión, la que al soltarla, se aplica con presión constante y uniforme.

Motor. Para trabajo vertical de alto poder arranque, la transmisión es por medio de bandas tropezoidales en polea ranurada.

Dispositivo de seguridad. Dos pequeños interruptores interconectados, - impiden que la máquina sea puesta en marcha con la tapa abierta, ó con el - freno aplicado. En caso contrario cuando la máquina está en operación se desconectará el motor inmeditamente al aplicar el freno ó abrir la tapa garantizando así una seguridad tanto para el operador, como para la centrífuga.

Costo aproximado $ 253 000 00 M.N.

Reactor para Alcohólisis Alcalina de Acetato de Polivinilo

Balance de Materia:

Según los resultados obtenidos del estudio preliminar de mercado y la investigación realizada en el laboratorio, se requieren procesar 12.18 Ton día de acetato de polivinilo para obtener 6.73 Ton/día de alcohol polivinílico con 88% de hidrólisis; se determinó también que el ciclo de reacción sería de 5 horas aproximadamente, incluyendo 1.0 h para cargar el reactor, 1.5 para realizar la solución del acetato de polivinilo en el metanol, tiempo de reacción de 0.5 h y un tiempo de limpieza y descarga de 2h.

$$12.18\ \text{Ton/día} \quad \times\ 1/\frac{24}{5}\ \text{horas} \quad = \quad 2.54\ \text{Ton Ciclo}$$

Dando un 10% como medida de seguridad

$$2.54 \quad \times \quad 0.100 \quad = \quad 0.254$$

$$2.54 \quad + \quad 0.254 \quad = \quad 2.8 \quad \text{Ton/ciclo}$$

Según la técnica hay necesidad de disolver el acetato de polivinilo en metanol en una relación 30:70 en peso por lo cual la cantidad requerida de metanol será:

$$2.8 \quad \text{Ton} \quad \times \quad \frac{70}{30} \quad = \quad 6.53 \quad \text{Ton de metanol}$$

Siendo el peso total de la solución metanólica de acetato de polivinilo un total de:

$$6.53 \quad \text{Ton} \quad + \quad 2.8 \quad \text{Ton} \quad = \quad 9.33 \quad \text{Ton.}$$

Se encontró experimentalmente que la densidad de la solución á la temperatura de 30°C es de 0.83 Kg/l con lo cual el volumen ocupado por la solución estará constituido por:

$$9{,}330 \quad \text{Kg} \quad \times \quad \frac{1}{0.83\text{Kg/l}} \quad = \quad 11\ 240\ \text{l}$$

Posteriormente según la técnica encontrada se deberá adicionar una solución metanólica de hidróxido de sodio que se utilizará como catalizador en un proporción de 8.5 ml por cada 50 gr. de acetato de polivinílo procesado por lo cual el volumen requerido por esta solución será:

$$2\ 800\ \text{Kg} \quad \times \quad \frac{.0085\ \text{l}}{.050\ \text{Kg}} \quad = \quad 476\ \text{l}$$

El volumen total de reacción será de :

$$11\ 240\ \text{l} \ + \ 476\ \text{l} \ = \ 11\ 716\ \text{l}$$

Dando 20% de espacios libres el volumen total será:

$$11\ 716\ \text{l} \ \times \ 0.20 \ = \ 14059.2\ \text{l}$$

Con el fin de obtener una mayor continuidad en la producción del alcohol polivinílico, se tomó la determinación de realizar el diseño de dos reactores con la mitad de la capacidad antes calculada, subsanándose así la eventualidad de que por desperfecto en uno de los reactores la producción se detenga, pudiéndose trabajar a la mitad de la capacidad con el otro reactor.

Según lo anterior el volumen requerido por cada uno de los reactores estará constituida por:

$$14059.2\ \text{l} \ \times \ \frac{1}{2} \ = \ 7030\ \text{l}$$

En base a éstos cálculos las dimensiones obtenidas se encuentran resumidas en la siguiente tabla.

Volumen requerido del reactor L.	Díametro Interno m	Largo Sección Cilindrica m.
7030	1.89	1.89
Volumen Sección Cilíndrica m^3	Volumen 2 Tapas Elípticas m^3	Volumen Total m^3
5.302	1.7674	7,069 m
Díametro de la chaqueta m		
2.042		

Agitación.

El propósito de la agitación es realizar la disolución del acetado de polivinilo en metanol, lograr la dispersión del catalizador en la mezcla anterior y posteriormente lograr una dispersión adecuada del alcohol polivinílico producido en la reacción.

En este caso los requerimientos de potencia para la agitación pueden ser calculados mediante la ecuación dimensional de White.

$$hp = 1.29 \times 10^{-4}(Dj)^{1.1}\ (L)^{2.72}(N)^{2.86}(Y)^{0.3}\ (Z)^{0.6}\ (\mu)^{0.14}$$

$$(\rho)^{0.86}$$

Se usará un agitador de propela localizado en el centro con

$0.3\ Dj$ y con una altura $h < L/6$

$$L = 0.416 \times 186\ \text{cm} = 78.624\ \text{cm}$$

$$L = 78.624\ \text{cm} \times \frac{1\ \text{pulgada}}{2.54\ \text{cm}} \times \frac{1\ \text{pie}}{12\ \text{pulgadas}} = 2.58\ \text{pies}$$

$$h = \frac{78.624}{6} = 13.1\ \text{cm}$$

La viscocidad de la mezcla de reacción se encontró experimentalmente de 21 poises a 30°C.

Sustituyendo

$$hp = 1.20 \times 10^{-4}\ (6.2)^{1.1}\ (2.58)^{2.72}\ (2.5)^{2.86}\ (0.43)^{0.3}$$

$$(7.02)^{0.6}\ (5082)^{0.14}\ (51.709)^{0.86}$$

$$hp = 1.29 \times 10^{-4}\ (7.44)\ (13.17)\ (13.74)\ (0.776)\ (3.2)\ (3.3)$$
$$(29.76) = 42\ hp$$

Cálculo del Area de Transferencia de calor

En este caso, se requiere estimar el área de calentamiento para un reactor enchaquetado, que aparte de las dimensiones ya calculadas anteriormente estará lleno hasta una altura de 7.2 pies (2.196 m), el agitador girará a una velocidad de 125 r.p.m. y la temperatura de reacción - será de 60°c (140°F) requiriéndose la adición de 555 157.1 BTU/hr para- proveer el calor endotérmico de reacción y mantener la temperatura. Se tomó la determinación de tener un factor de ensuciamiento de 0.005.

Ya que la reacción de alcohólisis es muy poco exotérmica se puede- considerar un cálculo a estado estacionario.

$L = 2.58$ pies

$N = 125$ rpm x 60 min $= 7\ 500$ rph

$\rho = 62.5$ lb/pie^3

$a\ t = 140°C = 0.44 \times 2.42 = 1.06$ lb/pie

$k = 0.38$ BTU/lb° F

$c = 1.0$ BTU/16° F

$$Re_j = \frac{L^2 N \rho}{\mu} = \frac{(2.58)^2 \times 7\ 500 \times 62.5}{1.06} = 353\ 2.288$$

$$h_j D_j = 0.36 \left(\frac{L^2 N \rho}{\mu}\right)^{2/3} \left(\frac{c\ \mu}{k}\right)^{1/3} \left(\frac{\mu}{\mu_w}\right)^{0.14}$$

$$\left(\frac{c\mu}{k}\right)^{1/3} = \left(1 \times \frac{1.06}{0.38}\right)^{1/3} = 1.41$$

$\left(\frac{\mu}{\mu_w}\right)^{0.14}$ puede considerarse como 1.0 para agua sustituyendo.

$$\frac{h_j D_j}{k} = 0.36 \quad (3532.288)^{2/3} \ (1.41) \ (1)$$

$$\frac{hj\ Dj}{k} = 0.36\ (23194)\ (1.41)$$

$$hj = \frac{11\ 773.3\ (0.38)}{6.2} = 721.60 \text{ BTU/hr pie}^2\ ^\circ\text{F}$$

Para vapor en la chaqueta referido al diámetro interno del recipiente

$$hoi = 1500 \text{ BTU/hr pie}^2\ ^\circ\text{F}$$

Usando la superficie interna como referencia

$$Uc = \frac{hjxhoi}{hj+hoi} = \frac{721.6\ \ x\ \ 1500}{721.6\ +\ 1500} = \frac{1082400}{224.6} = 487.2$$

$$Rd = 0.005$$

$$hd = \frac{1}{Rd} = \frac{1}{0.005} = 200 \text{ BTU/hr (pie)}^2\ (^\circ\text{F})$$

$$Ud = \frac{Uc\ \ hd}{Uc+\ hd} = \frac{487.2x\ \ 200}{487.2+\ \ 200} = \frac{97440}{687.2} = 141.8 \text{ BTU/(hr) pie}^2\ (^\circ\text{F})$$

Cálculo del área disponible

Debido a que el área requerida no es muy grande se utilizará solamente el área de la sección cilíndrica del reactor en 1/3 de su altura.

$$A= 1/3\ \ x\ \ \ \ \ \ x\ (6.2)\ \ x\ \ 6.2\ =\ 40.25 \text{ pie}^2$$

Balance de Energía.

El balance de calor comprenderá la energía de activación para llevar a cabo la reacción más el calor requerido para mantener la mezcla reaccionante a 40°C.

En la literatura se encontró que la energía de activación es de : 12.5 Kcal/gr mol.

$$1400000 \text{ gr} \ \ x\ \ \frac{1\text{gr mol}}{2873 \text{ gr}} = 487.5 \text{ gr mol}$$

Peso molecualr promedio obtenido mediante la realción entre viscocidad y peso molecular promedio.

12.5 Kcal/gr mol x 487.5 gr mol = 6093.75 K cal

$$6093.75 \text{ Kcal} \times \frac{1 \text{ BTU}}{0.252 \text{ Kcal}} = 24181.6 \text{ BTU}$$

24,181.6 BTU/15 min x 4 = 96726,4 BTU/hr.

Metanol

$$Q = m \ Cp \ AT$$

$$Q = 3265000 \text{ gr} \times \frac{\text{gr mol}}{32 \text{ gr}} \times 19.3 \times 40 = 78768.5 \text{ Kcal/hr}$$

$$Q = 78768.5 \text{ Kcal / hr} \times \frac{1 \text{ BTU}}{0.252 \text{ Kcal}} = 312573.5 \text{ BTU/hr}$$

Acetato de Polivinilo

$$1400000 \text{ gr} \times 0.389 \text{ cal/ gr}\,^{\circ}\text{C} \times 40 = 21784 \text{ Kcal/hr}$$

$$21784 \text{ Kcal/hr} \times \frac{1 \text{ BTU}}{0.252 \text{ Kcal}} = 86444.5 \text{ BTU/hr}$$

Sol de Hidróxido de Sodio

$$380000 \text{ gr} \times 0.985 \text{ cal/gr}\,^{\circ}\text{C} \times 40 = 14972 \text{ Kcal/hr}$$

$$14972 \text{ Kcal/hr} \times \frac{1 \text{ BTU}}{0.252 \text{ Kcal}} = 59412.7 \text{ BTU/ hr}$$

$$QT = 59412.7 \text{ BTU/hr} + 86444.5 \text{ BTU/hr} + 312573.5 \text{ BTU/hr} + 96726.4 \text{ BTU/hr} = 555157.1 \text{ BTU/hr}$$

Cálculo del Δ T

$$Qt = Ud \ A \ \Delta \ T$$

$$t = \frac{Qt}{Ud \ A} = \frac{555157.1}{141.8 \times 40.25} = 97.26\ ^{\circ}\text{F}$$

Ya que la reacción ocurre a 140°F la temperatura del vapor de calentamiento será de:

Tv = 140 + 97.26 = 237°F = 114°C

Material de Construcción.

Tomando en consideración que los principales reactivos que tomarán parte en la reacción serán el alcohol metílico, acetato de polivinilo y solución de hidróxido de sodio así como también los productos obtenidos serán alcohol polivinílico, acetato de metilo y acetato de sodio se procedió a checar en la literatura los materiales de construcción recomendados para manejar dichos compuestos (Recomendation Table for Metallic Materials of Construction. Chemical Engineering Plant Design Vilbrant). Obteniéndose en todos los casos como materiales recomendados el acero inoxidable(18-8)- y el acero inoxidable (18-8-Mo).

En vista de los datos anteriores se seleccionó como materia de construcción Acero Inoxidable 316 (18 Cr - 8Ni + Mo).

Determinación del grosor de placa de acero inoxidable para el reactor de alcohol polivinílico.

Para la presión atmosférica y siguiendo el método expuesto en el Brownell utilizando la gráfica 15 para determinación del grosor de la sección cilíndrica construida de acerosausteníticos 18 Cr - 8 N + Mo tipo 316 del código ASME 1956 el grosor de placa será de 5/16 de pulgada ó 7.9375 mm. Para el diseño de las tapas elípticas del reactor se utilizó la figura 2.11 del Unfired Pressure Vessels de Chose pag. 37 resultando un grosor de 5/16 de pulgada ó 7.9375 mm.

Seguridad.

Debido a que la reacción de alcohólisis que se efectuará en el reactor se trabaja a una temperatura relativamente baja, y la reacción es muy poco exotérmica, no se presentan grandes problemas en cuanto a seguridad se refiere.

El único punto que es conveniente tomar en consideración es el manejo del metanol debido a sus propiedades tóxicas debiendo evitarse la aspiración de los vapores que pudieran generarse por parte de los operadores.

Limpieza del Reactor.

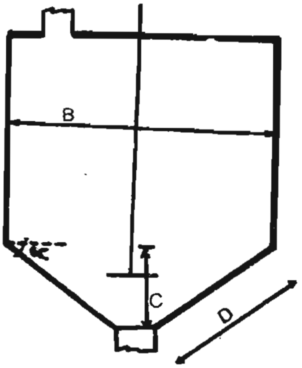
En base a las experiencias realizadas en el laboratorio el alcohol polivinílico no es soluble en el metanol y no se adhiere en ninguna forma a las paredes del reactor, por lo cual la limpieza del reactor quedaría reducida simplemente a tratar de eliminar mediante un lavado ligero con metanol los residuos del alcohol polivinílico precipitado que pudieran quedar en las paredes del equipo empleado.

Tanque de almacenamiento para lavado, filtrado y secado de alcohol polivinílico.

Aplicación. En forma inmediata a la terminación de cada proceso en los reactores utilizados en la fabricación de alcohol polivinílico, las cargas deberán depositarse en un tanque, para permitir la continuación de los ciclos de los reactores e iniciar el ciclo de filtrado, lavado y secado en la centrífuga seleccionada para este caso.

Requerimientos. Las características que deberá poseer un tanque de este tipo serán las de contener una carga completa de uno de los reactores, más una capacidad adicional del 20% como medida de seguridad, tendrá un fondo cónico, para auxiliar la descarga del producto sólido y tendrá una tapa en la parte superior como medida de seguridad debido a las características tóxicas del metanol empleado en el proceso.

Equipo seleccionado. Según los datos obtenidos del balance de materia el tanque deberá poseer un volumen de 70 0 l, teniendo las dimensiones especificadas en la siguiente tabla.



A	B	C	D	E
2.05	2.0	0.5775	1.153	0.1016

Material de Construcción

El material seleccionado para la construcción de este equipo será acero inoxidable 304 con placas de un grosor de 1/4 de pulgada ó 0.635 cm según código ASME 1956.

Centrífuga de Canasta para filtrado, lavado y secado de alcohol polivinílico.

Aplicación. Para realizar la filtración, lavado y secado del alcohol polivinílico producido en cada uno de los reactores y en vista a la experiencia obtenida en las pruebas de laboratorio, fué seleccionada una centrífuga de canasta para llevar a efecto este proceso.

Requerimientos. De acuerdo al balance de materia se requieren producir 6.73 Ton/día de alcohol polivinílico en 4.8 ciclos/día dando un resultado de 1.55 ton/ciclo; tomando en cuenta que el ciclo de los reactores dura 5 hrs. se tendrá:

1.55 Ton/ciclo de reactor x 1/5 hr/ciclo de reactor = 310 Kg/hr Como son dos reactores los que se operán 310 Kg/hr x /2 reactores = 155 Kg/hr en cada reactor.

Experimentalmente se concluyó el poder realizar dos ciclos en la centrífuga por hora, de donde la carga de producto seco estará constituida por 155 Kg/hr x 1/2 ciclos centrífuga/hr = 77.5 Kg/ciclo centrífuga.

Dicho producto ocupará un volumen de acuerdo a una densidad aparente del sólido seco de 0.65 Kg/dm^3 de 77.5 Kg/ciclo centrífuga x 1/0.66 Kg/dm^3 = 117.5 dm^3 ciclo centrífuga.

En base a estos datos se seleccionó, una centrífuga semejante a la empleada en el filtrado lavado y secado del acetato de polivinilo, que aunque se encuentra sobrada de capacidad permitiría realizar el proceso en 4 horas lo que daría un margen de seguridad mayor, tomando en cuenta también que un equipo de 30 no llenaría los requerimientos de volumen especificados anteriormente.

Características del equipo seleccionado.

Marca	Nacional
Tipo	Centrífuga extractora modelo SP de operación semi automática.
Distribuidor	Mexicana de Maquinaria, S. A.

Diámetro de la Canasta mm	1000
Capacidad máxima en Kg producto seco x ciclo	150
Capacidad total dm^3 por ciclo	338
Capacidad útil dm^3 por ciclo	229
Velocidad de la canasta rpm	930
Profundidad de la canasta mm	470
Diámetro de la boca de carga mm	724
Centro de la máquina al eje de la columna mm	663
Centro de la máquina al eje del motor mm	812
Diámetro de descarga de extracción mm	63(2)
Potencia del motor	5 Hp
Voltaje de operación	220/440
Ancho Total mm	1581
Largo Total mm	1480
Altura Total mm	968
Peso aproximado Kgs	1200
Espacio sobre piso m^2	2.34
Descarga	Manual

Cuerpo sólidamente construido en placa de acero inoxidable 304, totalmente soldado eléctricamente a prueba de fugas. El cuerpo puede ser fácilmente desmontado para un servicio de limpieza y mantenimiento.

Canasta. Consta esencialmente de tres partes, perfectamente ensambladas el cono central totalmente maquinado, para un ajuste preciso con el árbol de giro y el fondo de placa de acero al que va firmemente sujeto por tornillos del mismo material. El fondo así ensamblado es forrado con lámina de acero inoxidable. El envolvente, convenientemente perforado para obtener un máximo de efeciencia en la extracción se construye con lámina de acero inoxidable de 3 mm con perforaciones de 3.9 mm y en un paso de 19 mm.

Dichos envolventes, van reforzados exteriormente con 4 aros de acero Todo el conjunto así ensamblado es balanceado estáticamente, para un mínimo de vibraciones.

Baleros. El mecanismo de giro está diseñado para contener tres tipos de baleros, axial, radial - axial y radial, lo que permite soportar fuertes cargas.

Flecha de Transmisión. De acero, con alta resistencia a la torsión, la cual garantiza, una máxima seguridad a los esfuerzos originados por cargas desbalanceadas en el trabajo de extracción.

Freno. Tipo banda, opera a fricción sobre un tambor de freno, parte integral de la polea motriz el cual actúa por medio de una palanca con resorte de torsión, la que la soltarla, se aplica con presión constante y uniforme.

Motor. Para trabajo vertical de alto paro de arranque, la transmisión es por medio de bandas trapezoidales en polea ranurada.

Dispositivo de Seguridad. Dos pequeños interruptores interconectados, impiden que la máquina sea puesta en marcha con la tapa abierta, ó con el freno aplicado. En caso contrario cuando la máquina está en operación se desconectará el motor inmediatamente al aplicar el freno ó abrir la tapa garantizando así una seguridad tanto para el operador, como para la centrífuga.

Costo aproximado $ 253,000.00 M.N.

Procesos para recuperación de Solventes.

Los principales constituyentes en las aguas madres de la alcohólisis son metanol, acetato de metilo y acetato de sodio. Es importante económicamente hablando la recuperación de cada uno de estos constituyentes. En algunos casos la mezcla de metanol- acetato de metilo puede venderse como solvente para pinturas.

En otros casos las aguas madres se alimentan a una columna de destilación extractiva con agua. El acetato de metilo y el agua destilan de la parte superior de la columna y agua junto con metanol destilan del fondo.- El acetato de metilo se puede hidrolizar posteriormente en una columna de intercambio catiónico ó en presencia de un ácido fuerte, resultando ácido acético se concentra mediante la extracción ó destilación aleotrópica.

El acetato de sodio se convierte en sulfato de sodio y ácido acético añadiendo ácido sulfúrico.

En el presente trabajo, debido a la complejidad que presenta el diseño del equipo destinado a la recuperación de solventes, no fué realizado el diseño del mismo, por lo cual solo se deja constancia de los caminos a seguir para llevar a cabo estos procesos.

a) Tanque de Almacenamiento de Acetato de Vinilo.

Según el balance de materia efectuado se requieren 12.18 Ton de monómero de acetato de vinilo por día el cual tiene una densidad de 0.9338 Kg/dm^3. Se planea tener almacenado el equivalente de una semana de producción, lo que representan 85.26 Ton/semana que ocuparan un volumen de 91.3 m^3, para llevar a efecto este almacenamiento se puede disponer de 2 tanques verticales de fondo plano y techo cónico, con una entrada hombre de 0.4572 m (18 pulgadas) una boca de 0.01016 m (4 pulgadas) otra de 0.15 x 24 (6 pulgadas) y cuatro de 0.0508 m (2 pulgadas) con 4.88 de díametro y 4.88 de altura con una capacidad de 45.93m^3 cada uno. Contando además con un tubo de respiración y sello de agua.

b) Tanque para almacenamiento y disolución de iniciador al 3%

Por cada tonelada de acetato de vinilo procesada se requieren 100 l de solución al 3% de inicidor para 12.18 Ton/día se requerirán 1218 L de solución acuosa al 3% debido a que la solución de este iniciador debe ser de preparación reciente para poderse utilizar, el tanque deberá diseñarse para un día de trabajo, más un 10% de volumen debido a la agitación.

El tanque seleccionado tendrá un diámetro de 1.0 m, una altura de zona cilíndrica de 1.5 m y un fondo cónico de 0.30 m. de altura y 1 m, de diámetro para contener 1.34 m^3 de solución y estará provisto además con un agitador con doble propela de transmisión directa de 1 H.P. y- un serpentín para calentamiento.

c) Tanque para almacenamiento y disolución de Buffer

En este caso el tanque requerido deberá contener 1.125 m^3 de - solución al 2% de Buffer pues su preparación como en el caso anterior- deberá ser reciente; el tanque seleccionado tendrá un diámetro de 1.0m, una altura de la sección cilíndrica igual a 1.5 m y un fondo cónico de 0.30 m. de altura y 1 m. de diámetro para contener 1.33 m^3 de solución estando provisto además de un agitador con doble propela de transmisión directa de 1 H.P. y un serpentín para calentamiento.

d) Tanque de almacenamiento y disolución de Emulsificante.

Por cada tonelada de acetato de vinilo que se procesa se requieren 350 L de solución al 10% de emulsificante para una producción de - 12.18 Ton/día se requieren 4.375 m^3/día solución más 10% como medida de seguridad resulta un tanque de 4.8125 m^3 día.

Para este fin se podría disponer de un tanque horizontal de 1.45 m de diámetro, 2.5 de longitud, con dos tapas elípticas de 0.725 m de eje mayor y 0.3623 de eje menor, efectuándose la disolución mediante la - recirculación de los productos.

Antioxidante.

Los requerimientos para el producto son de 25l/día y su almacenamiento se efectuará directamente de los tambores en los cuales se distribuye.

Agua.

El abastecimiento del agua se realizará directamente de la cisterna que deberá poseer la planta para su uso general, no requiriéndose por lo tal un recipiente aparte para este caso.

Sulfato de Sodio

Para realizar la precipitación de la emulsión de acetato de polivinilo, se requieren 60.9 L diarios de solución concentrada, la cual podrá ser preparada en cualquiera de los tanques destinada a la solución Buffer ó Iniciador en cualquier intervalo y almacenada en tambores destinados a este fin.

e) Tanque de almacenamiento de Alcohol Metílico.

El alcohol metílico se recibe en pipas conteniendo de 23 a 25 - Toneladas, los requerimientos diarios de metanol serán de 15,694 Ton/día que con una densidad de 0.7924 ocuparán un volumen de 19.8 m^3/día haciendo el cálculo para 7 días se necesitará almacenar un volumen de 138.6 m^3/ 7 días.

Para llenar esta necesidad se propone disponer de dos tanques verticales de forma cilíndrica, fondo plano y techo cónico con capacidad por- unidad de 70 m^3 con 4.47 de diámetro y 4.47 m de altura, una entrada hombre de 0.4572 m, una boca de 0.152 m, otra de 0.1016 y 4 de 0.0508 m. y- un tubo de respiración con sello de agua.

f) Tanque de Almacenamiento y Disolución de Hidróxido de Sodio.

Según los cálculos efectuados en el balance de materia se requieren 2,070 L/día que se disolverán en un tanque de un fondo elíptico de 0.275 m de eje menor y 0.55 m de eje mayor, contando además con un agitador con doble propela de transmisión directa de 1 H.P. y un serpentín para calentamiento.

Estimación de Costo del Equipo

Reactores para polimerización en Emulsión de Acetato de Vinilo.

Según el CE Cost File- IV del Chemical Engineerins pag 7 para recipientes enchaquetados de acero inoxidable 316 el costo aproximado para un reac—tor con capacidad de 5089 l (1344.6 Gal) incluyendo el recipiente, chaqueta, agitador termoposo, válvulas de seguridad, aislamiento, material y mano de -obra sería de 21800.00 dolares para una fecha de referencia de Marzo de 1958 con un índice de Marshall y Stevens de 232.3 y para 1976 de 486.3 con una cotización del dolar de 22.4 pesos/dolar.

$$21800 \text{ dólares} \times \frac{486.3}{232.3} = 45636 \text{ dólares} \times 22.4 \text{ pesos/dolar}$$

= 1,022,255.77 pesos x 2 reactores = 2'044,511.54 pesos.

Tanque para precipitación de emulsión de acetato de Polivinilo.

Según el CE Cost File - IV del Chemical Engineering pag 6 incluido totalmente para una capacidad de (1344.6 Gal) para una fecha de referencia de Marzo de 1958 con un índice de Marshall y Stevens de 232.3 y para 1976 de 486.3 —con una cotización del dolar de 22.4 pesos/dolar.

8,700 x 486.3 x 22.4 = 407964.45 pesos.

Centrífuga para Filtrado, Lavado y Secado de Acetato de Polivinilo.

El precio de la centrífuga destinada a este fin se obtuvo de la cotización directa del fabricante y es de 253000.00 pesos.

Reactor para la producción de alcohol Polivinílico

Según el CE Cost File - IV del Chemical Engineering pag 7 para reactores enchaquetados de acero inoxidable 316 el costo aproximado para un reactor —con capacidad de 6892 L (1844 Gal) para una fecha de referencia de Marzo de 1958 con un índice de Marshall y Stevens de 232.3 y para 1976 de 486.3 con -una cotización del dolar de 22.4 pesos/dolar.

25900 x 486.3 = 54,219 dólares x 22.4 pesos/dolar = 1214514.8 pesos.

1214514.8 pesos x 2 reactores = 2,429,029.77 pesos.

Tanque de almacenamiento para Lavado, Filtrado y Secado de Alcohol Polivinílico.

De acuerdo a el CE Cost File - IV del Chemical Engineering pag 6 incluido totalmente para capacidad de 1844 gal para una fecha de referencia de Marzo de 1958 con un índice de Marshall y Stevens de 232.3 y para 1976 de 486.3 con una cotización del dolar de 22.4 pesos/dolar.

Si

7000 dólares x $\frac{486-3}{232.3}$ = 14653.89 dólares x 22.4 pesos/dolar

= 328247.26 Pesos.

Centrífuga para Lavado, Secado y Filtrado de Alcohol Polivinílico.

El precio de la centrífuga destinada a este fin se obtuvo de la cotización directa del fabricante y es de 253000.00 pesos.

Tanques de Almacenamiento de Monómero de Acetato de Vinilo

Tomando los datos del costs of process Equipment Chemical Enginneerins Marzo 16, 1964 para un índice de Marshall y Stevens de 238.8 página 139 se obtuvo un costo de 2000.00 dólares para una capacidad de 12,060.7 Gal.

2000 x 486.3 = 4072.56 dólares x 22.4 pesos/dolar

= 91232.16 pesos x 2 tanques = 182,464.32 pesos.

Tanque de Almacenamiento de Alcohol Metílico

Según el Costs of Process Equipment del Chemical Engineerins de Marzo 16 1964 pag 139 para un índice de Marshall y Stevens de 238.5 se obtuvo un costo de 4000.00 dólares para una capacidad de 18309 Gal 69300 l.

4000.00 dólares x 22.4 pesos/dolar = 89600 pesos

39,600.00 pesos x $\frac{486.3}{238.8}$ = 182464.32 pesos

182,464.32 pesos x 2 tanques = 364,928.64 pesos.

Tanques de Almacenamiento y disolución de Iniciador y Buffer.

De acuerdo a las mismas referencias que en el caso anterior para un volumen de 300 Gal se obtiene un costo de:

380 dólares x $\frac{486.3}{238.8}$ = 773.84 dólares

773.84 dólares x 22.4 pesos/dolar = 17334 pesos

17334.00 pesos x 2 tanques = 34668.00 pesos

Tanque de Almacenamiento de Emulsificante

Continuando con la misma referencia para un volumen de 1155.8 Gal la estimación de costo:

700 dólares x $\frac{486.7}{238.8}$ = 1425.5 dólares

1425.5 dólares x 22.4 pesos/dolar = 31931.25 pesos

Tanque de almacenamiento de Solución de Hidróxido de Sodio

Para una capacidad de 2070 L (546.89 Gal) según la misma referencia anterior se obtuvo un costo de:

600 dólares x 486.3 = 1221.85 dólares

1221.85 dólares x 22.4 pesos/dolar = 27369.64

Condensadores de reactores de polimerización de Acetato de Vinilo

Según los datos obtenidos del "Costs of process Equipment pag. 137 el -- costo de acuerdo al cálculo realizado del área de los tubos será:

$$550 \times \frac{486.3}{238.8} \times 22.4 = 25088.99$$

Costo total del Equipo

Sumando los costos parciales anteriores se obtiene un costo total del -- Equipo sin instalar de $6'407,292.7 M.N.

V.- LOCALIZACION DE LA PLANTA

V.- Localización de la Planta.

① La localización óptima para una planta química depende de un número de factores. El lugar lógico será aquel en el cual el costo de producción y distribución sea mínimo, ó donde el costo adicional de las materias primas, elaboración, ventas y transportación de los productos terminados al mercado sea menor. La situación de una planta química esta determinada por el análisis cuidadoso de los siguientes factores.

A.- Abastecimiento de Materias Primas.

Las materias primas en la elaboración de alcohol polivinílico consideradas para este estudio son el acetato de vinilo, metanol y sosa cáustica. Con respecto al acetato de vinilo el único proveedor es Celanese Mexicana, S.A. en su planta de Celaya, Guanajuato con una capacidad instalada en 1975 de 13,200 Ton/año existiendo el proyecto de una ampliación por 4,300 Ton/año.

En relación al metanol éste es fabricado en la planta de Pemex localizada en San Martín Texmelucan, Puebla, con una capacidad instalada de 31,500 Ton/año existiendo también un proyecto de ampliación a 150,000 Ton/año en el mismo lugar para el año de 1978.

En cuanto a sosa cáustica se refiere los principales productores son; Celulosa y Derivados, S.A., Compañía Industrial San Cristobal, S. A. , El Pilar, S.A., Guanos y Fertilizantes de México,S.A., Industria Química del Istmo, S. A. Pennwalt, S.A. de C.V., Sosa Texcoco, S.A.

B.- Mercado

Originalmente se hizo este proyecto con miras a satisfacer unicamente la demanda nacional, pero no hay que descartar la posibilidad de exportar alcohol polivinílico a algunos países de Latinoamérica, pues como miembro de la ALALC, México tendría preferencia como exportador y según estudios realizados por el IMCE se considera posible la exportación.

C.- Distribución de Consumidores.

Se estima que el consumo actual del alcohol polivinílico se encuentra distribuido geográficamente como sigue:

Distrito Federal	25%
Estado de México	58%
Jalisco	3%
Nuevo León	13%
Otros Estados	1%

D.- Descentralización

Otro aspecto considerado consiste en las medidas que ha tomado el Gobierno para la descentralización de la industria mediante la creación de las Ciudades Industriales con el fin de:

1).- Obtener un desarrollo regional equilibrado.

2).- Propiciar un crecimiento urbano ordenado, en los actuales centros de población de México.

3).- Evitar la contaminación ambiental.

4).- Desarrollar una infraestructura industrial, que permita la atracción de nuevas inversiones.

5).- Utilizar en forma racional, los recursos humanos y naturales de la región.

6).- Crear condiciones socioeconómicas favorables para la integración rural a este nuevo tipo de desarrollos.

E.- Incentivos Fiscales.

Se han establecido tres categorías de zonas industriales de acuerdo a su grado de industrialización, a las cuales se le aplican incentivos consistentes en exención ó reducción de impuestos, principalmente Sobre la Renta y de los impuestos de importación de maquinaria y equipo. Por medio de estos incentivos se intenta promover la industrialización de los Estados menos desarrollados en este aspecto. Como ejemplo está el Edo.de México al cual alguna vez se le concedieron incentivos fiscales bastante atractivos, pero debido a su gran desarrollo industrial, actualmente tiene un réjimen fiscal sumamente gravoso.

Incentivos semejantes se otorgan a las empresas que venden sus productos en las zonas fronterizas y perímetros libres.

Del análisis de los elementos anteriores se concluyó que la ciudad Industrial de San Juan del Río, Queretaro, es la más adecuada para instalar la planta en cuestión, ya que:

a) Se encuentra en el corredor natural para abastecimiento de materias primas básicamente la del monómero de acetato de vinilo, por la proximidad de la planta de Celanese Mexicana, S. A.

b) Debido a que solo se consideraron las necesidades del mercado nacional, cuenta con las vías expeditas y de buena calidad, para realizar las entregas de producto terminado, ya que los consumidores se encuentran concentrados en el centro del país.

c) Cuenta con los medios suficientes para satisfacer las demandas de agua, electricidad, eliminación de productos de deshecho, etc.

d) Al estar localizada la planta fuera del perímetro metropolitano se contribuiría a descentralizar la Industria.

e) El costo de la mano de obra al estar situado en la zona económica 58 correspondiente a Querétaro Sur, con un salario mínimo general de $\$6\overset{0}{1}.30$ y de campo de $\$4\overset{6}{9}.00$ es uno de los más atractivos en relación a los demás puntos de localización considerados.

f) Las condiciones de impuestos e incentivos Fiscales son adecuadas.

g) Las condiciones climáticas y de vida son adecuadas.

h) Se contaría con el terreno apropiado y suficiente para futuras expansiones.

VI.- ESTUDIO ECONOMICO PRELIMINAR

VI.- ESTUDIO ECONOMICO PRELIMINAR.

1.- Ventas Estimadas

2.- Costo de lo Vendido

3.- Gastos de Administración y Ventas

4.- Inversión Fija

5.- Costo del Límite de Baterías

6.- Costo de Arranque y Seguros

7.- Impuestos Sobre la Renta y Reparto de Utilidades

8.- Efectivo en Caja

9.- Cuentas por Cobrar

10.- Inventarios

11.- Activo Circulante

12.- Capital de Trabajo

13.- Depreciación y Amortización

14.- Gastos Preoperativos

15.- Gastos Financieros

16.- Costo Total de Producción y Utilidad antes de Impuestos

17.- Inversión Total

18.- Utilidad Neta.

1.- Ventas Estimadas.

Las ventas estimadas de los ejercicios de 1978 a 1982, se han determinado de acuerdo con el estudio de mercado presentado en el primer capítulo del presente trabajo y en el que se muestran tanto unidades como precio.

No se indican ventas de exportación debido a que se estima que la empresa únicamente satisfacerá el mercado nacional de un producto que no se fabrica en México.

Volumen de Ventas de Alcohol Polivinílico.

Se considera un precio de venta de $ 50.00

Año	Volumen de Ventas (Ton / año)	Volumen de Ventas (Miles de pesos)
1978	1494	74 700
1979	1623	81 150
1980	1840	92 000
1981	2028	101 400
1982	2221	111 050

Volumen de Ventas de Acetato de Metilo

Tomando en consideración que por cada Kg. de alcohol polivinílico se producen 0.641 Kg. de Acetato de Metilo cuyo precio de venta es de $ 12.50 tomando en cuenta un costo de recuperación de solventes por cada Kilogramo de Acetato de Metilo para fines de estimación se obtendra una ganancia adicional de 6.25 por cada Kg. de Acetato de Metilo.

Año	Volumen de Ventas de Acetato de Metilo - (Toneladas)	Volumen de Ventas Acetato de Metilo (Miles de Pesos)
1978	958	5 987.5
1979	1040	6 500
1980	1180	7 375
1981	1300	8 125
1982	1424	8 900

Volumen de Ventas Total

Año	Volumen de Ventas Total (Miles de pesos)
1978	80 687.5
1979	87 650
1980	99 375
1981	109 525
1982	119 950

2.- Costo de lo Vendido

El costo de o vendido se determinó según estado de costo de producción que se muestra a continuación, con los incrementos respectivos en realción a las unidades vendidas en cada uno de los años proformas.

Este renglon incluye:

Materias Primas

Servicios de Proceso

Mano de Obra

Supervisión

Mantenimiento y Material de Mantenimiento

Suministro de Operación

Material en General

Laboratorio

Gastos Generales

Materias Primas

Consumo de Materias Primas por Unidad de Producto
(precios referencia febrero de 1977)

Materia Prima	Kg/kg de AP*	Precio ($/kg)	Costo/Kg AP
Acetato de Vinilo	2	16.18	32.36
Catalizador y Emulsificantes	0.120	11.53	1.39
Metanol**	0.625	7.5	4.7
Sosa Caústica	0.153	2.6	0.4
		Sub-Total	38.49

Servicios de Proceso

Servicio	Consumo	Costo	Importe
Vapor	1.25 kg/kg de AP	0.25 $/kg	0.3125
Electricidad	0.5 kwh/kg de AP	0.55 $/kg	0.275
Agua de Enfriamiento y Proceso	0.125 m^3/kg de AP	3.2 $/kg	0.4

Sub-Total 0.9875

Total 34.4775

* AP Alcohol Polivinílico

** Se toma en cuenta la recuperación de metanol dando un 20% de pérdidas

*** Fuente ESCAFE Report y datos de costo obtenidos empíricamente.

De acuerdo al plan de ventas, los costos de materias primas y servicios de proceso estarán constituidos por:

Año	Volumen de Ventas Ton/año	Costos de Producción (Miles de Pesos)
1978	1494	58 979.38
1979	1623	64 071.98
1980	1840	72 638.6
1981	2028	80 060.4
1982	2221	87 679.52

Supervisión de Operación

Puesto	No.de Personas	$/Mes	$/Año
Jefe de Producción	1	20,000	240,000
Ingenieros de Turno	3	15,000	540.00

Total 780,000.00/Año

Salarios de Operación

Mano de Obra directa de Operación

Puesto	No. de Personas	$/mes	$/Año
Acetato de Polivinilo			
Encargados de los Reactores	3	5,000	180,000
Ayudantes de Reactores	3	3,000	108,000
Relevo	1	4,000	48,000
Operador Centrífuga	3	3,000	108,000
Alcohol Polivinílico			
Encargados de los reactores	3	5,000	180,000
Ayudantes de Reactores	3	3,000	108,000
Relevo	1	4,000	48,000
Operador Centrífuga	3	3,000	108,000
Relevo Operador Centrífuga	1	3,000	36,000
Sub-Productos			
Operadores	3	5,000	180,000*
Ayudantes	3	3,000	108,000
Relevo	1	4,000	48,000
Servicios			
Encargados de Generación de Vapor	4	5,000	240,000

Total 1,500 000.00/Año.

Mantenimiento

Puesto	No. de Personas	$/Mes	$/Año
Mecánico	1	7,000	84,000
Electricista	1	7,000	84,000
Instrumentista	1	7,000	84,000
Ayudantes	2	3,000	36,000

Total 288,000/Año

Material de Mantenimiento

288,000.00/Año

Suministros de Operación

15% de Supervición y sueldos de Mantenimiento *

43 200.00/Año

Materiales

1.6 de mano de obra de mantenimiento *

Laboratorio de Control e Investigación

Puesto	No. de Personas	$/Mes	$/Año
Jefe	2	10,000.00	240,000.00
Laboratorista	2	10,000.00	108,000.00
		Total	348,000.00

Materiales de Laboratorio

15% de mano de Obra de Operación *

252,000/Año

* Datos obtenidos del artículo Inversión Fija, Capital de Trabajo y costos de operación Revista IMIQ y Tesis "Analisís de la Estructura actual de la Industria de la rama de propileno y estrategias de desarrollo UNAM 1976.

Comprenden personal de oficina, de limpieza, de seguridad, la comunicaciones (teléfono, telégrafo, correo, telex) el comedor, vigilancia - pesos por aguinaldo Infonavit y Seguro Social, y fueron estimados como - el 30% de la suma de los costos anteriores.

1 188 000 00/Año

Costo Total 5 148 000 00/Año

Costo de lo vendido
(miles de pesos)

1978	64 127.38
1979	69 219.98
1980	77 786.6
1981	85 208.4
1982	92 827.52

3.- Gastos de Administración y Ventas

Los gastos de administración y ventas se aplican a continuación incluyendo sus incrementos anuales con sus bases.

Desglose

a) Gastos Administrativos

Sueldos y Salarios a personal de Administración

Asesoría

Comunicaciones, Mantenimiento y Materiales.

b) Gastos de Mercado y Distribución

Desglose de gastos administrativos

Puesto	No.de Personas	$/Mes	$/Año
Gerencia			
Gerente	1	24 000	288 000
Secretaria Ejecutiva	1	5 000	60 000
Contabilidad			
Contador	1	20 000	240 000
Auxiliar de Contabilidad	1	5 000	60 000
Secretaria	1	4 000	48 000
Ventas			
Ing. de Ventas	1	16 000	192 000
Secretaria	1	5 000	60 000
Oficina en el D.F.			
Directivos Oficina en D.F.	1	20 000	240 000
Secretaria	1	4 500	54 000
Mensajero	1	4 000	48 000

Total 1 290 000 00/Año.

Asesorías*

Este renglón toma en cuenta los honorarios por asesorías Jurídicas Impuestos, Actuarias etc. y se obtubo por un factor empírico de 7.3% - de sueldos y salarios a personal administrativo.

$ 94 170/Año

Comunicaciones, Mantenimiento y Materiales*

Este aspecto fué estimado en 541 800/Año

Total 1 925.97/Año

* Determinados ampíricamente

b) Gastos de Mercado y Distribución.

Corresponden al 5% del Costo de lo vendido

Año	Costo de lo Vendido (Miles de Pesos)	Gastos de Mercado y Distribución (Miles de Pesos)	Gastos Adm. (Miles de Pesos)	Total (Miles de Pesos)
1978	64 127.38	3 206.4	1 925.97	5 132.4
1979	69 219.98	3 461.00	1 925 97	5 387.0
1980	77 786.60	3 889.33	1 925.97	5 815.3
1981	85 208.40	4,260.20	1 925.97	6 186.2
1982	92 827.52	4 641.40	1 925.97	6 567.4

Gastos Imprevistos y Preoperativos

Los gastos imprevistos se estimaron como el 15% del costo directo de Planta y repartidos en 1.5 años de pre-operación.

Año	Gastos Imprevistos (Miles de pesos)
1977	1 609.76
1978	1 609.76

4.- Inversión Fija

Equipo comprado		6,407.00
Instalación	.43	2,755.13
Instrumentación	.20	961.05
Tubería	.36	2,306.52
Equipo Eléctrico	.15	961.03
Terreno	.06	384.43
Acondicionamiento de Terreno	.10	640.70
Servicios	.35	2,242.45
Edificios	.35	2,242.45
Costo físico de la Planta		18,900.77
Ingeniería y Construcción (40% del equipo sin instalar)		2,562.80
Costo Directo de la Planta		21,463.57
Contratista (7% de Costo Directo de la Planta)		1,502.45
Imprevistos (15% de Costo Directo de la Planta)		3,219.53
		26,185.55

5.- Costo del límite de Baterías

		Costo (miles de pesos)
Equipo		6 407.0
Tubería		2 306.52
Instrumentación		961.05
Equipo Eléctrico		861.05
	Sub-Total	10 635.62
	Imprevistos	3,219.53
	Total	13,855.15

6.- Costo de Arranque y Seguros

Inversión Fija	26 185.55	
Costo de Arranque (3% de Inversión Fija)		785.96
Seguros (1% de Límite de Baterías)		138.55

Año	Miles de Pesos
1978	924.11
1979	138.55
1980	138.55
1981	138.55
1982	138.55
1983	138.55
1984	138.55
1985	138.55

7.- Impuestos Sobre la Renta y Reparto de Utilidades

El impuesto sobre la renta se calculó sobre el ingreso global de las empresas y deberá aplicarse la taza del 42% sobre la utilidad neta antes de impuestos.

Se consideró el 8% sobre la utilidad antes de ISR, como participación de los trabajadores en las utilidades de la empresa, según experimentos anteriores.

Desglose del Impuesto Sobre la renta y reparto en los ejercicios.

Año	Impuesto sobre la renta.	Reparto de utilidades.
1978	3 233.51	615.90
1979	3 678.6	700.7
1980	4 825.25	919.09
1981	5 838.78	1 112.15
1982	6 974.48	1 328.47

8.- Efectivo en Caja

El efectivo en Caja para la operación normal de la compañia se ha supuesto igual al 5% del citado de pérdidas como porcentaje aproximado lo cual es función directa del costo de producción, sin considerar la depreciación.

Año	Costo Total de producción Estado de Pérdidas	Efectivo en
1978	70 519.065	3 526
1979	76 421.4	3 821
1980	85 416.32	4 271
1981	93 153.73	4 568
1982	100 874.08	5 044

9.- Cuentas por Cobrar

La cuentas por cobrar provenientes de clientes se han supuesto iguales al monto de ventas totales en 60 días de producción ya que la política que se piensa seguir es de vender a 60 días de plazo promedio.

Año	Cuentas por cobrar (Miles de pesos)
1978	13 263.70
1979	14 408.21
1980	16 335.61
1981	19 339.72
1982	19 717.80

10.- Inventarios

La inversión en inventarios se calculó de la manera siguiente:

a) 15 días de consumo de materias primas y materiales.

b) 15 días de costo de producción para producto terminado.

c) 7 días de costo de producción para producto en proceso y para mantener una existencia de herramientas y accesorios para la operación normal de la planta industrial.

Año	Materia Prima	Producto Terminado	Producto en Proceso	Inventarios
1978	2 423.81	2 898.04	1 352.42	6 674.27
1979	2 673.09	3 140.60	1 465.61	7 239.3
1980	2 985.14	3 510.30	1 638.12	8 133.56
1981	3 290.15	3 828.23	1 786.51	8 904.89
1982	3 603.26	4 145.51	1 934.57	9 683.34

11.- Activo Circulante

El activo circulante es la suma de:

Cuentas por cobrar

Efectivo en Caja

Inventarios

Año	Activo Circulante $ 50
1978	23 463.97
1979	25 468.51
1980	28 740.17
1981	32 902.61
1982	34 445.14

Miles de Pesos.

12.- Capital de Trabajo

El capital de trabajo puede ser obtenido restándole al Activo Circulante las cuentas por pagar. Las Cuentas por Pagar se estimaron como 30 días de materia prima necesaria para la producción.

Año	Cuentas Por Pagar	Capital de Trabajo $ 50
1978	4 847.52	18 616.45
1979	5 266.18	20 202.33
1980	5 970.28	22 769.89
1981	6 580.30	26 322.31
1982	7 206.52	27 238.62

13.- Depreciación.

La inversión en inmuebles, planta y equipo es suficiente para producir anualmente 2221 toneladas de alcohol polivinílico.

La inversión en este renglón y su porciento de depreciación anual está formada como sigue.

Equipo de proceso	6 407.00	9	576.63
Tuberías	2 306.52	9	207.58
Equipo Eléctrico	961.03	9	86.50
Instrumentación	961.05	9	86.50
Servicios	2 242.45	9	201.82
Montaje	2,755.13	9	247.96
Fletes	961.00	9	86.49
Edificios	2 242.45	3	67.27
Terreno	384.42	0	
Acondicionamiento de terreno	640.7	3	19.22
Seguros	138.5	5	6.92
Gastos Pre-Operativos	1 385.5	5	69.28
Honorarios Contratistas	1 502.45	5	75.12
Imprevistos	3 259.53	9	293.35
Ingeniería de Detalle	7 368.05	5	368.4
Ingeniería y Construcción	2 562.8	3	76.88

Total por Año 2 469.92

14.- Los gastos preoperativos y cargos diferidos fueron estimados como el 10% del costo del límite de baterías en 1 385.51 y están formados por los siguientes conceptos:

a) Gastos de organización

b) Gastos de proyectos e investigación de mercados

c) Costos directos e indirectos de arranque

d) Gastos financieros del periodo preoperativo

Año	Gastos Preoperativos (Miles de pesos)
1977	692.76
1978	692.76

15.- Gastos Financieros.

Se estimó solicitar un financiamiento del 40% de la Inversión Fija para ser solicitado en 1977 con un interés de 16% Anual sobre saldos Insolutos a 8 años de Amortización y 2 años de gracia que es lo usual en este tipo de financiamiento solicitando el 20% en el año de 1977, y el 80% restante en 1978.

Monto de la Inversión Fija	$	26 135 550.00
Monto del Financiamiento		10 474 220.00

Año	Saldo	Amortización 1	Amortización 2	Amortización Total	Gastos Financieros 16% de Int.
1977	2 094.844	———	———		———
978	10 474.22	———	———		335.175
1979	10 474.22	349.40	———	349.40	1 675.87
1980	10 124.82	349.40	1 396.56	1 745.96	1 675.87
1981	8 378.86	349.40	1 396.56	1 745.96	1 619.98

1982	6 632.9	349.40	1 396.56	1 745.96	1 340.61
1983	4 886.94	349.40	1 396.56	1 745.96	1 061.264
1984	3 140.98	349.40	1 396.56	1 745.96	781.91
1985	1 396.56	—	1 396.56	1 396.56	502.56
1986	—	—	—	—	223.45

16.- Costo total de producción

Los costos totales de producción son el resultado de la suma de lo siguiente:

Costos de lo vendido

Costos de Arranque y Seguros

Costos de Administración y Ventas

Costos Financieros

Costo total de producción

Año	(Miles de pesos)
1978	70 519.065
1979	76 421.4
1980	85 416.32
1981	93 153.73
1982	100 814.08
1983	100 874.08

Utilidad Antes de Impuestos

Fué calculada restándole el volumen de ventas, el costo total de producción y la depreciación, puesto que por ley esta ultima es - deducible de Impuestos y se calculo para el precio de Venta de $50.00

Año	Costo total de producción y Depreciación	Utilidad antes de Impuestos. $ 50
1978	72 989.065	7 698.84
1979	78 891.4	8 758.62
1980	87 886.32	11 488.68
1981	95 623.73	13 901.87
1982	103 344.08	16 605.92

17.- Inversión Total

La inversión total se calcula mediante la suma de la inversión fija capital de trabajo y gastos de pre-operación.

Año	Inversión Total Miles de pesos $ 50
1978	46 187.51
1979	47 773.39
1980	50 340.95
1981	53 893.37
1982	54 809.68

18.- Utilidad Neta.

La utilidad neta corresponde a la utilidad antes de impuestos menos los impuestos y reparto de utilidades.

Año	Utilidad Neta
1978	3 849.42
1979	4 379.3
1980	5 744.34
1981	6 950.94
1982	8 303.0

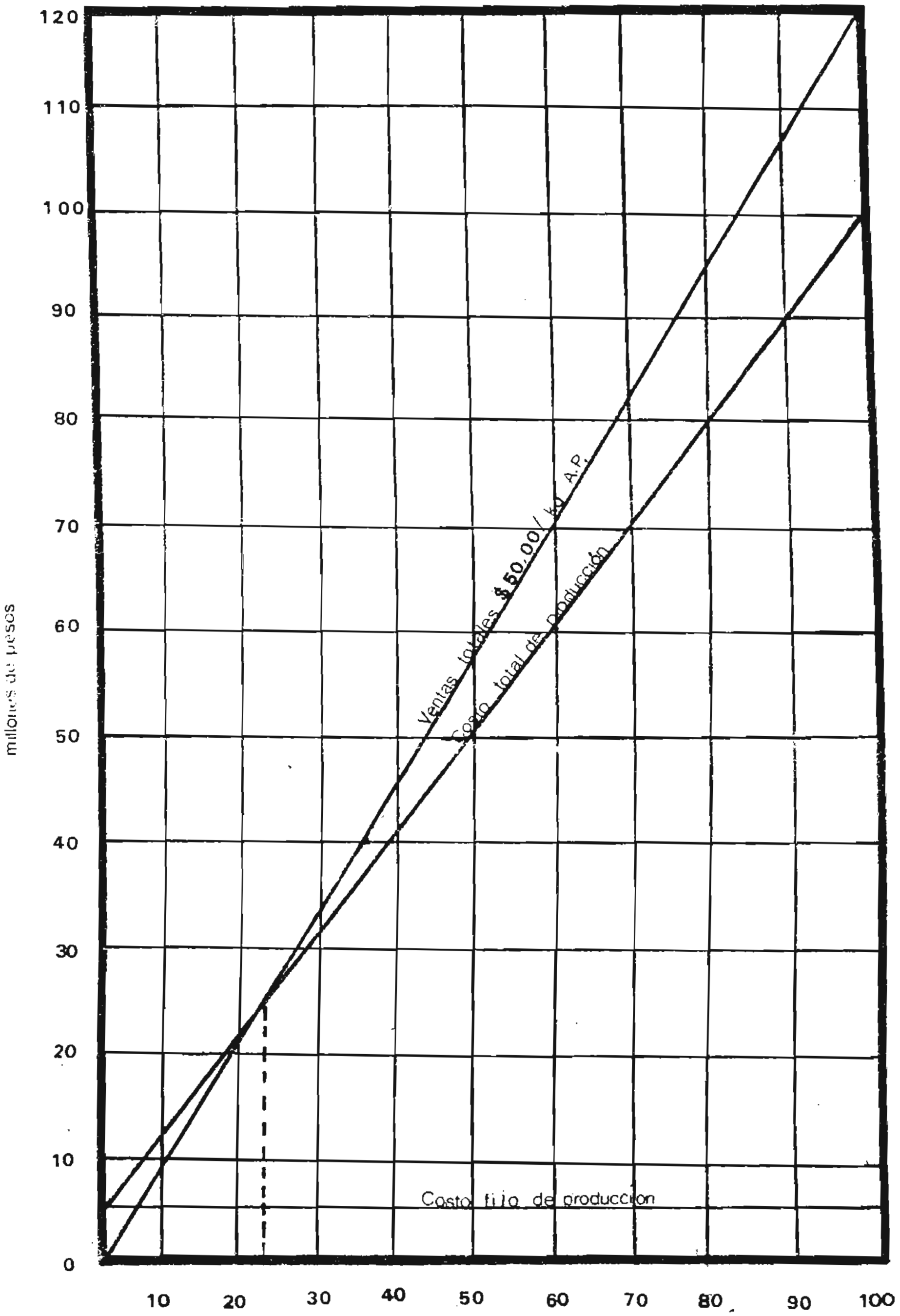
(Miles de pesos)

VII.- ESTADO DE PERDIDAS Y GANANCIAS

ESTADO DE PERDIDAS Y GANANCIAS PROFORMA; PRECIO DE VENTA $ 50.00/kg
Capacidad 2221 Ton/año
(miles de pesos)

Ejercicio social terminado al 31 de Diciembre de 1982	1977	1978	1979	1980	1981	1982
Unidades Vendidas Ton/año.	—	1494	1623	1840	2028	2221
Ventas Netas.	—	80687.5	87650	99375	109525	119950
COSTOS Y GASTOS DE OPERACION						
Costo de lo vendido	—	64 127.38	69 219.98	77 786.6	85 208.4	92 827.52
Depreciación y Amortización	—	2 470.0	2 470.0	2 470.0	2 470.0	2 470.0
Gastos de Administración y Ventas	—	5 132.4	5 387.0	5 815.3	6 186.2	6 567.4
UTILIDAD DE OPERACION	—	8 958.12	10 573.02	13 303.1	15 660.4	18 085.08
Gastos Financieros	—	335.175	1 675.87	1 675.87	1 619.98	1 340.61
Utilidad antes de otros		8 622.95	8 897.15	11 627.23	14 040.42	16 744.47
Gastos de Arranque y Seguros	—	924.11	138.55	138.55	138.55	138.55
Gastos Imprevistos	3 219.53	—	—	—	—	—
Gastos Preoperativos	1 385.51	—	—	—	—	—
UTILIDAD ANTES DE ISR	—	7 698.84	8 758.6	11 488.68	13 901.87	16 605.92
I S R	—	3 233.51	3 678.6	4 825.25	5 838.78	6 974.48
Utilidad antes de R.U.	—	4 465 33	5 080.0	6 663.43	8 063.09	9 631.44
Reparto de Utilidades		615.90	700.7	919.09	1 112.15	1 328.77
Utilidad Neta		3 849.42	4 379.3	5 744.34	6 950.94	8 303.0
% de Utilidad Neta a Ventas Netas		4.8	5.0	5.8	6.4	6.93
Capital Social		10.77	11.74	14.41	16.00	18.73

VIII.- GRAFICA DE PUNTO DE EQUILIBRIO


millones de pesos
120
110
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
Ventas totales $ 50.00/ kg A.P.
Costo total de producción
Costo fijo de producción

IX.- Estudio Bibliográfico

a) Análisis

b) Hidrólisis

c) Polimerización

a) Análisis

Determination of molecular parameters of the viscosity equation of such polymers through consideration of the draining effect. Kenji Kamide and Toru Kawai (Tokyo Inst. Technol.). *Kobunshi Kagaku* 20(8), 506–11(1963)(Japan); cf. *CA* 56, 6158a, following abstr. The intrinsic viscosity $[\eta]$ of a polymer soln. is given by $[\eta] = KM^a$, where K is a const., M the mol. wt., and a a mol. parameter; $a = 0.5 + a_1 + \Delta$. Three different procedures which enable the sepn. of the free-vol. effect, a_1, and the draining effect, Δ, are presented by using the Krigbaum relation (*CA* 54, 23409e) between $[\eta]$ and the 2nd virial coeff. and Yocks relation (*CA* 53, 18508b) between a and the expansion factor. Examples of analysis of the existing data by the 3 methods gave consistent values of Δ, the av. values being as follows: poly(Me methacrylate) in MeCOEt 0.040, poly(vinyl acetate) in Me$_2$CO 0.031, atactic polystyrene in PhMe 0.040, isotactic polystyrene in PhMe 0.060, poly(vinyl alc.) in H$_2$O 0.082, polyacrylonitrile in HCONMe$_2$ 0.121, atactic polypropylene in C$_6$H$_6$ 0.120, and cellulose trinitrate in EtOAc 0.46. The derived Δ did not depend on M owing to inadequate approxns. involved. The Δ for cellulose trinitrate varies according to the degree of esterification. Hideaki Chihara

Relation between the parameters in the Mark-Houwink equation for the intrinsic viscosity of polymer solutions. Kenji [illegible]

1881

modification (K., *et al.*, *CA* 55, 39d) of the Flory theory (F. and Fox, *CA* 45, 7409f) was applied to the Mark-Houwink equation $[\eta] = KM^a$ to improve the evaluation of excluded-vol. effect. The result shows that the draining effect Δ estd. by this improved method is smaller than the estimate based on the Flory theory (cf. Kamide and Kawai, preceding abstr.) as shown

Polymer	Δ (Flory)	Δ (Kurata)
poly(vinyl alc.)	0.99	0.22
atactic polypropylene	0.11	0.005
cellulose trinitrate	0.39	0.35

5764

Electron paramagnetic resonance spectra of free radicals in the decomposition products of solid oxygen-containing polymers. V. A. Radtsig and P. Yu. Butyagin. *Vysokomolekul. Soedin.* 7 (5), 922–7(1965)(Russ). The E.P.R. spectra are presented for specimens of the following polymers subjected to mech. degradation: polyformaldehyde, poly(ethylene oxide), poly(propylene oxide), and poly(vinyl alc.). The intensities and line widths are tabulated, as are the decompn. temps. For polyformaldehyde, the fact that an E.P.R. spectrum could be obtained at all indicates a free-radical mechanism for its mech. degradation. The data indicate that in chains of the structure –C–C–O–C–C–, rupture occurs predominantly at the C–C bond. The spectra indicate the presence of more than just one type of radical in the degraded polymers on a matrix of inert solvent. R. H. Albert

b

5767

Concentrated solutions and gels of poly(vinyl alcohol). I. Gelation processes and elasticity-viscosity characteristics of gels. L. I. Khomutov, G. P. Trofimova, E. P. Korchagina, and S. A. Glikman. *Zh. Prikl. Khim.* 38(3), 638–43(1965)(Russ). The differential curves of mol.-wt. distribution were detd. on 1% aq. solns. of 2 samples of com. poly(vinyl alc.) (I). Fractional freezing out and viscosity detn. of fractions were used (Loconti and Cahill, *J. Polymer Sci.* 49(152), S2(1961)). Sample II (av. mol. wt. 41,500, $\eta_{abs.}$ of 10% soln. 364) was not uniform with respect to its mol. wt., while sample III (mol. wt. 38,000, $\eta_{abs.}$ 280) showed a much more homogeneous mol.-wt. distribution corresponding to a peak in the 0.6–0.8 × 10^{-3} poise viscosity range. II and III had the same content of Ac groups (1.30%). Six percent iodo-I (IV) gels were prepd. from II and III upon addn. of a soln. of iodine in KI and of H$_3$BO$_3$. The IV gel from III had a higher mech. strength, greater elasticity, and higher viscosity than that from II. The capacity of IV to form mech. strong gels is important for medical applications, e.g., as a gel for filling the cavities in lungs of tuberculosis patients (Ushakov, (*CA* 55, 14018b). With increasing amts. of iodine (9–15%) and H$_3$BO$_3$ (2–6%) embodied in the IV gel from III, its mech. properties improved. The gelation capacity (as indicated by the no. of days required for ripening of the gel) was higher for I gel from III than for that from II. The mech. properties of the gel from III were superior to those of the gel from I. With a decreasing content of Ac groups in I, the gelation capacity increased and the mech. stability of the gels improved. GZJR

Concentrated solutions and gels of poly(vinyl alcohol). II. Thermal characteristics of gels. L. I. Khomutov, E. P. Korchagina, and S. A. Glikman. *Zh. Prikl. Khim.* 38(4), 786–91 (1965)(Russ); cf. preceding abstr. The thixotropic temp., T_t, and the gel formation temp., T_g, of gels of 6% poly(vinyl alc.) +15% I + H$_3$PO$_4$ were detd., the former by the temp. at which the gel broke at a given load P and the latter by the temp. at which the viscosity detd. with a falling sphere did not increase over 3 hrs. Extrapolation of T_t vs. P to $P = 0$ gave the m.p. of the gel. The plot of $1/T_g$ vs. the gel concn. was a linear function from which the energy of a single bond in the system was found to be 10.21 kcal./mole. GBJR

5804

Supermolecular order in chemical fibers and the increase of their stability. I. Analysis of some rheological factors affecting the structure of poly(vinyl alcohol) fibers. A. Ya. Sorokin, L. M. Pyrkov, and S. Ya. Frenkel. *Khim. Volokna* 1965(3), 2–7(Russ). In wet spinning, there are 3 regions after the spinneret: (*1*) the still liquid jet, (*2*) the coagulating, viscoelastic fiber, and (*3*) the coagulated, solid, highly swollen fiber. Exptl. fibers were spun from 10.4% poly(vinyl alc.) (I) in H$_2$O (0.48% acetate groups, intrinsic viscosity 100 ml./g.). The soln. was heated for 24 hrs. to 95° and filtered (Schott no. 1). Acetone, PrOH, iso-PrOH, aq. Na$_2$SO$_4$ (400 g./l.), and AcOH were used as coagulants. The spinning device allowed the following variations: uptake 0.5–85 m./min., bath length 100–900 mm., stretching 0–15,000%, bath temp. 0–200°. The spun fibers were tested

h

the stabilization process of I is more than a depression of the adverse effects of HCl. A. P. Mueller

5827

Spectrophotometric investigation of poly(vinyl alcohol) during heating. Mirosław Mrozowski, Wacław Sopicki, and Gabriel Włodarski (Inst. Syn. Fibers, Lodz, Poland). *Faserforsch. Textiltech.* 16(5), 260–72(1965)(Ger). The intensity of the 1146 cm.$^{-1}$ line in the ir spectrum of isotropic poly(vinyl alc.) film, characterizing the magnitude of the cryst. fraction, was detd. in the 0–210° temp. range. The intensity increased with increasing temp. until a max. was reached at 180° and then decreased to 0 at 205°. The 2nd-order transition was indicated by a dip in the temp. *vs.* intensity curve in the 80–100° area. Rapid cooling from 200° tended to stabilize the cryst. fraction, indicated by the disappearance of the 1146 cm.$^{-1}$ line. G. J. Ernyei

6351

New method of the experimental study of the desorption of surface-active substances from liquid phase boundaries. R. A. Kul'man (M. V. Lomonosov State Univ., Moscow). *Dokl. Akad. Nauk SSSR* 162(5), 1095–6(1965)(Russ). The desorption from liquid-gas and liquid-liquid boundaries were studied by using the lying bubble or drop method. In an optical cell with the soln. of the surface-active substance, a gas bubble (drop) was formed and the soln. was then slowly replaced by pure solvent. The surface tension was detd. from contour dimensions of the bubble. For 0.01% aq. Na oleate and pH 11, the surface tension increased from 33.3 ergs/cm.^{2} up to 72.0 ergs/cm.^{2}, which is close to the value for pure water. The adsorption and desorption are thus reversible. However, for poly(vinyl alc.) soln., the surface tension (63.0 ergs/cm.^{2}) did not change after replacing the soln. by H_2O and the adsorption is irreversible.

K. Dusek

6487

Effect of potassium iodide on the iodine-poly(vinyl alcohol) color reaction. L. G. Tebelev and N. A. Silkina. *Dokl. Akad. Nauk SSSR* 161(5), 1096–7(1965)(Russ). The absorption spectra in the visible range (400–700 mμ) of the I_2-KI-poly(vinyl alc.) (PVA) system was studied by maintaining the concns. of PVA and I_2 at 0.02 and 1.0%, resp., at increasing concns. of KI of 1.3, 1.5, 1.65, 1.8, 2.0, and 2.6%. The 6 curves obtained indicated "shortwave" absorption bands at 490 mμ, at low iodide concns., due to a complex compd. of I_2 and PVA. With increasing iodide concn., the equil. was shifted to an increase in the "blue" ("longwave") complex, with absorption bands at 600 mμ. All the curves intersected in the 530-mμ region, indicating an equil. in this area of 2 color center forms. Free I_2 is essential to "shortwave" complex formation, corresponding to the 490-mμ band, while the 600-mμ band is due to the "blue" complex resulting from triiodide formation under conditions wherein an excess of KI is required for a practically complete binding of I_2 to form the triiodide ion. J. Beller

7128

Differential thermal analysis of polymers. III. Differential thermal analysis of poly(vinyl alcohol) and its derivatives. Yoshiro Nakamura and Hideo Terui (Iwate Univ., Morioka, Japan). *Kogyo Kagaku Zasshi* 68(4), 737–8(1965)(Japan); cf. *CA* **57**, 4839*e*, 13964*f*. The endothermic peak of poly(vinyl alc.) (I) above 200° becomes larger when a sapong. agent, such as H_2SO_4 or NaOH, is present. The exotherm starts around 250°, showing the accelerated decompn. of I by such impurities. I with different acetate group contents shows endothermic peaks at 120, 200–30, and 320–60°, corresponding to evapn. of adsorbed
c water, fusion, and pyrolysis, resp. These peaks are displaced to higher temps. as the acetate content decreases. This can be used to est. the acetate content in I. Formalization of sapond. I makes the peaks at 220 and 360° disappear and new ones appear at 150–250 and 445°. Hideaki Chihara

7163

Effect of some molecular structural factors on the mechanical properties of poly(vinyl alcohol). Waichiro Tsuji, Ryozo Kitamaru, and Tetsuo Ikeda. *Bull. Inst. Chem. Res., Kyoto Univ.* 42(2-3), 93–104(1964)(Eng). Effects of residual acetyl content, mol. wt. and its distribution in poly(vinyl alc.) (I) on some mech. properties of I film or fiber were studied. Some unfavorable effects of the small quantity (less than 0.5 mol. %) of Ac groups residue on the drawability at high temp. and tensile strength of I film or fiber were observed. The linear relation between tensile strength of max. stretched film of well fractionated I and the reciprocal value of the degree of polymerization was observed, while a linear relation was not observed with unstretched film or film stretched to some lesser degree. Examg. the effect of mol. wt. distribution on the mech. properties of I confirmed that tensile properties generally decreased with lower no. av. mol. wt. or with increasing inhomogeneity of mol. wt. distribution even if the samples had an equal viscosity av. mol. wt. and were tested at an equal degree of stretching.

Allan E. Sherr

7164

Rheological properties of concentrated poly(vinyl alcohol) solutions. II. Rheological properties of plasticized systems. N. S. Volkova and A. A. Konkin. *Khim. Volokna* 1965(3), 7–11(Russ); cf. *CA* 62, 14875*c*. Poly(vinyl alc.) (I) with d.p.
e 1600 was studied in a rotational viscometer at shear rates of 4.4×10^1 to 4.4×10^3 sec.$^{-1}$, concn. in H_2O c = 35–55%, and temp. 60–90°. The log-log flow curves show 2 straight-line portions: the 1st with slope 1 (Newtonian flow), the 2nd with slope 1 (nN = non-Newtonian flow). E.g., for c = 50 and 80°, the nN slope was 4.5. The junction point indicates the crit. gradient, D_{crit}, where the destruction of supermol. structures and thus nN flow begin (here 270 sec.$^{-1}$). The shear stress τ is lowered during the first ~8 sec. from its max. value to its stationary value due to thixotropy (e.g. from about 6 to 4×10^5 dynes/cm.^{2}). D_{crit} and the nN slope increase with c (e.g. D = 170 and 275, slope = 2.3 and 4.5 for 35 and 55%, resp.). The viscosity increases rapidly with c. D_{crit} is slightly raised with increasing temp.; the slope is not altered. The viscous-flow activation energies are 3.6, 7.97, 9.73, and 11.23 kcal./mole for c = 35, 40, 45, and 50%, resp.; for c = 40% they are 6.72 and 2.9 for D = 52.8 and 2430 sec.$^{-1}$, resp. If, instead of H_2O, mixts. of H_2O and ethylene glycol or $HCONMe_2$ are used for plasticizing, in equiconcd. solns., a higher viscosity results at low D, while at high D, nearly no difference is found. I plasticized with ethyleneglycol or glycerol, measured with c = 35% at 140°, gave flow curves of the usual form with a steeper nN branch. H_2O appears the most efficient plasticizer for I. J. Schurz

8486

Kinetics of polymerization of vinyl monomers prepared from dicarboxylic acids. I. Kinetics of polymerization of vinyl *N*,*N*-diisobutylglutaramate. G. N. Freidlin and K. A. Sclop (Branch State Inst. Nitrogen Ind., Severodonetsk). *Vysokomolekul. Soedin.* 7(6), 1060–4(1965)(Russ). The kinetics of polymerization of iso-$Bu_2NCO(CH_2)_3CO_2CH:CH_2$ (I) was studied in the presence of $(BzO)_2$ as catalyst. The dependence of the polymer yield with time on the monomer concn. (by dilg. in EtOAc in the range of 1.3–2.4 mole/l.) and $(BzO)_2$ concn.
d (0.0192–0.0587 mole/l.) was detd. at 60, 70, and 80°. In the polymerization of I (concn. 3.4 mole/l.) with $(BzO)_2$ (0.0385 mole/l.), the over-all reaction consts. at 60, 70, and 80° were 0.0261, 0.0529, and 0.1355, resp. The activation energy was 18.3 ± 0.2 kcal./mole. The rate consts. of transfer to monomer were calcd. from the mol. wt. of polymers detd. from the characteristic viscosity of poly(vinyl alc.) formed as a result of alk. sapon. of the appropriate polymers. The mol. wts. of the polymers studied were in the range of 42,800 to 58,400. Equations are derived to show that termination of the kinetic chain occurs mainly through transfer to monomer. S. Kaganoff

Determination of unperturbed dimensions of polymer molecules by viscometry of moderately concentrated solutions. C. F. Cornet (Koninkl./Shell-Lab., Amsterdam). *Polymer* 6(7), 373–84(1965)(Eng). It was demonstrated that unperturbed dimensions of high-mol.-wt. polymer coils can be detd. from viscosity data of moderately concd. polymer solns. by assuming that a uniform total segment d. is attained at the so-called crit. concn. The root-mean-sq. end-to-end distance is given by $(R_0^2)^{1/2} = 2.84 \times 10^{-8} (M/c_{cr})^{1/3}$, where M is the mol. wt. and c_{cr} is the crit. concn. $(R_0^2/M)^{1/2}$ values from different sources are shown for polystyrene in PhMe, poly(vinyl alc.) in H_2O, poly(vinyl chloride) in cyclohexanone, poly(α-methylstyrene) in PhMe, polyisoprene in *n*-heptane, and an ethylene-propylene copolymer in a θ mixt. Effects of polydispersity and branching can be neglected.
T. E. Muller

Electron-microscopic method of studying the supermolecular structure of polymers in solution. V. A. Kargin, N. F. Bakeev, S. Kh. Fakirov, and A. L. Volynskii (M.V. Lomonosov State Univ., Moscow). *Dokl. Akad. Nauk SSSR* 162(4), 851–2(1965) (Russ); cf. *CA* 62, 9248*d*. With a new method of prepg. samples for electron-microscopic investigations, the supermol. structure of polymers was studied in soln. As solvents, compds. with low crit. temps. were used, e.g. propane. Solns. of poly-1-butene (mol. wt. ~180,000) and atactic polypropylene (mol. wt. ~35,000) in propane were studied with concns. varying between 0.05 and 3 wt.-%. The new method enables the estn. of the character of the assocn. of macromols. in solns.
K. W. Gabbert

Cohesive-energy densities of high polymers. VI. Cohesive energy densities of poly(vinyl esters). D. Mangaraj, S. Patra, P. C. Roy, and S. K. Bhatnagar (Indian Inst. Technol., Kharagpur). *Makromol. Chem.* 84, 225–9(1965)(Eng); cf. *CA* 62, 14841*b*. The soly. parameters (δ) of poly(vinyl acetate) (I) and poly(vinyl propionate) were estd. by their swelling and soln. viscosity measurements in a series of alkyl acetates and propionates. The soly. parameter of poly(vinyl propionate) is smaller than that of I, indicating that the intermol. forces in a polymer decrease with an increase in the bulk of the side group. The soly. parameters of the polymers are slightly higher than the soly. parameters of their structural equivs., whereas in the case of polyacrylates and polymethacrylates the soly. parameters of polymers are much higher than those of their structural equivs. Although I and poly(Me acrylate) are close in their chem. structure, the former has a lower soly. parameter compared to the latter. The glass transition temp. of poly(Me acrylate) (273°K.) is lower than that of I (300°K.). If cohesive energy d., flexibility of the backbone chain, and bulk of the side group are detg. factors for glass transitions, then the contrary result should have been found.
I. C. Kogon

Configuration of vinyl polymers from high-resolution nuclear magnetic resonance spectra. I. Poly(vinyl chloride). W. C. Tincher (Chemstrand Res. Center, Inc., Durham, N. Car.). *Makromol. Chem.* 85, 20–33(1965)(Eng). High-resolution N.M.R. spectra of samples of the title compd. were obtained. The methinyl proton spectrum consists of 3 quintets which are assigned to isotactic, heterotactic, and syndiotactic triads. Detns. of the relative nos. of each triad in several samples show that the degree of stereoregularity is not affected by changes in polymerization solvent or temp. The 100-Mc. spectrum of poly(α-deuterovinyl chloride) indicates that the methylene proton spectrum consists of 2 overlapping triplets from isotactic and syndiotactic diads. It is possible that the methylene proton spectrum is complicated by the presence of branching in poly(vinyl chloride). **II. Polypropylene.** *Ibid.* 34–45. High-resolution N.M.R. spectra of polypropylene, poly(propylene-*3,3,3-d₃*), and poly(propylene-*1,1-d₂*) were analyzed. Although the methinyl proton spectrum is not influenced by the stereochem. configuration, differences appear in the methylene proton spectrum which can be related to tacticity. By comparison of calcd. methylene proton spectra, assuming different ratios of isotactic and syndiotactic diads with the observed spectra, information is obtained about the tacticity of the polypropylene samples. III. Poly(vinyl alcohol). *Ibid*, 46–57. High-resolution N.M.R. spectra of the title compd. were analyzed. The methinyl proton spectrum consists of 3 quintets as in poly(vinyl chloride). The methylene proton spectrum consists of 2 triplets from isotactic and syndiotactic diads. The spectra indicate that poly(vinyl alc.) (I), prepd. by hydrolysis of poly(vinyl acetate), is essentially atactic, I obtained from poly(vinyl *tert*-Bu ether) is predominantly isotactic, and I from poly(vinyl trifluoroacetate) is slightly syndiotactic.
D. V. Anders

The determination of the stereochemical microstructure of poly(vinyl alcohol) by H_1–H_1-spin uncoupling. J. Bargon, K. H. Hellwege, and U. Johnsen (Deut. Kunststoff Inst., Darmstadt, Ger.). *Makromol. Chem.* 85, 291–6(1965)(Ger). The exact detn. of the structure of poly(vinyl alc.) is possible by H_1–H_1-spin uncoupling. Therefore, the "sideband technique" was used, whereby emitter and magnetic field are modulated. PhOH and D_2O were used as solvents. Me_4Si (2%) was used as an internal standard for PhOH; cyclohexane (τ = 8.57) was used as an external standard for D_2O and converted for Me_4Si. Poly(vinyl alc.) (5 mg.) in 100 mg. PhOH at 180° gave the best results for uncoupling. D_2O as solvent gave, in the case of uncoupling, only a single line for the C–H resonance (Ramey and Field, *CA* 62, 9241*d*). Only with PhOH as solvent, was it possible to resolve the resonance of uncoupled α-protons into 3 sep. lines. They belong to the CH groups of the repeated vinyl unit (Bovey, *et al.*, *CA* 59, 7097*h*). The resonance of α-protons in syndiotactic triads is shifted towards lower field intensities to τ = 5.69, and in isotactic triads towards higher field intensities to τ = 5.86. In heterotactic triads, the resonance is at τ = 5.78. This correlation is made by analogy to poly(vinyl chloride) (B., *et al.*, *loc. cit.*), since the influence of an OH substituent on the resonance of the CH group is very similar to that of a Cl substituent. The intensity of the 3 signals in case of uncoupling depends upon the abundance of the types of microstructure in the polymer. This makes it possible to det. the proportion of isotactic and syndiotactic linkages and the av. length of sequency with high accuracy.
Judith Eisenbeiss

The effect of nonelectrolytes on association processes in solutions of poly(methacrylic acid) and poly(vinyl alcohol). E. B. D'yakonova, I. S. Okhrimenko, and I. F. Efremov (Lensovet Technol. Inst., Leningrad). *Vysokomolekul. Soedin.* 7(6), 1016–19(1965)(Russ); cf. *CA* 63, 2840*d*. Turbidimetric titrn. of a 1% aq. soln. of poly(vinyl alc.) (I) (mol. wt. 84,000) with 1% aq. poly(methacrylic acid) (II) (mol. wt. 87,000) showed that in the mixt. having the highest absorbance the ratio of I to II is 3:7. At higher concns. of the solns. (above 7%), a gel is formed, the compn. of which is independent of the ratio of the components and corresponds to the stochiometric value. The addn. of nonelectrolytes (MeOH, EtOH, $HOCH_2CH_2OH$, Me_2CO, dioxane, and $HCONMe_2$) in very small concns. lowered the absorbance and therefore the degree of assocn. of the macromols. The mechanism of the assocn. is discussed.
Ota Horak

Spectrophotometric analysis of the interaction of iodine with solutions of poly(vinyl alcohol). L. G. Tebelev, G. F. Mikul'skii, E. P. Korchagina, and S. A. Glikman (State Univ., Saratov). *Vysokomolekul. Soedin.* 7(1), 123–8(1965)(Russ). The effect of the concns. of iodine, poly(vinyl alc.) (I), and starch on the intensity of the absorption bands in the 600-mμ region is discussed, and a spectrophotometric method is proposed for characterization of certain properties of I mols. The color reaction is not only chem. in nature. The aggregation of the mols. is a necessary condition for the formation of a "blue complex." The dependence of absorptivities on I concn. was studied. The unleached I samples with a low content of Ac groups have a greater ability to form the "blue complex." Absorption curves for starch and I are different because of different penetration of iodine into the 2 materials. In starch, the penetration involves the cavities between the mol. aggregates as well as the contents of the aggregates, whereas in I only the interaggregate cavities are involved. 15 references.
V. Sychra

10080

Rotation of molecular groups in polymers. O. N. Trapeznikova and [illegible]. *Vestn. Leningr. Univ.* 20(10), *Ser. Fiz. i Khim.* No. 2, 60–75(1965)(Russ). The temp. dependences of the birefringence of poly(Me acrylate) (over the range 3–300°K.) and of poly(vinyl acetate) (I) (20–300°K.) were measured. The small temp. dependence in the former case is ascribed to rotational isomerism inside the ester group. The anisotropy of the polarizability of the ester group indicates a transition of this group from a cis- into nearly planar trans-configuration. The energy difference for the 2 isomeric states is 600 cal./mole. The temp. dependence in the case of I is ascribed to the rotational vibrations of the AcO group. The temps. of max. dielec. and mech. losses are compared with the data of the present work.
Jehudah Eliassaf

10120

Photosensitive resins. IV. The sensitization and spectral sensitivity of photosensitive resins. Jyong Sup Shim, Hideo Kato, Tadashi Yoshinaga, and Shinichi Kikuchi (Univ. Tokyo). *Kogyo Kagaku Zasshi* 68(5), 1002–8(1965)(Japan); cf. preceding abstr. The spectral sensitivities and uv absorption spectra of the cinnamate ester films of poly(vinyl alc.), phthalic anhydride–glycerol, and isophthalic acid–glycerol polycondensates were examd. with and without sensitizers. The sensitizers used were 1,2-benzanthraquinone, *p*-nitroaniline, *p*-nitrodiphenyl, 5-nitroacenaphthene, 2-chloro-1,8-phthaloylnaphthalene, and picramide, and the results were compared with Kodak Photo Resist and Kodak Ortho Resist. The films were prepd. by spraying the soln. of these resins in the mixed solvent of Cellosolve acetate with trichloroethylene or acetone on an Al plate and drying with an ir lamp. All these resins were photosensitized, and the larger the sensitization effect, the broader the sensitive range toward the longer wavelengths. The absorption peak coincides with the spectral sensitivity max., and the exposure used cured the resins. The best sensitizers were 5-nitroacenaphthene for the poly(vinyl alc.) and the phthalic polycondensate esters and 2,6-dichloro-4-nitroaniline for the isophthalic polycondensate ester. The spectral sensitivity of the furfural–acetone polycondensate was examd.; the photosensitization was small. On the basis of these spectral sensitivities a conventional method of sensitivity representation was proposed. **V. The photocuring reaction of photosensitive polycondensates.** Jyong Sup Shim, Tadashi Yoshinaga, and Shinichi Kikuchi (Univ. Tokyo). *Ibid.* 1009–12 (1965)(Japan). The mechanism of photocuring reaction was studied by examg. the ir spectra before and after the exposure of phthalic anhydride-glycerol and isophthalic acid-glycerol polycondensate cinnamate esters and furfural–acetone polycondensate, with and without sensitizers. The sensitizers used were 5-nitroacenaphthene for the phthalic, 2,6-dichloro-4-nitroaniline for the isophthalic and 1,2-benzanthraquinone for the furfural resins. The absorption bands of cinnamoyl group at 1639 and 983 cm.$^{-1}$ for the cinnamate esters and of furfurylidene group at 1608 and 972 cm.$^{-1}$ in the ir spectra were decreased or disappeared with extended exposure times, and the uv absorption spectra agree with the calcd. values. The curing is due to the intermol. cross-linking by the cleavage of the C:C bonds in the cinnamoyl or the furfurylidene groups. **VI. Application of photosensitive polycondensates in engraving.** Jyong Sup Shim, Takahiro Tsunoda, and Shinichi Kikuchi (Univ. Tokyo). *Ibid.* 1013–16(1965)(Japan). The resolving powers, conventional sensitivities, and reagent stabilities were examd. in relation to the applicability in engraving of phthalic anhydride–glycerol and isophthalic acid–glycerol polycondensate cinnamate esters and furfural–acetone polycondensate, 5-nitroacenaphthene, 2,6-dichloro-4-nitroaniline, and 1,2-benzanthraquinone, resp., being used as sensitizers, and compared with Kodak Photo Resist. The resolving powers before and after the corrosive treatment with HNO_3 and the sensitivities of these resins sprayed on Zn plate increase with the degree of polymerization of these resins and the duration of exposure, and they are comparable with or sometimes better than the Kodak materials; the stabilities of these resin films against HNO_3 and $FeCl_3$ soln. are also comparable. These resins may be applicable as practical engraving resists complying with their characteristics.
T. Okano

11719

Turbidimetric titration method for determining solubility distributions of polymers. W. H. Beattie (Shell Oil Co., Torrance, Calif.). *J. Polymer Sci., Pt. A* 3(2), 527–49([illegible]). Turbidimetric titrn. is a quick and accurate method for detg. mol. wt. distributions of polymers. Like many [illegible] of detg. mol. wt. distributions, this method also depends upon soly. differences. In the general procedure the turbidity of a dil. polymer soln. is measured as it is titrated with a precipitant. Initially, the higher-mol.-wt. species ppt., but with increasing amt. of precipitant added, the lower-mol.-wt. species ppt. and the turbidity increases. The turbidity is assumed proportional to the concn. of the pptd. polymer. This then allows calcn. of the wt. distribution of solys. of the polymer. Common difficulties of this procedure, such as the importance of relative refractive indices and the effect of particle size on the turbidity readings, are discussed. The turbidimetric titrn. method can also give mol. wt. distribution data provided that the relation between soly. and mol. wt. is known. The relation between turbidity and particle size is given by the Mie equations rather than Rayleigh's law. Since concns. are quite dil. (e.g., <0.05%), secondary scattering is ignored. Turbidity is almost independent of the degree of swelling of the particles even though their size is changed with swelling. Also, turbidity is approx. independent of particle size in the region of the max. turbidity value. Turbidity measurements were made until after this max. value was reached and the turbidity started to decrease. This decrease was a particle size effect and was not due to sedimentation. Exptl., a series of pptns. was made using different vol. fractions of precipitant. The concn. of pptd. polymer can be detd. and plotted as a function of vol. fraction of precipitant. This gives the soly. distribution curve. Using the method of max. turbidity measurements results in abs. soly. values. However, broad particle size distributions require a more complicated treatment than does a narrow particle size distribution. Expts. were performed using polystyrene in order to test the theory. A modified recording spectrophotometer was used along with a special turbidity cell. Approx. 30 ml. of soln. at 0.01% concn. was used for each sample. MeCOEt was the solvent while iso-PrOH was the precipitant. Exptl. findings agreed with the theory. The accuracy of this abs. method for turbidimetric titrns. was confirmed by using conventional fractionation techniques. Addnl. verification of the theory comes from the fact that use of different wavelengths gave almost identical results and also that the mixing conditions had little influence on the max. turbidity. Many of the usual precantions for a turbidimetric titrn. are not necessary with this method.
J. J. Krackeler

13437

Measurements of light scattering and viscosity during the degradation of polymers in solution by ^{60}Co γ-rays. Yoshito Ikada and Wolfram Schnabel (Hahn Meitner Inst., Berlin). *Makromol. Chem.* 86, 20–32(1965)(Ger). Polymers that had been γ-irradiated in solns. below the crit. concn. were studied for light scattering and viscosity. It could thus be deduced whether the polymers undergo intramol. cross-linking in dil. solns. or are predominantly degraded in the main chain. In all the cases investigated, degradation was observed. Poly(vinylpyrrolidinone) showed practically no branching after irradiation below the crit. concn.; above this concn., branching increased with dose. Poly(vinyl acetate) degraded in dil. acetone soln. Polystyrene and poly(dimethylsiloxane) degraded in C_6H_6 at low concns. The results are discussed with respect to Henglein's theory (*CA* 54, 5213*b*; Schnabel and H., *CA* 55, 20919*g*) concerning degradation and cross-linking of polymers in org. solvents.
Paul J. de Meester

16484

Determination of head-to-head arrangement in poly(vinyl alcohol). Hung Chen. *Ko Fen Tzu T'ung Hsun* 7(1), 65–8 (1965)(Ch). The head-to-head arrangement in poly(vinyl alc.) is detd. by using ceric salt instead of HIO_4. RCTT

Solvation of macromolecules in binary solvents. III. Number of adsorbed molecules on polystyrene in methyl ethyl ketone–C_6H_6 solvent mixture. H. Lange (Deut. Kunststoff Inst., Darmstadt, Ger.). *Makromol. Chem.* 86, 192–9(1965)(Ger); cf. *CA* 62, 11841*e*. The no. of the solvent mols. in the adsorption layer of one monomer unit of polystyrene (*I*) in the mixed solvent C_6H_6–MeCOEt were detd. as a function of the temp. and the compn. of the solvent by using light scattering and density measurements described previously (*CA* 62, 2835*h*). The no. of adsorbed mols. at 20–70° did not depend on the temp. at all compns. of the solvent, including limiting cases, where the solvent consists only of one component. Mols. of C_6H_6 are adsorbed preferentially. The no. of the adsorbed mols. on one monomer unit of I in pure MeCOEt was 0.7 ± 0.2 as compared with 3.1 ± 0.4 in pure C_6H_6, which is known from earlier measurements (*CA* 62, 14841*c*). B. K. Mikelsaly

16485

Viscoelastic properties of poly(vinyl acetates). III. Mechanical loss and molecular weight distribution. Yasuji Oyanagi and John D. Ferry (Univ. of Wisconsin, Madison). *Proc. Intern. Congr. Rheol., 4th, Providence* 1963, Pt. 2, 491–503(Pub. 1965)(Eng); cf. *CA* 60, 679*c*. The mech. loss tangent (tan δ) was measured for 4 fractions of poly(vinyl acetate) and 24 binary blends of fractions, at frequencies between 0.08 and 5 cycles/sec. and various temps., in the region where tan δ passes through a min. For each fraction and blend, the temp. dependence was described by the method of reduced variables, with shift factors related to the free vol. and hence the no.-av. mol. wt. (M_n) as in previous creep studies on similar samples. For the fractions and the blends in which both mol. wts. exceeded the crit. value for entanglement coupling (M_c), the magnitude of tan δ at its min. was expressed by the linear relation log tan δ_m = 3.63–0.80 log M_n, whose slope agrees with the theory of Marvin. For the blends in which only 1 mol. wt. exceeded M_c, tan δ_m was smaller than would be predicted by this relation and it could not be expressed by any simple empirical equation involving mol. wt. averages. In blends of 2 components with mol. wts. exceeding M_c, the frequency location of the min. shifted down with increasing proportion of the component of higher mol. wt. In blends with 1 component of mol. wt. less than M_c, the location of the min. was nearly independent of compn. It appears to be impossible from loss measurements alone on a single blend to det. whether components of mol. wt. less than M_c are present.

16586

Temperature variation of unperturbed chain dimension of stereoregular poly(vinyl alcohols) from thermoelasticity measurements in diluents. Ichiro Sakurada, Akio Nakajima, and Kyoichiro Shibatani (Univ. Kyoto, Japan). *Makromol. Chem.* 87, 103–18(1965)(Eng). Thermoelastic measurements were carried out on isotactic (I), syndiotactic (II), and atactic (III) poly(vinyl alcs.) in ethylene glycol–H_2O mixts. as a function of temp. from 20 to 90°. The energy and entropy components of the retractive force and the temp. variation of the unperturbed mean-sq. end-to-end distance $\langle R_0^2\rangle$ were detd. by thermodynamic analysis of the stress-temp. exptl. results. It was found that $\partial \ln\langle R_0^2\rangle/\sigma T$ is neg. for all samples and their abs. values are in the order of I > III > II. These results are discussed by considering the effects of stereosp. configurations on the chain conformation assocd. with bond rotations. I. C. Kogon

18281

The specific heat of high polymers as a function of the previous state of the material. H. Tautz, M. Glueck, G. Hartmann, and R. Leuteritz (Deut. Akad. Wiss., Berlin). *Plaste Kautschuk* 11(11), 657–61(1964)(Ger). The effect was measured of annealing above the softening temp., of cooling in liquid N, and of stretching the sample on the sp. heat of poly(vinyl acetate), poly(vinyl chloride), a vinyl acetate–vinyl chloride copolymer, low- and high-pressure polyethylene, isotactic polypropylene, polystyrene, poly(Me methacrylate), and poly-ε-caprolactam. Cooling has no effect on amorphous substances; stretching produces a max. near the glass-transition temp. which is related to orientation in the material. Cooling decreases the melting temp. of the polyethylenes and increases that of polypropylene. The enthalpy gain between room temp. and 180° is smaller for the treated samples than for the annealed ones.

18279

Structural viscosity of polymer solutions. Franz Patat and Gottfried Sperr (Tech. Hochsch., München, Ger.). *Makromol. Chem.* 87, 8–20(1965)(Ger). Non-Newtonian flow of solns. of polyisobutylene, poly(vinyl acetate), polyethylene glycol, and polyisoprene were studied in relation to mol. wt., concn., temp., and solvent. The increase of viscosity was caused by polymer associates-solvent interactions, which were dependent on the rate of shearing stress. Millard Maienthal

The effect of particle size and distortions on the x-ray diffraction patterns of polymers. R. Bonart, R. Hosemann, and R. L. McCullough (Chemstrand Res. Center, Durham, N. Car.). *Polymer* 4, 199–211(1963)(Eng). The theory of the paracrystal developed by Hosemann (*CA* 45, 4131*g*) is used for the development of a general method by which the effects of short-range displacement distortions, long-range, liquidlike distortions, and particle size on the diffraction diagrams are sepd. and analyzed. The application of the method to polymer systems requires that ≧2 orders of interference be observed. An amorphous phase, if present, contributes to the diffuse background and must be considered. A further requirement is that the particle size be reasonably large. From *CZ* 1964(49), Abstr. No. 912. M. G. Moore

X-ray diffraction method for determining the degree of crystallinity of polymers. M. A. Martynov and K. A. Vylegzhanina. *Plasticheskie Massy* 1965(8), 50–3(Russ). Existing x-ray methods for detg. the degree of crystallinity of polymers, based on the measurement of integrated intensities, are subject to many errors. It is more satisfactory to measure 2 quantities, *A* and *K*, proportional to the content of amorphous and cryst. polymer, resp., and to find the degree of crystallinity from a calibration chart. With Cu K_α radiation, *A* for polyethylene was taken as the difference between the diffracted intensities at 2θ = 16° (the background value) and at 19°30′, and *K* as the difference between the intensities at 19°30′ and at 21°24′ (110 reflection). For polypropylene, the corresponding values of 2θ were 10°, 15°03′, and 16°50′ (040 plane of the α modification). Graphs of *K* vs. *A* are linear, as they should be. The crystallinity values are closer to those from d. measurements than are those from other x-ray detns. Gordon G. Evans

Phenomenological theory of spherulitic crystallization: primary and secondary crystallization processes. Fraser P. Price (Gen. Elec. Res. Lab., Schenectady, N.Y.). *J. P*

Sci., Pt. A 3(9), 3079–86(1965)(Eng). The theory of high-polymer crystn. developed takes into account: (*1*) a transformation which follows the usual Avrami kinetics of nucleation and growth of spheres, and (*2*) a stage with decreased crystn. rate, where vol. fraction transformation increases approx. as ln time. All the crystn. is assumed to occur within the spherulites, but the amt. of crystallinity at any particular point within the spherulite depends on the length of time that the region has been inside a spherulite. Hence it is shown that the transformation curves so derived resemble those obtained from actual polymer crystn. F. Learmonth

18282

Structure of macromolecules at liquid-solid interfaces. *F. R. Eirich, R. Bulas, E. Rothstein, and F. Rowland* (Polytech. Inst., Brooklyn, N.Y.). *Ind. Eng. Chem.* 57(9), 46–52(1965) (Eng). The adsorption of polymers is the primary step in the
l formation of all polymeric interfacial bonds, such as occur in org. adhesion, in coatings, in dispersion stabilization (affecting viscosity), and in biol. membranes. All adhesives are macromol. in character and form bridges of multiple van der Waals strength between adjacent phases. The function of primers or the adherence of various paints or coatings can be understood on the same basis, as can the action of fillers. The stabilization of a dispersion functions via solvated protective jackets formed by adsorbed macromols. Many biol. structures are of composite nature and contain folded or helical macromols. in contact with solid materials (e.g. inorg. constituents of bone or teeth). More
e specific information than is available from adsorption isotherms was obtained in 2 types of expts. In the 1st, the flow rate of polymer solns. and of corresponding pure solvents through capillaries or sintered glass disks was measured. In the 2nd, viscosities of coated and uncoated dispersions were measured. Expts. were carried out [redacted]merized poly(vinyl acetate), mol. wt. 75,000-1,200,000; [redacted]ions of comm. polystyrene, mol. [redacted], and a poly(Me methacrylate) freed from gel and sepd. into 5 fractions, mol. wt. 75,000–1,400,000. In the case of polystyrene on a polar surface, the thickness adsorbed rose rapidly to almost the free coil value at 50,000–100,000 mol. wt. and then declined. With polymers
f of Me methacrylate and vinyl acetate, it eventually rose to about half the free coil diam. All data confirmed the view that the polymers were adsorbed in the form of monolayers of coils, somewhat, but not much, denser than in soln., and with dimensions perpendicular to the surface which were substantial fractions of the free coil diams. 28 references. GRJN

The surface tension of aqueous solutions of poly(vinyl alcohol) esterified by fatty acids in homogeneous systems. Sadao Hayashi, Chiyoko Nakano, and Takuhiko Motoyama (High Polymer Chem. Ind. Ltd., Osaka, Japan). *Yukagaku* 14(1), 24–6(1965)(Japan). Poly(vinyl alc.) (PVA) was esterified by
g HCO_2H, HOAc, and $EtCO_2H$ in homogeneous systems contg. water with HCl as catalyst and the surface tensions of these esterified PVA were measured. The lowering of the surface tension with esterified PVA was in the order HCO_2H < HOAc < $EtCO_2H$. It was presumed that the surface chem. properties of aq. solns. of partially sapond. polyvinyl ester became more active with increase in the hydrophobic properties of the ester group if the residual ester content and the distribution of ester groups in a polymer chain were the same. RCYS

Relation between parachor and Zisman's critical surface tension of polymers. Irene J. Lee, William M. Muir, and
h Donald J. Lyman (Stanford Res. Inst., Menlo Park, Calif.). *J. Phys. Chem.* 69(9), 3220–2(1965)(Eng); cf. *CA* 45, 4109*b*. The addivity of parachor for low-energy polymer solids is expressed as $\gamma_p^{0.25} = P(\text{polymer})/V_m(\text{polymer}) = nP(\text{monomer})/nV_m(\text{monomer}) = P(\text{monomer})/V_m(\text{monomer})$, where γ_p is the surface tension of the constituent group, P the parachor,

18290

Densities of radiation-grafted copolymers. Kh. U. Usmanov, R. S. Tillaev, and U. N. Musaev. *Vysokomolekul. Soedin* 7(8), 1310–13(1965)(Russ). Acrylonitrile was radiation-grafted on polystyrene, poly(vinyl chloride), chlorinated poly(vinyl chloride) and poly(vinyl alc.) (*CA* 61, 13479*c*). Densities of the grafted polymers (as detd. by the hydrostatic method in iso-BuOH) were different than the additive mean value of densities of the polymer components, showing the structural changes of the polymers due to grafting. O. Elsner

Dynamic determination of the elasticity modulus of polymers exposed to γ-rays and fast electrons. A. I. Kurilenko, O. F. Tatarenko, and V. L. Karpov. *Vysokomolekul. Soedin.* 7(8),
d 1422–6(1965)(Russ). The elasticity modulus and shear modulus of the hardened condensation polymers and some thermoplastics before irradiation and after the action of γ-rays of fast electrons were detd. by the dynamic method of free oscillations. Unsatd. polyester type PN-1, poly(Me methacrylate), and poly(vinyl chloride) were irradiated at 25° with ^{60}Co γ-rays at intensities of ≦800 rads/sec. and doses of ≦15 megarads or with fast electrons of energy 0.3 Mev., at intensities of ≦1.5 megarads/sec. and doses of ≦498 megarads. No reversible changes in the elasticity and shear modulus were observed. I. Brzezinski

18351

Transition of external friction to viscous flow in the surface melting of polymers. G. V. Vinogradov, V. A. Mustafaev, Yu. Ya. Podolskii, and Yu. M. Malinskii (Inst. Petrochem. Synthesis, Moscow). *Dokl. Akad. Nauk SSSR* 163(6), 1419–22(1965) (Russ). A study of the external friction of polymers is an effective method for detg. changes in the various states of polymers, such as transitions from the glass-like, high-elastic, and plastic states. The transition from a glass-like to a high-elastic state is accompanied first by an increase, and then by a decrease of friction force (Elkin, *Iznos i Trenie Metallov i Plast. Mass, Sb.* 1964, 101 pp.). Measurements of external friction were carried out on a Tr-7 tribometer (friction gage) in a wide temp. range (40–200°) and in a vacuum of 10^{-4} torr, at const. loads of 10 g., and slip rates of 5×10^{-3}, 10^{-2}, 10^{-1}, and 1 cm./sec. The results are presented in the form of friction force (*F*)-temp. (*t*) curves. The following cryst. and amorphous plastics were studied: low-pressure (I) polyethylene (Alkathene 2) and high-pressure (II) polyethylene (Hostalen GD), I and II with different degrees of radiation cross-linking, polypropylene, polystyrene, poly(oxymethylene), poly(vinyl acetate) and poly(Me methacrylate). A. Plochocki

18353

Radiation cross-linking of nylon 66 and poly(vinyl alcohol). Bruce S. Bernstein, George Odian, Gyula Orban, and Sebastian Tirelli (Radiation Applications, Inc., Long Island City, N.Y.). *J. Polymer Sci., Pt. A* 3(10), 3405–12(1965)(Eng). The process of radiation-induced cross-linking of polymers in the presence of polyfunctional monomers, disclosed in an earlier communication (*CA* 61, 5803*h*, 9627*g*), was extended to nylon 66 and to poly(vinyl alc.) (I). Nylon extruded tape was cut into strips ~2.5 cm. in length, swollen to equil. in vol. mixts. of $MeOH/H_2O$/allyl methacrylate, flushed with N, irradiated by ^{60}Co at 0.02–0.06 megarad/hr., vacuum dried at 120° for 16 hrs., and weighed. White, fluffy, fibrous gel fractions were obtained by immersion of the irradiated strips in 97–100% HCOOH. The extn. was continued for 8–12 days at room temp. Under these conditions, similarly treated monomer-free species had dissolved in less than one day. The primary effect of radiation on nylon 66 was cross-linking. The results obtained upon varying the solvent/monomer compn. and upon conducting control expts. using straight irradiation of the polymer either in N or in $MeOH/H_2O$ mixts. in the absence of polyfunctional monomers, suggest that MeOH/-monomer mixts. reduce the radiation dose required for gelation, while H_2O aids in increasing the total gel fraction. Increases in the radiation dose, as well as increases of the monomer content in the initial system, caused a corresponding increase in the extent of gelation. I films were cast from 7% aq. solns., immersed in $MeOH/H_2O$/allyl methacrylate solns., irradiated by ^{60}Co at 0.04 megarad/hr., washed with cold H_2O, dried, and weighed. Gel fractions were detd. by extn. for 4 days either in refluxing H_2O or in triethylenetetramine at room temp. Results obtained by varying the solvent/monomer compn. at const. radiation dose showed that H_2O markedly affects the amt. of monomer incorporated into the polymer. The monomer consumption also increased with increasing radiation doses; however, very rapid cross-linking was observed even at low doses, e.g. 75% gel was obtained after only 4–5 megarads of radiation. In the absence of monomer under otherwise equal conditions, no gel formed. The mechanism of ^{60}Co radiation-polyfunctional monomer cross-linking is interpreted as occurring via radiation-induced radical formation on the polymer backbone, followed by radical interaction to form a three-dimensional network. G. W. Scherf

18357

Pyrolysis and oxidation of plastics. B. Kaesche-Krischer (Bundesanstalt Materialpruefung, Berlin). *Chem.-Ingr.-Tech.* 37(9), 944–51(1965)(Ger). Auto-ignition of plastics is a problem in fire-prevention research. The possible mechanisms of pyrolytic decompn. and oxidn. of poly(vinyl alc.), polyacrylonitrile, and polypropylene are treated. Results are reported for thermogravimetric and differential thermal analysis expts. in vacuum and at O pressures up to 500 torr, over temps. ≦500°. Karl Kammermeyer

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High-resolution nuclear magnetic resonance analysis of vinyl acetate copolymers. Martin W. Dietrich and Robert E. Keller (Monsanto Co., St. Louis, Mo.). *Anal. Chem.* 36(11), 2174-7 (1964)(Eng). N.M.R. spectra of the title copolymers were measured on 80-20 wt./vol. solns. in CCl_4 by using a Varian HR-60 spectrometer. Reference standards of copolymers of known compn. were prepd. as latex emulsions, cast on glass, allowed to dry, and dissolved in CCl_4. Characteristic peaks for
h dibutyl fumarate (I), dibutyl maleate (II), dioctyl maleate (III), and 2-ethylhexyl acrylate (IV) in the presence of vinyl acetate (V) and the copolymer were identified and calibration curves of relative peak heights of monomer and copolymer peaks were prepd. From these curves, the mole % compn. of samples was detd. with a claimed accuracy of 2 mole % abs. N.M.R.

657

Properties and structure of poly(vinyl alcohol). Waclaw Wojciak (Univ. Poznan, Poland). *Zeszyty Nauk. Univ. Poznaniu, Mat., Fiz., Chem.* No. 6, 44-53(1962); cf. *CA* 56, 15004i. Aq. (6%) solns. of poly(vinyl alc.) were fractionated by sedimentation in cylinders 40 cm. high. After 20 days, samples of the solns. were taken from the top and the bottom layers, KI, was added, and transparency studied with the aid of a Pulfrich colorimeter by using a filter of λ_{max} = 533 mμ. The amt. of aldehyde groups in the samples was detd. by the Willstatter and Schudel method (*CA* 13, 406). The transparency of the solns. was higher and the amt. of I adsorbed lower in samples taken from the bottom layer. Thus, the end aldehyde groups in particles of poly(vinyl alc.) in the bottom layer are more susceptible to reaction with oxidizing substances, probably because the polymer chains are more straight there. None of these differences were observed for solns. heated on a steam bath before sedimentation. Irena Kloczko

1794

Dependence of the mechanical properties of poly(vinyl alcohol) on its cross-linking. N. Inoyatov and B. I. Aikhodzhaev (Inst. Polymer Chem., Acad. Sci. Uzbek S.S.R., Tashkent). *Vysokomolekul. Soedin., Khim. Svoistva i Modifikatsiya Polimerov, Sb. Statei* 1964, 118-21; cf. *CA* 59, 14122h. The dependence of the mech. properties of poly(vinyl alc.) (I) on cross-linking induced by S_2Cl_2 in PhMe solns. at 110° was studied. Graphs of the breaking stress *vs.* elongation at 25° for samples contg. 0,
c 1.1, 4.7, 7.01, 17.3, and 26.8% S and graphs of elongation, residual elongation, and breaking stress at 25-250° and of the elasticity modulus at 25° *vs.* the amt. of combined S showed that cross-linking of I increased the breaking stress and the elasticity modulus while the elongation decreased, esp. at higher temps. The mech. properties are due to the cross-links and to the cryst. areas of I. Roentgenograms showed that I with 15-20% combined S, substituting practically all OH groups, was fully amorphous. In such samples, the mech. properties depended only on the degree of cross-linking. M. Kalfus

2835

Polarography in the determination of the molecular weight of poly(vinyl alcohol). V. D. Bezuglyi and E. K. Salichuk (Inst. Monocrystals, Scintillators and Highly Purified Materials, Kharkov). *Dokl. Akad. Nauk SSSR* 158(6), 1390-2(1964)(Russ). The effect of the mol. wt. of poly(vinyl alc.) on the lowering of the polarographic max. of the 2nd order on the Cu wave was investigated in 1*M* KCl solns. The extent of inhibition of the max. height decreased linearly when the mol. wt. increased in the range 5000–10^6. When a mixt. of 2 equal fractions of mol. wts. M_1 and M_2 were polarographed, the actual mol. wt. observed was $(M_1 + M_2)/2$. The accuracy was ±4%. From the calibration curve obtained, the mol. wt. of unknown fractions was detd. The height of the max. of the 1st order was almost independent of the mol. wt. of poly(vinyl alc.). G. Thirot

Solvation of macromolecules in binary solvents. I. A method for determining the number of solvated molecules. H. Lange (Deut. Kunststoff Inst., Darmstadt). *Kolloid Z.* 199 (2), 128–35(1964). The mol. wt. of polystyrene in mixts. of *n*-docosane, *n*-dodecane, *n*-hexane, and C_6H_6 detd. by light scattering was compared with the no. of solvent mols. in the adsorption layers of the macromols. If $\alpha = \lim_{c \to 0} dx_1/dc$, where x_1 is the mole fraction of the solvent component preferentially solvating the macromols. and *c* is the wt. concn. of the macromol. substance, then $\alpha = [V_M x_1x_2/M]\{(N^*_{1s}/x_1) - (N^*_{2s}/x_2)\}$, where V_M is the mol. vol. of the solvent mixt., x_2 is the mole fraction of the other solvent component, *M* is the true mol. wt. of the polymer, and the N^* terms are the no. of solvate mols. in the adsorption layers of a macromol. By approxn., the no. of C_6H_6 mols. in the adsorption layer of one polystyrene monomer unit at 20-70° was 3.1 ± 0.4. Thomas A. Wilson

4641

Thermal behavior of poly(vinyl alcohol) crystallites. I. Thermal expansion. Kau Shirakashi, Kinzo Ishikawa, and Keizo Miyasaka (Tokyo Inst. Tech.). *Kobunshi Kagaku* 21 (234), 588-93(1964). The thermal dimensional changes of poly(vinyl alc.) (I) crystallites were studied by x-ray diffraction method from room temp. to ~200°. The crystallites expand anisotropically with the increase in temp.; the expansion coeff. in the direction of the *a* axis is much larger than that of the *c* axis, and that of the *b* axis (mol. direction) is somewhat neg. at higher temp. The thermal expansion coeff. of the crystallites changes discontinuously at ~120°. This characteristic temp. corresponds to the 2nd-order transition point of I crystallites. Since the temp. coeff. of β (angle between the *a* and *c* axis) is neg., I crystallites may approach orthorhombic with the increase in temp. Eiichi Wada

7883

Tacticity of poly(vinyl acetate) by NMR. Kermit C. Ramey and Nathan D. Field (Atlantic Refining Co., Glenolden, Pa.). *J. Polymer Sci.* Pt. B. 3(1), 69-72(1965)(Eng). N.M.R. studies were made on poly(vinyl acetate) and its derivs. The resonance at 100 Mc./sec. of the α proton decoupled from the β protons shows 3 components with the same relative areas as that of the 3 Me components. The undecoupled spectrum of poly(vinyl acetate) in CH_2Cl_2 consists of the α proton and the Me and β proton resonances. The decoupled α proton resonance shows components at τ = 5.03, 5.07, and 5.10. The β proton resonance decoupled from the α proton shows only a singlet. A. A. Hiltz

7923

Light stabilization of polyamides by graft copolymerization. N. P. Gnip, N. V. Kulik, A. A. Kachan, and E. E. Chervyatsova. *Khim. Prom., Inform. Nauk.-Tekhn. Zb.* 1964(4), 9–10 (Ukrain). Irradiation with uv light decreases the strength of polyamide fibers. When Kapron (I), or I graft-copolymerized with 6% or 12% polyacrylonitrile or 2% poly(vinyl acetate), were irradiated for 100 hrs. with 365 μm uv light, their strength decreased by 18, 12, 9, and 8%, resp. Irradiation of I or I-copolymerized fibers for 40 hrs. with uv light of 320 μm decreased their strength by 55 and 40%, resp. Graft copolymerization made polyamides light-stable by blocking their amide bonds. BMJW

7024

Graft copolymerization of styrene onto poly(vinyl alcohol) fibers impregnated with catalysts. Ichiro Sakurada and Yasuyoshi Sakaguchi (Univ. Kyoto, Japan). *Sen-i Gakkaishi* 20(8), 518-5[illegible](196[illegible])(Japan). Untreated and heat-treated (at 180 or 225°) poly(vinyl alc.)(I) fibers, impregnated with solns. (1 g./g. of fiber) of various catalysts, were heated with styrene (1.8 g./g. of fiber) in sealed tubes for graft copolymerization. When $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ were used as catalysts, the grafting generally proceeded smoothly, and grafting efficiencies of ~90% were obtained. The grafting efficiencies were affected only slightly by catalyst concns. (0.3-3%), solvents (H_2O, 15:85 H_2O-MeOH, 30:70 H_2O-Me_2CO) of the impregnating solns., and heating temps. With H_2O_2 as catalysts, grafting efficiencies were generally lower than with persulfates, but efficiencies of ~80% were obtained under favorable conditions. The grafting efficiencies increased with decreasing catalyst concns., heating temps., and increasing H_2O contents of the impregnating solns. With azodiisobutyronitrile and Bz_2O_2, grafting did not proceed as smoothly as with persulfates; the efficiencies were only ~55% even under favorable conditions, and they were affected considerably by catalyst concns. and heating temps. The grafting was affected only slightly by previous heat treatment of the fiber when the H_2O contents of the impregnating solns. were high, but considerably affected when the H_2O contents were lower. In another series of expts., dry I fibers impregnated with catalysts were heated with styrene-MeOH mixts. for grafting. The reaction proceeded as smoothly as with fibers impregnated with catalyst solns. Grafting took place only slightly when dry fibers were heated with pure styrene. Graft polymerization of styrene in emulsion onto I fibers was also investigated. High-efficiency grafting could be obtained by using 2% polyethylene glycol oleyl ether as an emulsifier. The grafting behavior of the I-styrene system was generally similar to that of the cellulose-styrene system, with some small differences. From *Polymer Rept.* 1964(77), 32-3.

TCPM

8475

Measurement of dielectric properties of substances by the method of a stationary probe at 1.18 cm. wavelength. I. E. Ezhik (Polytech. Inst., Kharkov). *Pribory i Tekhn. Eksperim.* 9(5), 187-90(1964)(Russ). The app. and method of the stationary probe are described for studies of dielec. properties of solids and liquids, which make it possible to follow continuously changes in the temp. dependence of dielec. properties of substances. The parameters are recorded automatically in a wide [illegible] temps. The [illegible] dependence of tan δ are presented, realizing mol. transformations of acetophenone and poly(vinyl acetate). The curves are obtained at a frequency of 10^{10} cycles/sec. The app. may also serve for the investigation of the influence of monochromatic light on dielec. properties of substances.

J. Hejduk

9253

Structure of polybutadiene grafted onto cellulose or poly(vinyl alcohol). Ichiro Sakurada, Toshio Okada, and Ayako Torikai. *Nippon Hoshasen Kobunshi Kenkyu Kyokai Nempo* 4, 89-94 (1962)(Japan). The structures of polybutadiene (I) and of I grafted onto cellulose or poly(vinyl alc.) were detd. by ir analysis. I polymerized by γ-irradiation did not contain the cis-1,4 structure, and the ratio of the trans-1,4 structure to the vinyl structure was ~4. In the case of I grafted onto cellulose by a mutual irradiation, the cis-1,4 structure could not be found either. The value of the trans-1,4/vinyl ratio was 1.5-2 for this expt. The amt. of vinyl structure increased with increasing percent graft. The value of trans-1,4/vinyl was ~2 in the case of I grafted onto poly(vinyl alc.).

RCTT

10528

Determination of the molecular polydispersity of poly(vinyl alcohol) by the method of summation fractionation. Henryk Sibinski and Halina Jaron. *Polimery* 9(7-8), 321-5(1964)(Pol). The following method has been developed: 8-12 test tubes containing polymer solns. of equal concn. are prepd. By adding to the tubes different amts. of a substance, in which the polymer does not dissolve, the polymer is divided into 2 fractions; 8-12 fractions of different sizes and different av. d.p. are thus obtained from the concd. phases, and 8-12 fractions from the dil. phases. If the concd. phase is a ppt. the polymer is recovered by washing and drying the ppt. The polymer from the dil. phases is generally rejected. The fractions thus obtained are dried to const. wt. and their wt. fractions and intrinsic viscosities $|\eta|$ are detd. The av. d.p. X is calcd. by the equation $|\eta| = 8.33 \times 10^{-4} X^{0.11}$.

P. Neta

11926

Differential thermal analysis of polymers. V. O. Gorbacheva and N. V. Mikhailov. *Vysokomolekul. Soedin.* 7(1), 28-32 (1965)(Russ). A thermographic study was made of the processes of heating and cooling poly(ethylene terephthalate) (I), poly(vinyl alc.) (II), polycaproamide (III), polyacrylonitrile (IV), poly(tetrafluoroethylene) (V), and polypropylene (VI) under different conditions of synthesis and processing. Data are given to show that with the increase of mol. wt. of I (11,500-30,000) the region of phase transitions widens, heat of crystn. decreases, and the initial temp. of the process can be lowered. The temp. range of transition of II into a viscous state depends upon the method of prepn., apparently assocd. with the degree of stereoregularity of the polymer mols. Thermograms for III show that an increase in mol. wt. is accompanied by a decrease of the area of the peak in the melting range of polymer, i.e. by a decrease of the amt. of heat needed to destroy the initial structure of polymer. Independently of the method of processing IV, its thermogram shows a spread-out endothermic effect. On heating highly oriented fibers of IV, its thermogram shows no reversible effects, thus indicating that the polymer is amorphous. Heating and cooling V gives a thermogram indicating absorption and evolution of heat owing to melting and crystn. of polymer. Differing from other polymers, VI, owing to its stereoregularity, crystallizes over a comparatively narrow temp. interval of 3-5°.

S. Kaganoff

11954

Radiation-induced graft copolymerization to poly(vinyl alcohol). X. Grafting of vinyl monomers to poly(vinyl alcohol) fibers and some mechanical properties of the grafted fibers. Ichiro Sakurada, *et al.* *Doitai To Hoshasen* 4(4), 363-74(1962)(Japan); cf. *CA* 62, 7916e. Grafting of styrene, Me methacrylate, acrylonitrile, and 2-methyl-5-vinylpyridine to poly(vinyl alc.) fibers by γ-ray irradiation was carried out and the mech. properties of the grafted fibers were detd. The fibers used in the expts. were: dried fibers, heat-treated fibers, and formalized fibers. Regardless of the monomer used, the ease of the grafting is in the following order; dried fiber > heat-treated fiber > formalized fiber. In some cases, the grafted fibers were further subjected to after-treatments such as heat treatment or formalization. When the fibers were grafted with styrene or Me methacrylate, they became more thermoplastic and their elastic recoveries and heat setting properties were improved. Fibers grafted with 2-methyl-5-vinylpyridine showed good dyeability when the degree of grafting was >5%. **XI.** Grafting of styrene to dry poly(vinyl alcohol) films in styrene-methanol solution at higher temperatures by γ-irradiation. *Ibid.* 375-82. Grafting occurs in styrene-MeOH soln. without the presence of water at >40°. The favorable effect of solvents is far less remarkable for other org. liquids than for MeOH. The effect of MeOH seems to be related to the swelling power, for the degree of swelling of poly(vinyl alc.) films also becomes appreciable first at 40°. When the styrene:MeOH ratio is varied, the rate of grafting is highest at a higher MeOH concn. The optimum temp. for the grafting is 70° at the dose rate of 1.1 × 10^4 r./hr. and 55° at the dose rate of 4.8 × 10^3 r./hr., resp. From *Nucl. Sci. Abstr. Japan* 3(4), Abstr. No. 00933-4(1964).

TCNK

Determination of lanthionine in wool hydrolyzates. P. Miro and J. J. G. Dominguez (Dept. Textil Patronato "Juan de la Cierva", Barcelone, Spain). *Bull. Inst. Textile France* 18(115), 953-66(1964)(Fr). Various methods for detn. of lanthionine (I) by paper chromatography of wool hydrolyzates were examd. With use of a 2:1:1 BuOH/AcOH/H_2O mixt. as a developer, sepn. of I and cystine (II) requires several days. Oxidn. of the hydrolyzate improves sepn., due to greater differences in the R_f of the I sulfoxide and cysteic acid (III) formed

13256

Structure formation in poly(vinyl alcohol) solutions. P. I. Zubov and E. A. Osipov (Inst. Phys.-Chem., Moscow). *J. Polymer Sci., Pt. A* 3(2), 423-31(1965)(Eng). Supermol. structures of colloidal sizes were obtained by cooling poly(vinyl alc.) (I) solns. in anhyd. $HCONMe_2$. The diam. of these ℓ particles depends on the concn. of soln. and on the temp. at which the I solns. are cooled. The globular particles formed are quite stable. They keep their structure after complete removal of solvent. The presence of small amts. of H_2O (<1%) causes a redistribution of intermol. and intramol. bonds, as h shown by a gradual increase of viscosity and transformation of the soln. to a transparent thixotropic gel. Bond redistribution takes place rapidly upon heating the soln. to 120°. The structure formation in I solns. has a great influence on the mech. and adhesion properties of I films. Films prepd. from globular I solns. obtained by acetalation with succinaldehyde show better

13328

Statistical analysis applied to film development: grafted poly(vinyl alcohol)-based water-soluble film. Alan F. Bentz and Roy W. Roth (Am. Cyanamid Co., Stamford, Conn.). f *J. Appl. Polymer Sci.* 9(3), 1095-1105(1965)(Eng). A statistically designed expt. was used to predict the optimum properties and conditions for formation of a water-sol. film. The film was made from an 88%-hydrolyzed low-mol.-wt. poly(vinyl alc.) (I) (PVA-L) to which poly(Et acrylate) was grafted by the Ce ion technique of Mino and Kaizerman (*CA* 54, 10400e). An 88%-hydrolyzed high-mol.-wt. I (PVA-H) was blended with the graft in order to increase the tensile strength. The exptl. design included 5 different levels of Ce ion concn., of $CH_2:CHCO_2Et$, and of PVA-H. The properties tested were tensile strength, tab tear strength, Elmendorf tear strength, % elongation at break, modulus, rupture time in water, and soln. time in water. g The exptl. responses were submitted to statistical analysis and a digital computer was used to fit approx. functions (2nd degree polynomials) to the data by the method of least sqs. When the quadratic components could not be reliably estd., linear approximations were used. Contour surfaces were drawn for each of the responses with the 3 exptl. variables as coordinates. From the results, 6 films were designed which were predicted to have overall good properties. These were prepd. and cast both by hand and on a heated drum. Generally, good agreement was obtained between predicted and observed values and between hand- and drum-cast samples. Thus, statistical analysis permitted, with h a min. no. of expts., the establishment of reliable estimates of interaction of the variables in prepn. of the film, from which a film suitable for com. use could be designed. R. H. Loeppert

14847

Properties of graft copolymers of poly(vinyl alcohol) with vinyl acetate or methyl acrylate. Seikon Ren (Univ. Kyoto, Japan). *Kyoto Daigaku Nippon Kagakuseni Kenkyusho Koenshu* 18, 1-8 (1961)(Japan). Graft copolymers of partially acetylated poly(vinyl alc.) with vinyl acetate or Me acrylate were synthesized by emulsion polymerization in aq. soln. with $K_2S_2O_8$ as catalyst or with irradiation. The swelling behavior in acetone and deswelling in water of these graft copolymer films were examd. by measuring the dimensions of and the stresses in the films as a function of the degree of grafting and of acetylation. The ratio of the film dimensions in acetone and in water indicated that the swelling is nearly reversible. This was also confirmed by the measurement of the change of the stresses in the film during swelling. The stress in the film is nearly proportional to the water content of the swelling medium, and has a nearly linear relation with the square root of the time after the immersion of the film into the medium. The diffusion of acetone and water into the graft copolymer films was discussed. Graft copolymers of highly acetylated poly(vinyl alc.) become opalescent upon swelling. T. Okano

14825

Interference refractometry of polymer solutions. E. Èlbing and A. G. Parts (Univ. Sydney). *Makromol. Chem.* 82, 270-6 (1965)(Eng). The specific *n* increments of polystyrene, poly(vinyl chloride), poly(vinyl acetate), and polyacrylonitrile in ℓ PhMe, Me_2CO, and $HCONMe_2$ polymer-solvent systems were measured by an interference refractometer. The technique described permits rapid and precise evaluation of d*n*/d*c* and eliminates the difficulties normally associated with interferometric measurements in org. solvents. Peter Marcel Barna

Nuclear magnetic resonance spectra of poly(methyl methacrylate) in solution. II. The calibration of the infrared absorption method and some applications to study of the polymerization mechanism. Yoshinori Kato, Haruaki Watanabe, and Atsuo Nishioka (Elec. Commun. Lab., Tokyo). *Bull. Chem. Soc. Japan* 37(12), 1762-8(1964)(Eng); cf. *CA* 62, 4128b. Stereoregularity measurements were made and a statistical method applied to an investigation of anionic polymerization of Me methacrylate. Two types of catalysts were used: RMgBr, with R = Et, *n*-Bu, *n*-Pr, *n*-Am, *n*-heptyl, and Ph; and R_2Mg, with R = Et, *n*-Bu, iso-Pr, iso-Bu, Ph, and cyclohexyl. The polymerization temperatures were −78° to 150°. The proportions of syndiotactic and isotactic triads were determined by use of 2 pairs of bands in the ir spectra of polymer films: 1063 and 1393 cm.$^{-1}$ for *S* triads and 749 and 757 cm.$^{-1}$ for *I* triads. The infrared method was calibrated with mixts. of 2 polymers of known stereochem. compositions and the calibration was verified by the N.M.R. method described in Part I (*loc. cit.*). An extension of the Ising model of the linear chain (cf. Kramers and Wannier, *Phys. Rev.* 60, 252-62(1941)) and of a treatment of polymer chains by Miyake and Chujo (*CA* 55, 12967d) was developed and applied to interpretation of the exptl. data. Polymerization with R_2Mg catalysts occurs by 2 mechanisms which yield both atactic and stereoblock polymer chains, and stereochem. configurations of the polymers are rather const., regardless of polymerization temp. and the identity of R. On the other hand, polymerization with RMgBr produces more isotactic polymers, the stereoregularity is dependent on polymerization temp., and only a single mechanism is involved.

Raymond C. Ferguson

Properties of polymer solutions from the comparison of uv and ir spectra of polymers and their hydrogenated monomers. I. Poly(vinyl acetate)-ethyl acetate system. M. F. Mayaki and A. H. Al-Taiar (Univ. Baghdad, Iraq). *J. Polymer Sci., Pt. B* 3(4), 331-7(1965)(Eng). The band of max. uv absorption of poly(vinyl acetate) and of EtOAc shifts towards lower wavelengths as the concn. of the solutes in dioxane and MeOH is reduced. The short range effect of mol. interactions for poly(vinyl acetate) in dioxane and MeOH is zero. In $CHCl_3$ the absorption peak shifts to longer wavelengths for poly(vinyl acetate). The explanation is found in the varying extent of stabilization of the excited state of the CO group in the H-bonding and the non-H-bonding solvent. The absorbance of poly(vinyl acetate) is higher than that of EtOAc in $CHCl_3$ at the same concns. The difference is less marked in dioxane and in MeOH. There is little or no difference between the CO group vibrations in the ir of poly(vinyl acetate) and of EtOAc. I. C. Kogon

14851

Photocatalytic oxidation of poly(vinyl alcohol) by benzophenone. Yves Tradelle and Jean Néel (Ecole Super. Phys. Chim., Paris). *Compt. Rend.* 260(7), 1959-2(1965)(Fr). Partial oxidn. of poly(vinyl alc.) by Ph_2CO in 1:1 vol./vol. HOAc-H_2O has been studied. When photocatalyzed by uv light, the oxidn. leads primarily to partial conversion of secondary OH groups of the polymer to carbonyl groups, with redn. of the Ph_2CO to benzopinacol (I). The reaction is accompanied by subsequent degradation of the polymer and the formation of terminal CO_2H groups. Under the reaction conditions, the CO_2H groups combine immediately in lactone rings or in intra-mol. linkages. Aq. poly(vinyl alc.) (50 ml. 8.8% or 9.3%) was mixed with 200 ml. HOAc and approx. 3 g. Ph_2CO, and the mixt. was irradiated with uv at 25° under N. The resulting carbonyl and CO_2H groups were detd. in the oxidized polymer, the carbonyl groups by reaction with $H_2NOH.HCl$ and the CO_2H groups by sapon. with KOH and back-titration with excess alkali (which includes the lactone formations). The viscosity of the reaction mixts. decreases only slightly during irradiation, no decrease being apparent in absence of Ph_2CO. Slight yellowing of the soln. and pptn. occur during the reaction. The soln. contains the oxidized polymer, which was sepd. either by stabilization and removal of impurities by extn. with benzene, or by repeated pptn. with acetone. The ppt. consists mainly of I. When (*A*) 17 parts oxidant/100 parts polymer was irradiated 72 hrs., it gave 5.3 carbonyl and 5.5 CO_2H groups/100 parts oxidized polymer. Similarly, (*B*), 17 parts oxidant/100 parts polymer, irradiated 72 hrs. gave 7.5 carbonyl and 11.6 CO_2H groups/100 parts oxidized polymer, and (*C*) 18 parts oxidant, irradiated 60 hrs. gave 2.34 carbonyl and 2.75 CO_2H groups/100 parts oxidized polymer. In *A* and *B*, the oxidized polymer was obtained from the soln. after removal of the I ppt. from the reaction mixt., and contained nos. of carbonyl and CO_2H groups/100 moles requiring amts. of oxidant in excess of the Ph_2CO present. To obviate the slow filtration, in *C* the oxidized polymer was pptd. directly from the reaction mixt. with acetone and purified by repptn., the excess Ph_2CO and I dissolving in the acetone. The polymer thus obtained had considerably fewer oxidized groups, indicating the effect of atm. oxidn. Lactone ring formation is shown by the very slight decrease in the viscosity of the oxidized polymer, and by the absence of free acid given by direct alk. estimation of the oxidized polymer. The yellow coloration is due to slight intramol. dehydration of the carbonyl groups, with formation of conjugated ethylene double bonds. The presence of a large no. of carbonyl groups is confirmed by ir spectroscopy of samples of the oxidized polymer dispersed in KBr pellets. F. Learmonth

Noncompensating potentiometric method for determination of monomers. D. B. Gurvich, V. A. Balandina, and A. G. Ivanyuk. *Zavodsk. Lab.* 31(3), 288-90(1965)(Russ). The presence of monomers changes the physicomech. properties of polymers. A rapid method was developed for detn. of monomers based on double-bond titrn. with 0.1*N* Br in AcOH. The course of titrn. was followed directly by means of a microammeter connected in the potentiometer circuit. Standard calomel and Pt electrodes were used. Before the titrn. the microammeter light spot was turned down to zero by changing the resistance of the potentiometric wire by 2000-3000 ohms. The equivalence point was reached when there was no change in the microammeter deflection during 1 min. after addn. of 1 drop of Br soln. The time required for the detn. was 5-10 min. and the monomers were titrated in the range 0.1-12 mg. with a relative error of 10-0.1%. The procedure is recomended for detn. of following compds.: vinyl acetate (I), vinyl propionate, vinyl butyrate, vinyl stearate, vinyltoluene, vinylpyridine, styrene, α-methylstyrene, β-vinylnaphthalene, and acenaphthylene. In a 100-ml. calibration flask contg. 15 ml. EtOH (or 50% AcOH for the detn. of I), 0.6-0.8 ml. of the compd. is placed (solid compds. are weighed as such and the flask filled with EtOH to the mark. Then, 10 ml. of this soln. is added to 60 ml. of an EtOH-H_2O mixt. (3:2) (or 80% AcOH in the case of I) and the soln. is titrated as above. For detn. of the monomer content in polymers, the weighed samples are dissolved in 10 ml. of 50% AcOH for the analysis of poly(vinyl acetate) or C_6H_6 or $C_2H_4Cl_2$ for polystyrene and poly(vinyltoluene) and the mixt. titrated after addn. of aq. EtOH (3:2). B. Svatek

16386

Infrared analysis of poly(vinyl chloride)-poly(vinyl acetate) copolymers. Tsugio Takeuchi and Sadao Mori (Univ. Nagoya, Japan). *Anal. Chem.* 37(4), 589-90(1965)(Eng). A calibration curve was constructed by correlating the absorption intensity ratio of the 5.71 μ band (C=O stretching vibration) to the 7.02 μ band (CH_2 scissors vibration) in a range of samples. The corresponding vinyl chloride content of the copolymers was obtained from prior Cl analysis. Five types of absorption intensity were calcd.: (*A*) absorbance ($A = \log_{10} I_0/I$); (*B*) absorbance times the half-intensity band width in cm.$^{-1}$; (*C*) integrated absorption intensity ($B' = 1/bc \int \log_{10} I_0/I d\nu$, where ν is wavenumber in cm.$^{-1}$); (*D*) peak height in cm. times the width of the band in cm. at 1/2 the peak height; and (*E*) the wt. of the paper inside the band contour. Both the thin solid-film method and the KBr-disk technique were used, and 10 calibration curves of the copolymers were constructed and compared. The curves obtained with types *B* and *C* for films were linear and passed through the origin. Other types of intensity data gave curved lines. No linear relations were found for samples prepd. as KBr pellets. Thus, type *B* and *C* intensity data are preferred. Although samples can be prepd. quickly and easily by the KBr pressed-disk technique, the results from the films are more accurate. Seymour M. Kaye

16395

Molecular weight of poly(vinyl alcohol). Agnieszka Marciniak-Fabianowa (Univ. Poznan, Poland). *Zeszyty Nauk. Univ. Poznaniu, Mat., Fiz., Chem.* No. 8, 33-46(1964)(Pol). The av. mol. wt. of poly(vinyl alc.) (I) was measured nephelometrically in 0.5-2% aq. solns. and the influence of various methods of treatment was detd. The mol. wt. depended on the concn. of I during prepn. of the soln. and varied from 307,000 to 621,000 for concns. of 0.5-2%. Heating for 1 hr. at 100° decreased the mol. wt. from 625,000 to 147,000. The mol. wt. depends on the rate of cooling and is different for solns. of different concn. Fractionation by foam analyses gave fractions of mol. wt. from 726,000 to 214,000, but gravitational fractionation was unsuccessful. Centrifuging at 16,000 r.p.m. for 4 hrs. decreased the mol. wt. from 307,000 to 74,000. Comparison of nephelometric data with viscometric data implies the existence of aggregates of macromols., detectable only by optical methods for mol.-wt. detn. Irena Kloczko

16430

Properties of poly(vinyl alcohol) (P.V.A.) derived from the polymerization catalyst, tri-n-butylboron. IV. The effect of the polymerization solvents on the properties of P.V.A. and P.V.A. fiber. Masao Ishii and Masasin Imai. *Sen-i Gakkaishi* 18(4), 320-30(1962)(Japan); cf. *CA* 57, 1106*f*. The effect of the polymerization solvents at 20° in the presence of tri-*n*-butylboron catalyst on the properties of P.V.A. was studied. MeOH was the best solvent. The degree of swelling of the P.V.A. film, the I adsorption, the rate of pptn. in a dimethylsulfoxide-water system, and the boiling water resistance of the heat-treated fiber were affected by the polymerization solvents. Such phenomena depend on the solvent, which affects the polymer structure in the propagation reaction. RCTT

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The LET-dependence of the radiation reaction of poly(vinyl acetate) in solution. Edgar Heckel (Hahn-Meitner-Inst. Kernforsch., Berlin). *U.S. At. Energy Comm.* NP-12303, 28 pp. (1961). The strong effects of linear energy transfer (LET) on the behavior of poly(vinyl acetate) in soln. (at concns. of 15 and 19 wt. %) under the influence of ionizing radiation are described. The solvent was a mixt. of 78.6 wt. % trimethyl ester of H_3BO_3 and 21.4 wt. % MeOH. The observed effects were, at times, independent of the dosage, but depended very strongly on the sp. ionization of the radiation. Radiation of higher LET, such as ^{4}He and ^{7}Li particles, were produced in the reaction $^{10}B + n \rightarrow {}^{7}Li + {}^{4}He + \gamma$ by irradiation of the soln. itself with thermal *n*. The av. LET of this radiation amounted to 28 e.v./A. corresponding to an av. sp. ionization of about 10,000 ion pairs/μ. By means of x- and γ radiation the poly(vinyl acetate) was converted into a 3-dimensional network, while ^{4}He/^{7}Li radiation caused a mol. wt. decrease by degradation of the chief chain. Various reaction mechanisms are discussed for explanation of these effects. From *Nucl. Sci. Abstr.* 17(5), Abstr. No. 6127 (1963).
TCNC

729

Properties of poly(vinyl alcohol) used for emulsion polymerization of vinyl acetate. E. Florea and Ecaterina Pop. *Rev. Chim.* (Bucharest) 15(1), 18–22(1964). The properties of poly(vinyl alc.) as an emulsifying agent and as a protective colloid were studied. Detn. of the emulsifying capacity and of the Ag no. permitted establishment of the characteristics of I when applied in the emulsion polymerization of vinyl acetate (II). Good results in the polymerization of II were obtained with partially hydrolyzed I with the following characteristics: sapon. no., 100–145; emulsification capacity, max. 40% sepn. of the components of a II emulsion after 24 hrs. with a 1% I soln.; surface tension for a 1% I soln. (capillary method), max. 56 dyne/cm.; polymerization degree, *K* = 70–80; Ag no. detd. as min. amt. of I which does not permit the change in color of 10 cc yellow Ag sol on the addn. of 1 cc. 33.3% K tartrate soln., max. 15 mg. Emulsion polymerization of II was also accomplished by using a practically completely hydrolyzed I with a *K* value of 40–50 (the type of I used for fibers) with max. Ag no. of 30 mg. Two types of partially hydrolyzed I were completely unsuitable for the emulsion polymerization of II. These were I with sapon. no. <80 even at *K* = 70–80 and I with a high sapon. no. such as 150 when *K* = ~40. The latter I showed a sudden worsening of the emulsifying and protective colloid properties, characterized by increasing Ag no. and by poor polymerization results.
M. Lapidot

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Fractionation of poly(vinyl alcohol). Florica Butaciu (Inst. Chem. Res., Bucharest, Romania). *Rev. Chim.* (Bucharest) 14(11–12), 643–6(1963). A method for characterization of poly(vinyl alc.) (I) by fractionation was established, being based on direct extn. of the I film. The results obtained were reproducible, and the method itself was more rapid and accurate than the indirect method applied to the reacetylated I. The I sample was dissolved in H_2O at 10% concn., and 0.4 mm. thick Al foils (1000 cm.^{2}) were passed through the heated (40°) soln. to give a thin and continuous layer of I lacking agglomerations and air inclusions. For improved adherence the Al foils were first perforated and then rubbed with sandpaper in 2 perpendicular directions (followed by careful washing and drying). The coated foils were dried on a support and cut into small bands (5–50 mm.), which were folded and vacuum dried at 60° to const. wt. The bands were introduced into the extn. vessel (similar to that used by Fuchs, *CA* 46, 2*d*) and kept at the optimum temp. of 65° by a circulating-water jacket. A series of aq. PrOH solns. (varying from 58:42 PrOH:H_2O in the 1st soln. to 45:55 in the 9th and to water only in the 10th) were introduced successively, and were agitated each for 20 min. (for 2000 cm.^{2} of surface coated with 1 g. I, 100 cc. aliquots of these mixts. were applied). The exts. were evapd. (sand bath) to 5–10% vol., and then transferred to graduated flasks and dild. to 25% of the initial vol. The viscosity of the exts. was detd. in an Ostwald viscometer (25 ± 0.02°). The concn. of the exts. was detd. by evapn. on a sand bath until almost dry, further drying at 80° and vacuum drying at 60° to const. wt., followed by weighing the residue. The method enabled examn. of the effects of the prepn. processes of the polymer on the mol. wt. distribution. The mol. wt. distribution of I was improved with decreasing conversion in the vinyl acetate polymerization, and with thermal treatment and washing of the I. Cross-checking of the method showed that practically no degradation or material loss occurred during the fractionations.
M. Lapidot

The specific heats of polymers in the temperature range of −150 to 180°. H. Tautz, M. Glueck, G. Hartmann, and R. Leuteritz (Deut. Akad. Wiss., Berlin). *Plaste Kautschuk* 10 (11), 648–53(1963). An adiabatic calorimeter for measuring the sp. heat of 4–6-g. polymer samples from −150 to 180° is described. Sp. heat *vs.* temp. curves are shown for high- and low-pressure polyethylene (I), isotactic polypropylene (II), polyamides (III), polystyrene (IV), poly(Me methacrylate), poly(vinyl chloride) (V), poly(vinyl acetate) (VI), and copolymers. The following glass transition temps. were derived: IV, 79–86° (variation between different sources); V, 74–9°; VI, 39°; vinyl chloride-vinyl acetate copolymer, 61° (tempered), 70° (chilled). The following polymer m.ps. were derived: low-pressure I, 130–3°; high-pressure I, 111–14°; isotactic II, 166° (tempered), 175° (chilled); III, >200°.
Olden E. Paris

Determination of polymer isophasic transition by measuring absorption of β-radiation. R. Zannetti, P. Manaresi, and L. Baldi (Soc. Montecatini, Ferrara, Italy). *Chim. Ind.* (Milan) 43(11), 1310(1961). The isophasic transition temp. is detd. by the change in the course of the curve of β-ray absorption. The exptl. app. consists of HgCl labeled with ^{36}Cl (0.71 m.e.v.) as β-ray source and a Geiger-Mueller counter with a mica window and Ar–Cl as quenching gas. Results for atactic polypropylene, atactic poly-1-butene, and amorphous polystyrene obtained by the new method agree well with previous results.
S. C. Ceccotti

A molecular kinetic theory of volume and enthalpy relaxation in the freezing point region of organic glasses. Gerold Adan (Philipps Univ., Marburg/Lahn, Ger.). *Kolloid-Z.* 195(1) 1–8(1964). Math. Results calcd. by a mol. kinetic theory developed to explain certain aftereffects noted in the f.p. regio in terms of the relation between enthalpy and vol. relaxation agreed quant. with results obtained with polystyrene, poly(viny acetate), and glucose. The agreement was only qual. if th original state of the sample was changed before the appearance o the aftereffects, since the change in the necessary parameters could not be evaluated.
Thomas A. Wilson

The low-temperature transition of polymers. Michael Lorant. *Kunststoffe-Plastic* 11(1), 5–6(1964)(in English). An app. for the detn. of low glass-transition temps. is described. Low-temp. gases are used as media in a dilatometric technique.
William A. Swarts

1963

Mechanism of radiation-induced gelation in monomer-polymer mixtures. Bruce S. Bernstein and George Odian. *U.S. Atomic Energy Comm.* RAI-329, 89 pp.(1963); cf. *CA* 58, 8054*d*. Polyethylene (I), I equil.-swollen with 4.5% allyl methacrylate (II) or allyl acrylate (III), and I swollen with 0.3% diallyl maleate (IV) were each irradiated with ^{60}Co γ-rays up to 12 megarads and Van de Graaff electrons up to 200 megarads. At doses to 100 megarads, a higher gel fraction was formed in I with monomer than in I alone. I contg. II gave a higher gel fraction than I contg. IV, although IV is more efficient considering the lower concn. All results follow the Flory relation, with the vol. swelling ratio inversely proportional to the $^{3}/_{5}$ power of cross-link d. or radiation dose. Tensile strength at 25° and 115° of irradiated I with II was greater than that of irradiated I alone over the entire dose range. Elongation at break of irradiated I with II at 25° and 115° was lower at all doses than that for irradiated I alone. At 115°, above the m.p. for I, the moduli increase with increasing radiation dose, with greater moduli for I with II than for I alone. Polypropylene (V), equil.-swollen with II (5.0–5.7%), was irradiated with ^{60}Co in N at 0.07–4.0 megarads/hr. for a dose range of 0.01–175 megarads. At 4 megarads/hr., incipient gelation occurs at 0.05 megarad compared to 80 megarads for V alone. Gel formation is not significantly dependent on the dose rate. In air, 233 megarads by Van de Graaff on V contg. II gave a max. gel content of 59%, indicating O inhibition. The dose-swelling ratio relation for V contg. II over 0.2–63 megarads follows the Flory-Rehner equation, as does I. For both V and I, the infinite dose scission/cross-linking ratio does not change with added monomer. The tensile strength of V decreases upon irradiation, but more rapidly with O present. The deleterious effect of radiation on the tensile properties is probably due to a loss of crystallinity. Heat aging at 225° for 16–45 hrs. in air and *in vacuo* shows that V irradiated with any monomer has a better heat resistance than V irradiated alone or unirradiated. Polyisobutylene (VI) normally degrades on irradiation; but with 16% II (equil.-swollen), the gel fraction formed at 4.0 megarads/hr. increased rapidly to about 75% at 0.7 megarad and then decreased. Lower dose rates appear to be more effective than higher dose rates below 0.7 megarad. Samples of VI cross-linked with II and heat-aged at 180° for 7 hrs. remained unmelted, although unirradiated or monomer-free irradiated polymer flowed. Normally degrading cellulose acetate (VII) was mixed with II or III and formed a 100% gel after 1–3 megarads with slight degradation after 50–200 megarads. Monomer incorporated is 16% II and 25% III after 0.5 to 1.0 megarad, which is the max. gelation dose. The tensile strength of a polymer contg. II and III increased 35–50% after 1–3 megarads, but VII without monomer showed a decrease in strength. Poly(vinyl alc.) (VIII), after swelling with MeOH/H_2O/II in various proportions was irradiated to 0.7 megarad at 0.04 megarad/hr. by ^{60}Co. Without H_2O, grafting occurs to less than 5% at 35% II, but with H_2O present almost 80% grafting occurs from a 15% II mixt. At const. II, grafting increases with increased H_2O. Extn. expts. indicated that true cross-linking occurred with II. Increased gelation with larger amts. of H_2O is probably due to an enhanced penetration of the monomer into VIII. The incipient gelation dose for all VIII systems is 0.06 megarad. Polystyrene (IX) was exposed to 3–5 megarads above a pool of II or III. At 5 megarads, the gel fractions were 51% with 49% III incorporated and 64% with 26% II incorporated. IX alone requires 45 megarads for a 60% gel. Nylon 66 (X) could not be satisfactorily swollen with monomers alone, even at 55°. X swollen with 1:3 MeOH/III or divinylbenzene (XI) and irradiated to 3 megarads at 0.04–0.08 megarad/hr. gave 6.8% III incorporated with 27% gel and 12% XI incorporated with 25% gel. The addn. of H_2O to the swelling soln. increases swelling, does not affect III incorporated by irradiation, and causes a slight increase in gel formation. The addn. of *m*-cresol to the swelling soln. increases swelling, causes a slight increase in II incorporated by radiation, and decreases the amt. of gel formed. The addn. of HCO_2H to the swelling soln. caused a slight decrease in swelling, gel formation, and II incorporated. Irradiation of the monomer-swollen X above 50 megarads does not significantly increase gelation. 33 references.

Raymond W. Angelo

1964

VI. **Radiation protection and promotion in aqueous solutions of poly(vinyl alcohol).** *Ibid.* 123–30. The effects of a no. of additives were measured for irradiation of deaerated and aerated aq. solns. of poly(vinyl alc.). Systems containing thiourea, MeCOEt, EtOH, $FeSO_4$ + 0.8*N* H_2SO_4, $CuSO_4$, or KBr were examd. in detail. These additives modified the rate of cross-linking as well as the degradation of polymers. On the contrary, MeOH, K_2SO_4, or NaCl did not have any appreciable effect on polymer reactions, although their concn. was fairly high compared with that of the former additives. The various effects of additives could be explained mainly in terms of recombination processes and radical transfer in the case of org. additives and electron transfer in the case of inorg. additives. The min. no. of additive mols. per initial polymer mol. required to affect the cross-linking was 0.08 (thiourea), 0.27 ($FeSO_4$ + 0.8*N* H_2SO_4), 0.5 ($CuSO_4$), 3 (MeCOEt), 10 (KBr), and 17 (EtOH). A discussion of the mechanism of radiation protection and promotion was

2606

Effect of pressure on the infrared spectra of some hydrogen-bonded solids. Joseph Reynolds and Sanford S. Sternstein (Rensselaer Polytech. Inst., Troy, N.Y.). *J. Chem. Phys.* 41(1), 47–50(1964). By using a diamond-anvil pressure cell, the infrared spectra of oxalic acid, poly(vinyl alc.), nylon 6–6, and other materials at various pressures up to 25,000 atm. were obtained. Studies on 2 of the pressure-induced changes, (*1*) the shift to lower frequencies of the H-bonded OH and NH stretching bands, and (*2*) the intensity changes of the 2 CH_2 stretching bands are reported.

RCJQ

3218

Infrared spectrometry of polymers in the overtone and combination regions. George N. Foster, Stuart B. Row, and Richard G. Griskey (Virginia Polytech. Inst., Blacksburg). *J. Appl. Polymer Sci.* 8(3), 1357–61(1964). Samples of low-d. and high-d. polyethylene, nylon 66, polyisobutylene, polypropylene, polystyrene, poly(vinyl chloride), a vinylidene chloride–vinyl chloride copolymer, and poly(vinyl acetate) were examd. by infrared spectroscopy in the 1.0–2.7 μ range. All were in film form except polyisobutylene, which was in a CCl_4 soln. Wavelength assignments were made for CH_2, NH, CO, OH, Me, CH, HO_2, and CH_2:CH groups.

R. Bostwick

3223

Cross-linking of poly(vinyl alcohol) by light-sensitive tetrazonium salts. Takahiro Tsunoda and Tsuguo Yamaoka (Chiba Univ., Matsudoshi, Japan). *J. Appl. Polymer Sci.* 8(3) 1379–90(1964). The mechanism of the light-hardening effects in poly(vinyl alc.) (I) contg. the $ZnCl_2$ double salt of tetrazotized *o*-dianisidine, and the hardening effects on I of amine-derived diazonium and tetrazonium salts were investigated. Tetrazonium salts with 2 diazonium groups on each mol. had a better hardening effect on I than diazonium salts. Tetrazonium salts, under ultraviolet radiation, form Ph ether bonds with the OH groups of I.
D. V. Anders

Reversible discoloration reaction of poly(vinyl alcohol) in water. Makoto Shiraishi (Kurashiki Rayon Co., Okayama, Japan). *Kobunshi Kagaku* 19, 598–602(1962). Aq. solns. of poly(vinyl alc.) (I) derived by alk. methanolysis of poly(vinyl acetate) (II) polymerized in the presence of aldehyde showed a reversible color change with the change of pH, i.e., yellow-brown in alk. and colorless in acid soln. However, I derived from II polymerized in the presence of Me_2CO was colorless, even in the alk. state. From the resemblance of the ultraviolet absorption spectrum between the former I and 2,4-hexadienal, it is considered that the tautomeric keto-enol isomerization of the terminal carbonyl group is the cause of the above color change.
Eiichi Wada

Degradation of poly(vinyl alcohol) in hot aqueous alkali solution. Makoto Shiraishi and Masakazu Matsumoto (Kurashiki Rayon Co., Okayama, Japan). *Kobunshi Kagaku* 19(212), 722–7(1962). Poly(vinyl alc.) (I) was heated in aq. NaOH soln. in air and the change in carbonyl content was observed. The increase (a_0) in the C:O content (mole % referred to the monomer) is given by $a_s(1-\alpha)+C$, where a_s, C, and α are the observed C:O content, the C:O content of the original I, and the const. at the given temp., resp. The carbonyl group produced by oxidn. in alk. soln. causes cleavage of the polymer by a reverse aldol reaction (rate const. k_1) and enolization (rate const. k_2). The const. α is the fraction of the C:O group which participates in the cleavage of the polymer. α = 0.5, 0.75, 0.87, and 1.00 at

4500

Osmometry with a nonselective membrane and evaluation of molecular weights of solutes. Fanny Boyer-Kawenoki (C.N.R.S, Bellevue, France). *Compt. Rend.* 258(17), 4274–7(1964). The osmometric method with a nonselective membrane (*CA* 57, 6098*f*) was used to det. the mol. wts. of fractions of poly(vinylpyrrolidinone) and poly(vinyl alc.) of the order of 6,000 to 13,000 units.
Alex Stassinopoulos

4502

A relation between reactivity and structure of poly(vinyl alcohol). Waclaw Wojciak and Kazimierz Mikolajczak (A. Mickiewicz Univ., Poznan, Poland). *Poznan. Towarz. Przyjaciol Nauk, Wydzial Mat.-Przyrod., Prace Komisji Mat.-Przyrod.* 10(2), 99–112(1962). In continuation of earlier work (*CA* 55, 17161*a*), the reactivity of 2 fractions of a 5% aq. soln. of poly(vinyl alc.) [illegible] →

[illegible]

4507

Oxidation of poly(vinyl alcohol) with chromic acid. Yves Trudelle and Jean Neel (Ecole Super. Phys. Chim., Paris). *Compt. Rend.* 258(17), 4267–70(1964). Poly(vinyl alc.) was partially oxidized by 0.207 *N* $Cr_2O_7^{--}$ (0.1–0.3 equiv. per monomer unit) in 3*M* H_2SO_4 and Cr^{+++} was pptd. with a base. The soln. absorbed at 325, 270, and 205–225 mμ. The no. of C:C and CO groups were detd. by HBr and $NH_2OH.HCl$, resp. The anal. results indicate the existence of double bonds conjugated to carbonyl groups. The probable mechanism is oxidn. of CH_2OH to CO, followed by intramol. dehydration and further rupture of double bonds in excess oxidant.
Alex Stassinopoulos

5761

Pyrolysis of polymers. I. Thermogravimetric analysis of polymers. Chwa-Kyung Sung (Natl. Ind. Inst., Seoul). *J. Korean Chem. Soc.* 7(2), 96–105(1963). Eighteen polymers were studied thermogravimetrically in N and air, resp., at a rate of temp. increase of 1°/min. The rate of wt. decrease *vs.* temp. plots together with the thermograms were used to classify the polymers into 3 types. Polystyrene, poly(Me methacrylate), and acetal resins (type I) depolymerize mainly into their monomers over a short interval of temp. Poly(vinyl chloride), poly(vinyl acetate), nylon, polyurethans, and polycarbonates (type II) decomp. in 2 steps. Poly(vinyl alc.) and diene polymers (type III) decomp. over a much wider range of temp. due to the various irregular chain scissions and side-chain splittings as well as depolymerization to monomers. Generally, polycondensation polymers are more stable toward heat than addn. polymers, and polymers with aromatic nuclei show good thermal stability. Decompn. of polymers with tertiary C atoms, such as polystyrene or polypropylene and acetal resins, starts at lower temp. in air than in N (by ≧50°). **II. Identification of polymer pyrolysis products by gas chromatography.** *Ibid.* 106–14. The pyrolysis products of various polymers at 450° were analyzed by gas chromatography with bis(2-ethylhexyl) sebacate, silicone oil, silica gel, and tetraethylene glycol di-Me ether columns; the latter were esp. useful in the analysis of gaseous hydrocarbons (*CA* 61, 4117*f*). Preliminary results of the detn. of the mechanism of polymer pyrolysis are reported and patterns of polymer pyrolysis are discussed. **III. Identification of gases**

5787

Structures in poly(vinyl alcohol) solutions. P. I. Zubov, E. A. Osipov, and L. A. Sukhareva (Inst. Phys.-Chem., Moscow). *Vysokomolekul. Soedin.* 6(5), 811–17(1964); cf. *CA* 52, 16786*b*. Conditions for the coiling of the poly(vinyl alc.) (I) macromols. were developed. The viscosity of aq. solns. of I (mol. wt. 31,000 and 2.86% AcO groups) decreased with increasing temp. from 5 to 95° for the concns. 1.25–160 g./l. The concd. solns. easily formed gels. Reaction of I in 5–9% solns. with HCHO (4–10%) in the presence of H_2SO_4 (0.2–8%) at 20–80° increased the viscosity of the solns. of I from 20 to 60–180 cp. with subsequent rapid decrease after the loss of soly. by the macromols. The increase in viscosity was due to stiffening of the macromols. by the introduced 6-membered rings. Substitution of OH groups by HCHO did not lead to coiling into spheres. An elastic gel network was formed by reaction of I (0.125–4.0%) with 0.06% succinaldehyde (II) in the presence of H_2SO_4 (0.1–0.5%) at 20°. Due to the stable cross-links formed when the concn. of I was ≧1.5%, the network was stable when heated on a steam bath. At concns. of I <0.5%, instead of network formation, coiling into spheres took place due to the formation of local intramol. bonds. The viscosities of the resulting transparent solns. were similar for all concns. of I when 10–15% OH groups were converted to acetals. When 30% of the OH groups were substituted by II pptn. occurred. Coiling of I into spheres occurred as well without a chem. reaction on addn. of $HCONMe_2$ (III) to the 0.125% soln. of I, when the concn. of III was ≧80%. The rate of coiling was highly dependent on temp. and concn. of III. The gels were opaque and the network was unstable. Transparent globular solns. were formed in H_2O-free III by rapid cooling to 10–30°, and the transparency was stable by evapn. (a 4% soln. was obtained from a 0.5% soln.) and by heating to 100°. The transformation into opaque gels occurred at 120° and was similar to the denaturation of proteins; it is believed due to the transformation of local intramol. bonds into intermol. bonds. The compn. of the binary mixt. of I and III also affected the magnitude of the ultimate internal stress in coatings from I solns. The films from the globular solns. of I were very unstable; on evapn. of the solvent *in vacuo* they formed a powder.
M. Kalfus

5789

Dilatometric studies of glass transitions of polystyrene and poly(vinyl acetate). A. V. Sidorovich and E. V. Kuvshinskii (Inst. High Molecular Compds., Acad. Sci. U.S.S.R., Leningrad). *Fiz. Tverd. Tela* 6(3), 888–95(1964). Ribbons 0.1 mm. thick made from polystyrene (I) of mol. wt. 700,000 and from poly(vinyl acetate) (II) of mol. wt. 10^6 were suspended in the measuring device, and their length was measured with an accuracy of 0.003%. Vol. changes were studied on cylindrical specimens from block polymers 3 mm. in diam. in Hg. All measurements were carried out after heating for 15–30 min. above the glass transition temp.(θ_g) in order to erase the effect of the previous thermal history of the sample. The thermal dilation of amorphous compds. at the temp. $\theta > \theta_g$ corresponds to vol. changes due to the increase of intermol. distances as well as to their mutual spacing. The kink in the curves occurs when the rate of packing falls. The activation energy of this process is 400 for I, and 300 kcal./mole for II, resp. The curves obtained on heating differ from the cooling curves, the difference being dependent on the rate of temp. changes. The comparison of dilatometric and calorimetric data indicates a near analogy between the changes in sp. vol. and the changes in enthalpy or sp. heat of amorphous compds. The activation energy cannot be explained based on relaxation processes only. 36 references.

V. Zvonar

5793

The phase state of poly(vinyl alcohol). M. I. Bessonov and A. P. Rudakov. *Fiz. Tverd. Tela* 6(5), 1333–42(1964). Transformations in poly(vinyl alc.) films were investigated by measuring variations in d., elastic modulus, birefringent structures visible in a microscope, and x-ray diagrams as a function of temp. A 1st order phase transition is found. Poly(vinyl alc.) is a cryst. polymer m. 232°.

A. Libacky

5802

Reaction of iodine with partially saponified poly(vinyl acetate). Sadao Hayashi, Chiyoko Nakano, and Takuhiko Motoyama (High Polymer Chem. Ind. Neyagawa, Osaka, Japan). *Kobunshi Kagaku* 20(217), 303–11(1963). Dil. aq. solns. of partially sapond. poly(vinyl acetate) (I) obtained by the ordinary alkali method turn red on treatment with iodine, as does undissolved I. Dil. solns. of partially acetylated poly(vinyl alc.) (II) prepd. from AcOH and fully sapond. II in homogeneous system do not turn red with iodine, even if both Ac contents are equal. Infrared absorption spectra and the water soly. of partially sapd. I films are studied. The coloring was caused by maldistributed groups of residual Ac in the polymer chain. The relation between conditions of sapon. and groups of residual Ac in the partially sapond. I is elucidated.

Eiichi Wada

Nitration of poly(vinyl alcohol). A. E. Akopyan, M. B. Ordyan, S. P. Ekmekdzhyan, and G. M. Belyaeva. *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* 17(1), 103–6(1964). Nitration of poly(vinyl alc.) (I) with the max. yield and safety is described. To fuming HNO_3 contg. 1–10% H_2SO_4 was added powd. I in the ratio 1:25 at −5 to +10° under N. The reaction mixt. was kept 1 hr. and the poly(vinyl nitrate) pptd. with H_2O. The presence of H_2SO_4 increased the yield of the poly(vinyl nitrate) to 92–3% and the N content to 16–16.3% against a content of 13.8% in the absence of H_2SO_4. N. Charmandarian

The synthesis of the ester of poly(vinyl alcohol) and dibutylboronic acid. S. N. Ushakov and P. Tudoriu. *Vysokomolekul. Soedin.* 6(5), 934–9(1964). Poly(vinyl alc.) (I) of mol. wt. 48,000, contg. 1.62 mol. % residual OAc, was treated with Bu_2BCl in pyridine, $HCONMe_2$, or Me_2SO. I was initially made more reactive either by swelling in a mixt. of 90% I + 10% H_2O for 2 days followed by repeated treatment with dry pyridine at room temp. or by heating at 100° for 4 hrs. In $HCONMe_2$, the mixt. with I was 1st heated to 100°. In Me_2SO, I dissolved in 30 min. at 50–60° giving a clear soln. stable at room temp. The Bu_2BCl:I ratio was varied between 1:1 and 4:1, the reaction temp. was 80 or 100°, and the duration 2–48 hrs. Reaction rate increased with increasing Bu_2BCl:I ratio and with increasing polarity of solvent ($Me_2SO > HCONMe_2 >$ pyridine). The max. observed esterification was 50% of theoretical. The esters are insol. in water, but dissolve on heating in pyridine, $HCONMe_2$, or Me_2SO. They are not hydrolyzed by boiling water. About 20–35% of the OH groups of I must be esterified to achieve soly. in pyridine, $HCONMe_2$, and Me_2SO. At 50% esterification the polymer is also sol. in benzyl alc. The glass temp. decreases from 80° for I to 27° for a polymer with 50% esterification. The rate of esterification is greater when Bu_2BOH or Ph_2BOH is used than when Bu_2BCl is the esterifying reagent.

C. H. Fuchsman

5803

The effects of γ-rays on polymers in aqueous solution. I. γ-ray irradiation of aqueous solutions of poly(vinyl alcohol) in the presence of oxygen. Akira Matsumoto (Tokyo Metropol. Univ.). *Kobunshi Kagaku* 20(216), 268–74(1963). The mols. of poly(vinyl alc.) (I) in aq. soln. are randomly degraded by γ-rays when mixed with O. If the amt. of O is small, cross-linking occurs. *G*-values for main chain scission are 0.2–0.6 and become larger at higher dose rate and concn. By the addn. of 10^{-2} mole/l. H_2O_2, *G* values for the degradation became 4 times as large as the original values. Main chain scission occurs predominantly at the 1,2-diol linkage, partially at the other structures. *G* values for the production of carbonyl groups in I are about 2. When the samples are kept at 100° for a few min. after irradiation, the *G* value is reduced to 1. Since the increase in no. of carbonyl groups produced by γ-ray irradiation is larger than that of main chain scission, the carbonyl groups produced are of ketone type in the main chain. **II. γ-ray irradiation of aqueous solutions of poly(vinyl alcohol) in absence of oxygen.** *Ibid.* 275–81. The viscosity of the soln. increases on irradiation. The crit. concn. for gel formation is 0.17 g./100 ml. or less. The crit. irradiation dose for gelation decreases linearly with the I concn. From the crit. concn., the radius of a I mol. of degree of polymerization 1500 is calcd. to be 200 A. or more in aq. soln. In the presence of EtOH, $EtNH_2$, dioxane, and phenol, gel formation is inhibited and the scission of the main chain occurs. In the I mols. irradiated in the presence of $EtNH_2$, the fragments of combined $EtNH_2$ are detected by the dinitrofluorobenzene addn. reaction. The viscosity decreases when aq. I solns. are irradiated at a concn. below 0.17 g./100 ml., but in this phenomenon main-chain scission is not responsible. Salts such as KCl, $Al(NO_3)_3$, and $CuSO_4$ and acid react for salting I out of soln. but such basic salts as Na_2CO_3, Na_2HPO_4, and NaOH do not. The formation of spherical microgel is confirmed by light scattering measurements. Alk. solns. irradiated with high doses become yellowish. Two weak absorption bands are observed at 240 and 290 mμ which may correspond to CH:CHCO and $(CH:CH)_2CO$.

Eiichi Wada

5847

The contraction of poly(vinyl alcohol) films in aqueous media. Hajime Noguchi and Jen Tsi Yang (Univ. of California Med. Center, San Francisco). *J. Phys. Chem.* 68(6), 1609–11(1964). A reversible contraction of poly(vinyl alc.) (I) film was observed in aq. NaCl and KF solns. The relative length of the polymer strip changed linearly with salt concn. up to 5*M*. The effect was independent of pH in the range 2–11.5. Sucrose caused a similar contraction. The shrinkage was attributed to osmotic contraction; osmotic pressure in the solvent caused the H_2O of hydration to diffuse out of the polymer. In contrast, LiBr, $CaCl_2$, $MgCl_2$, and $CuCl_2$ cause swelling in I, the latter irreversibly. The divalent cations and LiBr penetrate the film, probably break up the cryst. regions, and expand the polymer. Salts of the 2nd group are sol. in alc., while those of the former are only slightly sol. in alc. The different behavior of I with different salts is related to the affinity between the OH groups of I and these salts. I film is elongated in urea and guanidine hydrochloride, the latter being a more effective dispersing agent. A. Foxton

5848

Structure of poly(vinyl alcohol) films as influencing the mechanism of their pyrolysis process. G. I. Distler, P. S. Sotnikov, and E. I. Kortukova. *Dokl. Akad. Nauk SSSR* 156(3), 652-3 (1964). The supermol. structure of high-mol.-wt. polymers, such as poly(vinyl alc.) films (I), was studied by infrared spectroscopy polarization during their pyrolysis. The I were prepd. from a 4% aq. soln. with the addn. of 0.1*N* H_2SO_4, used as a catalyst during dehydration, until a pH of 2.25 was obtained. Thermal treatment at 150° was carried out in an atm. of air; infrared measurements were performed on a double-beam instrument. The orientation of films was achieved by 3-fold stretching. In the pyrolysis of oriented and nonoriented I, dehydration takes place with the formation of conjugated double bonds, the no. of which increases with the pyrolysis time; as a result of increasing intensity of the abs. bands corresponding to double bonds at 3000, 1670-1580, and 1000 cm.$^{-1}$, there occurs an intensity decrease of the abs. bands of the original film depending on the cleavage of H_2O mols. from the polymer chain. Only the abs. band at 1141 cm.$^{-1}$ of oriented I behaves anomalously; the intensity remains sometimes practically const. and then decreases sharply until its complete disappearance. In the pyrolysis of nonoriented films, the intensity of this band begins to decrease at once. These expts. indicate that, in oriented I, other structural formations are pyrolyzed first, and that pyrolysis of 3-dimensional-order surface films, leading to film amorphization, takes place only after their destruction, as evidenced by the disappearance of the 1141 cm.$^{-1}$ band and by diffusional reflexes on x-ray photographs. Pyrolysis of I is thus a sensitive indicator in differentiating diverse elements of a supermol. structure.
G. Wiener

6250

Toxicological characteristics of poly(vinyl alcohol), polyethylene, and polypropylene. G. N. Zaeva, M. D. Babina, V. I. Fedorova, and V. A. Shchirskaya. *Toksikol. Novykh Prom. Khim. Veshchestv* No. 5, 136-49(1963). Repeated enterogastric (30 times) administration of 500 mg./kg. doses of poly(vinyl alc.) brought about only slight reversible functional

7106

Effect of initiators and phase state of acetaldehyde on the chemical constitution of the macromolecules formed during its polymerization. I. M. Papisov, T. A. Pisarenko, A. A. Panasenko, V. A. Kabanov, and V. A. Kargin. *Dokl. Akad. Nauk SSSR* 156(3), 669-72(1964). Polymerization of AcH was initiated by Na or Mg and carried out in the cryst., amorphous, and liquid state. Cryst. AcH yielded 30% of a polymer, the infrared spectrum of which was similar to that of the usual polyacetaldehyde but distinct from that of polymers obtained by radiation-initiated polymerization in the solid state. It was insol. in MeOH or Me_2CO. The x-ray examn. indicates a stereoregular cryst. polymer. The amorphous AcH obtained by simultaneous condensation of AcH and 5-10% Na or Mg on a surface cooled to −196° did not crystallize up to −123.5° (m.p. of AcH) and did not polymerize at −130° for 10 min. Heating above −123.5° (liquid-state polymerization) yielded a polymer sol. in water, probably a poly(vinyl alc.) but its infrared spectra differed from those obtained by hydrolysis of poly(vinyl acetate). At lower concns. of the initiators (0.1-1%), amorphous AcH began to crystallize at −130° to −150°, and when heated to −130° for 10 min. formed polyacetaldehyde.
O. Elsner

7120

The rheological effect of solvate sheaths on poly(vinyl alcohol) in aqueous solution and its relation to molecular weight. S. Peter and H. Pashender (Tech. Hochschule, Hannover, Ger.). *Rheol. Acta* 3(2), 92-8(1963)(in German). Couette viscometry in the temp. range 20-50° of 10% aq. solns. of poly(vinyl alc.) fractions of mol. wt. 20,000, 85,000, and 180,000 revealed the existence of a solvate layer. Limiting viscosity nos. decreased with increase in temp. The temp. dependence corresponded to energies of viscous flow reaching 6.2 kcal. at high concn.
Raymond R. Myers

7127

Chromic [acid] oxidation of poly(vinyl alcohol). Yves Trudelle and Jean Neel (Lab. Chim. Macromol., Paris). *Compt. Rend.* 258(18), 4542-4(1964); cf. *ibid.* 4267-70. Poly(vinyl alc.) (I) was oxidized by adding CrO_3 dissolved in HCl, H_3PO_4, H_2SO_4, $HClO_4$, or HOAc to an aq. soln. of I at room temp. and under N for several hrs. The amt. of O equivs. (*r*) per 44 g. I varied from 0.373 to 1.988. The addn. of NaOH to pH 3 pptd. the modified I except where HOAc was used. The effect of the acids in reducing the sp. viscosity of I at equal values of *r* was in the order: $HClO_4$ > HCl > H_3PO_4 > H_2SO_4 > HOAc. The conjugated unsatn. measured by ultraviolet absorption did not increase regularly with increasing *r*. Degradation of I is by chain rupture α to a CO group (in $HClO_4$ or HCl), or at a double bond formed by dehydration (in H_3PO_4, H_2SO_4, or HOAc), with the 1st process being more degradative for a given *r*.
R. Bostwick

7130

Radiation effect on polymer binary systems. Fumio Kobayashi, Tatsuo Iwasaki, and Kosuke Tomita. *Nippon Isotope Kaigi Hobunshu* 4, 373-7(1961). Radicals on adjacent polymer chains, formed by high-energy radiation, are capable of combining to give crosslinks. In the presence of a 2nd, compatible polymer, the radical sites serve as junction points of cross-linking to give so-called "co-cross-linking. An attempt was made to produce co-cross-linking by using γ and ultraviolet rays. Poly(Me methacrylate)-poly(vinyl acetate) and nylon 6-poly(vinyl alc.) are selected. The latter was able to mix homogeneously with HCO_2H as a solvent, but in this case poly(vinyl alc.) was converted into poly(vinyl formate). From *Nucl. Sci. Abstr.* 17(18), Abstr. No. 29923(1963).
TCNG

Selectivity in radiation-induced scission of poly(vinyl alcohol). Yutaka Hirano and Ayao Amemiya (Univ. Tokyo). *Nippon Isotope Kaigi Hobunshu* 4, 367-70(1961). PVA is fractured under the influence of ionizing radiation at room temp. in the solid state. The degree of polymerization of irradiated PVA decreases with radiation dose. Most of the main chain of the usual PVA consists of 2 types of bonds—the 1,3-glycol type and the 1,2-glycol type. A certain selectivity in radiation-induced scission of these types of bonds occurs in PVA. The results show that, within exptl. error, only special types of bond can be fractured selectively. From *Nucl. Sci. Abstr.* 17(18), Abstr. No. 29921(1963).
TCNG

Irradiation effects on polyethylene. Sanyo Hori, Shozo Iida, Hiroshi Sakami, and Toshiaki Adachi (Govt. Ind. Res. Inst., Nagoya, Japan). *Nippon Isotope Kaigi Hobunshu* 4, 386-90 (1961). Cross-linking and decompn. are produced by the irradn. of polyethylene. The phys. properties of irradiated polyethylene were studied. From *Nucl. Sci. Abstr.* 17(18), Abstr. No. 29927(1963).
TCNG

Radiation effects on high polymers by high-dosage irradiation with γ-rays. Akibumi Danno, Mitsuru Koike, Kazuo Nagoshi, and Masao Inoue. *Nippon Isotope Kaigi Hobunshu* 4, 360-4 (1961). In order to study radiation effects of γ-rays with high dose, poly(vinyl alc.), polyethylene, and poly(tetrafluoroethylene) were irradiated with $>10^9$ r. by using a ^{60}Co source. The samples were irradiated in air or in vacuum at room temp. and low or high temp. Results of gas analysis, sol. fraction detn., and differential thermal analysis of irradiated specimens are presented. From *Nucl. Sci. Abstr.* 17(18), Abstr. No. 29919(1963).
TCNG

Irradiation effects on polymer blends. Sanyo Hori, Shozo Iida, Hiroshi Sakami, and Toshiaki Adachi (Govt. Ind. Res. Inst., Nagoya, Japan). *Nippon Isotope Kaigi Hobunshu* 4, 370-3(1961). The cross-linking and block or graft copolymerization by irradiation in polymer blends was discussed, in an attempt to achieve homogeneous blending. Polymer blends of high- and low-d. polyethylene, obtained by mech. and chem. methods, were γ-irradiated. The sp. heat-temp. relation and other characteristics of this system were measured. From *Nucl. Sci. Abstr.* 17(18), Abstr. No. 29922(1963).
TCNG

Radiation-induced reactions in swollen polymers. Zoila Reyes. *U.S. Atomic Energy Comm.* SRI A-120, 36 pp.(1963).

7194

Poly(vinyl alcohol) compositions. Societa Rhodiatoce (by Giacomo Bertolini). Ger. 1,172,043 (Cl. C 08f), June 11, 1964; Ital. Appl. Oct. 24, 1959; 2 pp. Granular, nondusty, easily H_2O-sol. poly(vinyl alc.) compns. contg. plasticizers, such as glycerol or ethylene glycol, are prepd. George S. Learmouth

7761

The behavior and streaming birefringence of solutions of different types of polyvinyl alcohol in water and in salt solutions. S. Peter and H. Fasbender (Tech. Hochschule, Hannover, Ger.). *Kolloid-Z.* 196(2), 125-35(1964). Poly(vinyl alc.) of mol. wt. 20,000-250,000, prepd. from the acetate by either acid or base hydrolysis, with acetate content of 1-11.5%, showed anomalous behavior of the streaming birefringence at 20-60° and 10 wt. % concn. that was connected with larger, rather stable aggregates, which disappeared above 40°. Another aggregation process caused by weaker energy of aggregation gave rise to non-Newtonian flow of the solns. favored by the presence of ions in the solns. Thomas A. Wilson

8428

Ultrasonic velocity and absorption of aqueous solutions of poly(vinyl alcohol). Kiyoshi Arakawa, Nobuo Takenaka, Mineo Watase, and Kazumari Kubota (Hokkaido Univ., Sapporo). *Bull. Chem. Soc. Japan* **37**(4), 559-63(1964). The ultrasonic velocity and absorption of completely sapond. poly(vinyl alc.) (I) and partially sapond. I were measured over the temp. range of 3-70° and the concn. range 5-15 wt. %. The compressibility of completely sapond. poly(vinyl alc.) in soln. was calcd. to be 26.5×10^{-12}. Charles Mader

9619

Oscillopolarographic study of some macromolecular compounds used in textile chemistry. A. Gergely, V. Komiszar, I. Rusznak, and I. Kralik (Vyskumny Ustav Textil. Chem., Budapest, Hung.). *Chem. Zvesti* 18, 391-8(1964)(in German). An oscillopolarographic method for the detn. of poly(vinyl alc.) (I) and carboxymethyl cellulose (II) was described. For the detn. of $dE/dt = f(E)$ curves of I or II, 10 mg. of I or II in 10 ml. of 5*M* LiCl was used. The depth of the cathodic deriv. peak is linearly dependent on the mol. wt. The results agree with those obtained by the viscometric method. Jan Micka

12108

Degradation of poly(vinyl alcohol) by hydrochloric acid. Ichiro Sakurada and Shuji Matsuzawa (Univ. Kyoto, Japan). *Kobunshi Kagaku* 20(218), 349-52(1963). Poly(vinyl alc.) (I) was degraded in 20% HCl at >60°. The rate of degradation increases with temp. Carbonyl and carboxyl groups formed by the degradation were detd. chem., while C:C and C:O bonds were detected from infrared absorption spectra. This degradation is a result of dehydration of I by HCl. I after a sufficient time of reaction with HCl in MeOH is insol. in boiling water. Chem. cross-linked I is formed by intermol. acetalization and esterification of degraded I mols. Eiichi Wada

14801

Radiation effects in poly(vinyl acetate). L. D. Maxim, R. H. Marchessault, V. Stannett, and C. H. Kuist (Syracuse Univ., Syracuse, N.Y.). *Polymer* 5(8), 403-17(1964). The behavior of poly(vinyl acetate) upon irradiation with high energy γ-rays (1.21 megarads/hr.) is described. A relatively linear polymer of no.-av. mol. wt. 270,000 was used. After 10 megarads (the gelation dose), an insol. network was formed. The sol. fraction decreased with increasing dose. The mol.-wt. variation up to the gel point was followed by osmometric and viscometric measurements. After gelation, the reaction course was studied by analysis of sol. fractions and swelling behavior in Me_2CO and MeCOEt. An app. for measuring equil. vapor sorption is described. The exptl. results are described in terms of current radiation theory. The polymer undergoes simultaneous cross-linking and chain scission. The scission:cross-linking ratio is 0.04:1. The cross-linking value *G*, is 0.1 cross-links /100 e.v. as detd. by mol. wt. and sol. fraction data. The *G* value from swelling measurements is higher. AcOH is evolved in an amt. proportional to the total radiation dose (*r*), according to the equation: % AcOH evolved

14849

III. Effects of gamma radiation on water-swollen films and aqueous solutions. Ichiro Sakurada and Yoshito Ikada (Univ. Kyoto, Japan). *Bull. Inst. Chem. Res., Kyoto Univ.* 39(2), 99-111(1961); cf. *CA* **53**, 18598*f*. The effects of γ irradiation both in air and *in vacuo* on aq. solns. and H_2O-swollen films of poly(vinyl alc.) were studied. The radiation-induced changes were followed by measurements of viscosity, sol fraction, and degree of swelling. For the H_2O-swollen films, remarkable differences were observed between irradiation *in vacuo* and in air, but for aq. solns. of higher concns. there were little differences between the 2 cases. For irradiation of H_2O-swollen films in air, the indirect effect of H_2O was quant. discussed. Calcn. indicated that the energy absorbed by H_2O was not completely dissipated, but only 69% of it was used for the main-chain fracture and the energy dissipated per main chain fracture was about 36 e.v. When the aq. solns. were irradiated, their viscosities were increased with dose and finally a gel was formed in the same manner observed in the case of vacuum irradiation of the H_2O-swollen films. The ratio of the no. of fractures and cross-linked units, p_0/q_0, was increased with the wt. fraction of the polymer; the values of p_0/q_0 were 0.27, 0.39, and 0.55:1 for wt. fractions of 10, 20, and 25%, resp. The results obtained by irradiation of the solns. contg. 10% by wt. polymer which had stood for some period before irradiation showed that the amt. of sol fraction decreased with standing time.

15459

Effect of molecular weight on dielectric absorption of poly(vinyl acetate). Toru Hara (Matsushita Res. Inst., Inc., Tokyo) and Shigeharu Okamoto. *J. Phys. Soc. Japan* 19(6), 1087-8(1964) (in English). The difference between static and high-frequency dielec. consts. for β-absorption, $\epsilon_0-\epsilon_\infty$, is 0.19 at −70° for polymerization degree $n = 240$, with temp. dependence, with activation energy ~10 kcal. For $n > 600$, $\epsilon_0-\epsilon_\infty$ is 0.09, substantially independent of temp. Apparently, end groups of the polymer contribute to β-absorption but not to α-absorption. Chelsey L. Brock

676

Molecular properties of amorphous high polymers. I. A cell theory for amorphous high polymers. A. T. DiBenedetto (Univ. of Wisconsin, Madison). *J. Polymer Sci.* Pt. A 1(10), 3459–76(1963). The concept of cell models is extended to describe the structure-insensitive properties of amorphous polymers. X-ray patterns indicate the presence of a short range order similar to the liquid state of a monomer. Taking a CH_2 unit as a cell center and assuming parallel alignment of chains, equations are derived for interaction energy and reduced potential energy. Characterizing an amorphous polymer as a homogeneous, one-component phase contg. *N* identical *n*-center segments, where *N* is Avogadro's no., and using the square well approxn., several equations describing thermodynamic behavior are derived. Their validity is limited to values of $v^*/v > 0.9$, where v^* is the vol. parameter for the 6–12 potential and v is the effective vol. per center. Application of these equations to polybutadiene to calc. force consts., heat of crystn., cohesion energy d., degrees of freedom/center, and coeff. of thermal expansion show agreement with values obtained by other means. Predicted and exptl. values are also shown for expansion coeffs., glass transition temp., lattice energy, and cohesion energy d. for natural rubber, neoprene, polyisobutene, poly(vinyl chloride) (I), poly(vinyl acetate) (II), a I-II copolymer, and polystyrene, with generally good agreement. Calcd. molar cohesion values for org. groups of these polymers compare favorably with values obtained from vaporization and sublimation data (*CA* 23, 743). II. **Interpretation of gaseous diffusion through polymers.** *Ibid.* 3477–87. The previous concepts are extended in order to interpret gaseous diffusion data through thin films of polymers. A sorbed gas mol. is considered as being trapped at an equil. site by surrounding bundles of parallel *n*-center polymer segments and behaving as a 3-dimensional harmonic oscillator. Segmental motion can produce a cylindrical void into which the gas mol. diffuses during an activated state of the unit cell. The activation process involves the partial destruction of Van der Waals bonds. Equations are derived for the instantaneous potential energy of a center and the activation energy for gaseous diffusion, leading to the calcn. of the no. of centers per unit cell, the length of a polymer segment, cohesion energy d., and mol. consts. An equation is also derived for the activation energy for self-diffusion by rotational exchange of positions of 2 polymer segments. When applied to polybutadiene (III), these equations give the av. no. of centers per segment as 8.3, the length of a polymer segment as 10.4 A., and the activation energy for self-diffusion as 9.6 kcal./mole at 298°K. Similar calcns. are shown for natural rubber (IV), neoprene, polyisobutene, II, and a I-II copolymer. Exptl. values for III and IV are very close to the calcd. energies for self-diffusion. The predicted linear relation between the activation energy for diffusion and the reduced potential charge is obtained for all but I, II, and the copolymer. R. Bostwick

682

Degradation of some polymers in aqueous solutions. Hans Vink (Univ. Uppsala, Swed.). *Makromol. Chem.* 67, 105–23 (1963)(in English); cf. *CA* 54, 5081*i*. Degradation of aq. solns. of hydroxyethyl cellulose (I), carboxymethyl cellulose (II), poly(oxyethylene), poly(vinyl alc.) (III) and poly(methacrylic acid) (IV) were studied. The reaction was followed by a viscometric method and was carried out in the viscometer at 25°. A special Ostwald-type instrument was necessary (due to the high surface activity of the solns.) to permit special gas atm. (N, O) to be used. Purified com. polymer samples were used. Purification was carried out by pptn. from a solvent (I, II, and III in H_2O; I in EtOH-benzene, IV in MeOH) with a nonsolvent (I, II, and III with Me_2CO; I with hexane, and IV with ether). Polymers having O bridges in the mol. backbone were degraded much more readily. Certain reaction conditions and impurities catalyzed the reaction, e.g. light or Fe^{+++} and Cr^{+++} ions. Thomas M. Laakso

679

Mechanical properties of substances of high molecular weight. XLII. Viscoelastic properties of poly(vinyl acetates). 1. Creep studies of fractions. Kazuhiko Ninomiya and John D. Ferry (Univ. of Wisconsin, Madison). *J. Phys. Chem.* 67(11), 2292–6(1963); cf. *CA* 58, 7379*f*. Tensile creep measurements on 3 poly(vinyl acetate) fractions and shear creep measurements on five sharp fractions are reported. The range of mol. wts. was from 5500 to 780,000 and the temps. were between 19 and 143°. The temp. dependence of the creep compliance was described by the method of reduced variables. The shift factors were identical for all fractions, provided that each was referred to a sep. reference temp. corresponding to iso-free vol. states. The treatment implies a fractional free vol. which decreases with increasing mol. wt. approaching an asymptotic value. At very high mol. wt., the fractional free vol. at 75° is $f_n = 0.0532$ (or $f_g = 0.026$) and its thermal expansion coeff. is $\alpha_f = 5.9 \times 10^{-4}$, in reasonable agreement with previous estimates. In the transition zone, the creep compliance and hence all viscoelastic properties are identical in the iso-free-vol. states. In the terminal zone, the viscoelastic properties are characterized by the steady-state compliance, whose value (for the sharp fractions) is near that predicted by the Rouse theory, and the steady-flow viscosity, which is proportional to the 3.4 power of mol. wt. The relaxation modulus in the terminal zone, derived from the creep compliance by approximation methods, agrees moderately well with the predictions of the Rouse theory for mol. wt. from 10,500 to 262,000. XLIII. **Viscoelastic properties of poly(vinyl acetates). 2. Creep studies of blends.** Kazuhiko Ninomiya, John D. Ferry, and Yasuji Oyanagi. *Ibid.* 2297–2308. Shear creep measurements were made on 18 binary blends of poly(vinyl acetate) fractions. In 5 blends, both component mol. wts. exceeded M_c, the crit. mol. wt. for onset of coupling entanglements; in 4, both were less than M_c; and in 9, 1 mol. wt., was less and one greater than M_c. The temp. range was 19–136°. The temp. dependence of the creep compliance was described by the method of reduced variables. The shift factors were identical for all the blends and also for the component fractions, provided that each was referred to a sep. reference temp. corresponding to iso-free-vol. states. From these reference temps. and the thermal expansion coeff. of free vol. obtained from the WLF equation ($\alpha_f = 5.9 \times 10^{-4}$), the fractional free vol. f, of each blend was calcd. at 40°. In each blend, f was nearly equal to $\nu_1 f_1 + \nu_2 f_2$, where the subscripts refer to the 2 components and ν is the vol. fraction. In terms of mol. wt., the expression $f = 0.0325 + 51.5/\bar{M}_n$ holds for nearly all the blends, where $\bar{M}_n$ is no.-av. mol. wt. In the transition zone of viscoelastic behavior, the creep compliances of all the blends are identical when reduced to iso-free-vol. states. In the terminal zone, the viscosities and terminal relaxation times depend on the combined effects of free vol. (a function of $\bar{M}_n$, governing the local friction coeff.) and mol. length (a function of $\bar{M}_w$, which includes entanglements if at least 1 species has $M > M_c$). The former effect can be eliminated by reducing the viscosities to iso-free-vol states (η_{0f}). For $\bar{M}_w < M_c$, η_{0f} is closely proportional to $\bar{M}_w$, and for $\bar{M}_w > M_c$ it is closely proportional to $\bar{M}_w^{3.4}$ up to $\bar{M}_w = 400{,}000$. The steady-state compliances of most of the blends were close to the values calcd. from the Rouse theory, $J_e = (2/5)M_{z+1}M_z/M_w\rho RT$, where ρ is the d., esp. when the possibility of some degree of mol. heterogeneity in the component fractions was taken into account by the method of Peticolas and Menefee. The ratio λ_2 of the terminal relaxation times of the component of higher mol. wt. in the blend to their values in that pure component was obtained for each blend by applying the method of N. to the relaxation modulus, calcd. from the creep compliance by approximation methods. For most of the blends, λ_2 was close to the value calcd. from the Rouse theory, $\eta_{01}M_2/\eta_{02}\bar{M}_w$. The data in the terminal zone were further analyzed by the phenomenological theory of viscoelasticity in terms of 2 auxiliary dimensionless parameters N_{21} and D. Here $D = \lambda_1^{\nu_1}\lambda_2^{\nu_2}$, where λ_1 is the ratio of terminal relaxation times of the component of lower mol. wt. in the blend to their values in that pure component. The data are all consistent with the assumption that $D = 1$ when the λ and η values are reduced to iso-free-vol. states, and that otherwise $\log D = (1/2.303)[1/f - (\nu_1/f_1) - (\nu_2/f_2)]$. The parameter N_{21} is the ratio of the contributions per unit vol. of the 2 components to energy dissipation in steady flow. When both $M < M_c$, $N_{21} = M_2/M_1$ as predicted by the Rouse theory. When both $M > M_c$, N_{21} exceeds M_2/M_1 by a factor which ranges from 6 to 10. When $M_1 < M_c < M_2$, N_{21} increases rapidly with ν_2. In such a blend, λ_2 is more dependent on compn. than λ_1, because component 1 participates in the entanglements to a limited extent. RCKG

723

High-energy electron radiation resistance of plastics. J. V. Pascale, D. B. Herrmann, and R. J. Miner (Bell Telephone Labs. Inc., Murray Hill, N.J.). *Mod. Plastics* 41(2), 239-40, 244-5, 248-9, 251-3, 374, 378(1963). The effects of ionizing radiation on the mech. and elec. properties of 45 plastics were detd. Styrene polymers and polyethylenes were most resistant to radiation, while acrylics, cellulosics, and fluorocarbons were least resistant.
C. A. Burkhard

1851

Osmotic coefficient of alkali salts of glyoxylic acid partial acetals of poly(vinyl alcohol) in water. Akio Nakajima and Hideto Sotobayashi (Kyoto Univ., Japan). *Kobunshi Kagaku* 19, 423-6(1962). Osmotic-pressure measurements were performed in dil. aq. solns. of an alkali salt of glyoxylic acid partial acetal of poly(vinyl alc.), contg. ~8 mole % COOH groups in the polymer chains. The osmotic coeff. calcd. from the exptl. data is very small and increases with the concn. of the polymer. This result conforms with that previously found for linear copolymers composed of vinyl alc. and acrylic acid units. To discuss this result more fully, the degree of swelling of the cross-linked copolyelectrolytes composed of the same components as that of the linear polymer was measured in H_2O. The osmotic coeff. evaluated from the results of the swelling equil. was compared with that for the linear copolymer.
Eiichi Wada

The orientation in atactic noncrystalline polymers. J. W. Breitenbach, A. Preisinger, and E. Tomschik (Univ. Vienna). *Monatsh.* 94(5), 807-8(1963). Microscopic examn. of thin sections of polymers of the "popcorn" type disclosed optically isotropic and also large optically anisotropic domains. These substances give x-ray diffraction patterns of amorphous matter. Parallel orientation of the polymer chains exists to a degree. The no. of optically anisotropic domains in the nonhomogeneous polymers is in direct relation to the ability to grow, in the case of monovinyl compds. After extended growth in monovinyl compds., polymers will be obtained which have almost no capacity for further growth and which have very few anisotropic domains.
Willem van Hees

Single crystals of poly(vinyl alcohol). Kiyoshi Tsuboi and Takaji Mochizuki (Kurashiki Rayon Co., Ltd., Kurashiki, Japan). *J. Polymer Sci.* Pt. B 1(10), 531-4(1963). The electron micrographs of single crystals of poly(vinyl alc.) show parallelogram-like platelets. The ratio of the length of the longer side to the shorter side is about 5, the lamella thickness 100-150 A., and the acute angle of the parallelogram 55°. The occurrence of corrugations inclined at 20-30° to the longer side of the platelet suggests that the lamellae grow as a semidome or a corrugated platelet during the crystn. The spacings and the intensities of the reflections of the electron-diffraction pattern of the single crystal nearly correspond to those of the x-ray reflections of fibers of poly(vinyl alc.).
G. W. Scherf

1857

Role of unsaturation in the radiation chemistry of polymers. I. Polyethylene. M. A. Crook and B. J. Lyons (Brit. Insulated Callender's Cables Ltd., London). *Trans. Faraday Soc.* 59(490), 2334-49(1963). The variation with ionizing radiation (Van de Graaf accelerator) dose of vinyl, vinylidene, and *trans*-vinylene unsatn. concn. in high- and low-d. polyethylene (I) was studied, including the effect of added allyl and vinyl unsatn. as triallyl cyanurate (II), 1,19-eicosadiene (III), and divinylbenzene. In both high- and low-d. I, suppression of *trans*-vinylene decay was observed in the presence of II or III. Expressions were derived to account for decay of vinyl, vinylidene, and added allyl unsatn. which allow for radical scavenging by the cyanurate group. The results were explained in terms of energy migration to or localization in the vicinity of unsatd. groups followed, in most cases, by chain reactions. Radiolytically formed *trans*-vinylene groups are postulated to be radical scavengers rather than chain carriers. II. Gel formation in polymer and triallyl cyanurate mixtures. *Ibid.* 2350-4. Gelling doses for I, poly(Me acrylate), and poly(vinyl acetate) are decreased by small addns. of III. Large amts. of III inhibit gelation at low doses, but increase gelation at high doses. At concns. of 0.5-5.0% of III in I, each mol. of III cross-links 2.5-3.0 polymer mols., indicating that, in this concn. range, hydrogenation or polymerization of allyl groups is insignificant. Cf. Dole, *et al.*, *CA* 52, 11464*e*.
T. W. Brooks

16052

Possible use of the dielectric method for studying the structure and intermolecular forces in the liquid state on a polymer-solvent model. P. F. Veselovskii (Polytech. Inst., Leningrad). *Ukr. Fiz. Zh.* 9(1), 99-100(1964). Measurements of the tangent of dielec. loss angle and the dielec. const. made with solns. of poly(vinyl acetate) (I) in H_2O or PhMe showed that, in the presence of H_2O, the max. of the tangent of dielec. loss angle and the dielec. const. are shifted to lower temps. The temp. shift is directly proportional to the no. of H_2O mols. introduced into the polymer. This effect is attributed to the interaction between H_2O and the polar polymer groups. PhMe has no effect on the polar I groups. Thus, H_2O blocks the polar polymer groups and decreases the effective dipole moment calcd. for a monomer link of the macromol. PhMe changes the geometrical configuration of the polymer-solvent mols., and therefore the effective dipole moment calcd. for the monomer link remains unaffected. The activation energy also decreases during plasticizing of the polymer with both H_2O and PhMe mols.
GPJW

1882

Poly(vinyl acetate) and poly(vinyl alcohol), an example of the employment of polymers in the textile industry. F. Linke and H. Seidel (Farbwerke Hoechst A.-G., Frankfurt/Main-Hoechst, Ger.). *Melliand Textilber.* 44(10), 1134-8(1963). A review of the different applications being made of poly(vinyl acetate) and poly(vinyl alc.) in their roles as textile assistants.
Thomas A. Wilson

3111

Structure and mechanical properties of "oriented" amorphous linear polymers. L. A. Laius and E. V. Kuvshinskii. *Fiz. Tverd. Tela* 5(11), 3113-19(1963); cf. *CA* 55, 26514*i*. Deformation-strength characteristics were investigated for poly(vinyl acetate) and poly(Me methacrylate) films which underwent uniaxial stretching at different temps. Strength and elongation at breaking are not found to be single-valued functions of the av. degree of orientation of macromol. chains. Analysis of expts. on isometric heating leads to the conclusion that films with the same birefringence but oriented at different temps. have different internal structures. This is reflected in their mech. properties.
H. Libackyj

4253

Determination of the diameter of large latex particles from the ratio of optical densities. Miroslav Hlousek. *Chem. Prumysl* 13(9), 492-7(1963). Previous reports (*CA* 55, 20488*i*; 58, 6216*h*) dealt with the detn. of the diam. of latex particles up to 0.2 μ. The method is applicable to det. the diam. of latex particles of poly(vinyl acetate) and other polymers up to 3 μ. Pulfrich's photometer is used for the detn. of optical ds.
R. C. Evans

4272

Gel formation in poly(vinyl alcohol) film by heat treatment after exposure to ultraviolet light. Masatake Mori and Michikazu Kumagai (Univ. Tokyo). *Japan. J. Appl. Phys.* 3(1), 11-15 (1964). The phys. properties of poly(vinyl alc.) (I) are changed by exposure to ultraviolet light followed by heat treatment as in the case of high energy radiations. When I is irradiated in air, carbonyl groups are produced. The heat treatment of irradiated I above 120° produces cross-linkages between mol. chains.
RCJD

Electrophysical properties of poly(vinyl alcohol) and its chelates. A. Ya. Gel'fman, E. F. Kvyatkovskaya, R. G. Luzan, and B. S. Skorobogatov. *Vysokomolekul. Soedin.* 5(10), 1534–7 (1963). Polychelates were prepd. by treating poly(vinyl alc.)

4304

(I) films with 10% $Ti(SO_4)_2$ or 10% $Cu(NH_3)_4SO_4$, and their electrocond. was measured at various temps. For Cu polychelates, the dependence of log σ *vs.* $1/T$ (σ is the sp. electrocond. and T the abs. temp.) in the heating cycle is represented by 2 straight lines with a break at 67°. This is caused by desorption of absorbed H_2O. By repeating the heating-cooling cycles *in vacuo*, the dependence becomes a single straight line for both the heating and cooling expts. For Ti polychelates, the temp. dependence of σ was measured only up to 68°; at this temp. the darkening of the sample occurs. The behavior of Ti polychelates is similar to that of Cu polychelates, including the effect of absorbed H_2O. The electrocond. is of 1st order with no sign of ionic cond. The electrocond. of I and its Ti chelates is 10^{-12}–10^{-13} ohm^{-1} cm.$^{-1}$ while that of Cu chelates is 10^{-14}–10^{-16} ohm^{-1} cm.$^{-1}$
K. Dusek

5641

Identification of organic polymers by pyrolysis and gas chromatography. H. Feuerberg and H. Weigel (Bundesanstalt Materialpruefung, Berlin-Dahlem). *Z. Anal. Chem.* 199(2), 121–32(1964). Identification of org. polymers is based on pyrolysis in a sep. tube followed by analysis of the pyrolyzate by gas chromatography. Polymers studied included polystyrene, silicone rubber, silicone oil, poly(Me methacrylate), polyacrylonitrile, poly(Bu acrylate), poly(Et acrylate), benzyl cellulose, Et cellulose, Me cellulose, cellulose acetate, cellulose acetatebutyrate, cellulose, poly(vinyl propionate), poly(vinyl acetate), and poly(vinyl alc.).
K. G. Stone

Identification reaction for poly(vinyl alcohol). M. M. L. Khosla and K. J. Balakrishna (Defence Res. Lab., Cawnpore). *LABDEV* (Kanpur, India) 1(1–2), 49(1963)(in English). Poly(vinyl alc.) (I) is distinguished from polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) by heating with resorcinol in the presence of concd. H_2SO_4. Only I produces a brownish-green fluorescence in visible light and strong blue fluorescence under ultraviolet light.
W. R. Browne

5652

Determination of the intrinsic viscosity at the theta point and molecular weight of a linear polymer from viscosity measurements in a nonideal solvent. V. S. R. Rao (Purdue Univ., Lafayette, Indiana). *J. Polymer Sci.* 62(174), S157–S159(1962). An equation is given for $[\eta]_\theta$, the intrinsic viscosity $[\eta]$ at the θ point for a given polymer sample, with any solvent. This equation eliminates the need of finding a θ solvent (which for many systems is difficult): $[\eta]_\theta = [\eta][1 - (1-2k)^{1/2}]$, where k is the Huggins const. (0.2–0.5). $[\eta]_\theta$ is calcd. for polystyrene dissolved in $CHCl_3$, toluene, Tetralin, C_2H_4–C_6H_6, dioxane, o-$C_6H_4Cl_2$, dichlorodiethylbenzene, chlorotriethylbenzene, MeCOAm, and MeCOEt, as well as for poly(vinyl acetate) in Me_2CO and amylose in Me_2SO. An equation is also given which, if used with the above equation, permits calcn. of the mol. wt. of a given polymer in any solvent: $[\eta]_\theta = K_\theta M^{1/2}$, where K_θ is a solvent-independent const., the values of which are available in the literature for many polymers, and M is the mol. wt. 13 references.
C. E. Beland

5660

Effect of stereospecificity on equilibrium acetalization of poly(vinyl alcohol) and pentane-2,4-diol. Kiyoshi Fujii, Junji Ukida, and Masakazu Matsumoto (Kurashiki Rayon Co., Okayama, Japan). *J. Polymer Sci.* Pt. B 1(12), 693–6(1963). The equil. const. (k) in the acetalization of pentane-2,4-diol (I) (meso type) is 8.7×10^3, of I (*dl*-type), 3.7×10^3. For poly(vinyl alc.) (II), corrected values of k are: for II-1 (isotactic) 3.01×10^3, II-2 (conventional) 1.14×10^3, II-3 (syndiotactic) 7.06×10^2. The degree of tacticity for each II sample is calcd. as: II-1 $I_0 = 0.746$, $S_0 = 0.254$; II-2 $I_0 = 0.47$, $S_0 = 0.53$; II-3 $I_0 = 0.329$, $S_0 = 0.671$, I_0 and S_0 denoting the isotactic and syndiotactic fractions, resp.
John H. Dittmar

Properties of polyacetylenes. V. I. Kasatochkin, A. M. Sladkov, Yu. P. Kudryavtsev, Z. S. Smutkina, T. M. Khrenkova, and V. V. Korshak (Inst. Heteroorg. Compds., Moscow). *Izv. Akad. Nauk SSSR, Ser. Khim.* 1963(10), 1766–71. The wt. losses of the previously described polyacetylenic polymers (*CA* 55, 18554*d*) on heating to 800° were detd. All yellow substances (polymers of *p*-diethynylbenzene, its copolymers with PhC:CH, EtC:CH, C_2H_2, 9,10-diethynyl-9,10-dihydroxy-9,10-dihydroanthracene, and the copolymer of PhC:CH with 2,6-dimethyl-3,5-diethynylpyridine) had linear structures and only a small loss of volatile matter on heating at 2°/min. At high temps., no carbonization was evident and there was only a small drop in C:H ratio at 400°, possibly because of reaction of macroradicals with water vapor. If the heating rate was raised to 8°/min., vigorous decompn. took place and much volatile material was lost at relatively moderate temps. Also examined were dark or black polymers of C_2H_2, its copolymers with 9,10-diethoxy-9,10-dihydroxy-9,10-dihydroanthracene and 2,6-dimethyl-3,5-diethynylpyridine, and polymers of the latter 2 monomers, as well as poly(vinyl alc.). These were studied in normal and in heated-treated states. The group was found to consist of semiconductors with an activation energy of cond. of 0.1–1.0 e.v. The probable gross structure consisted of aggregates of parallel chains with a high degree of azimuthal orientation, which depended on the space occupied by the substituent groups. Generally, Ph rings as end groups improved the longitudinal orientation and appearance of cryst. regions in the aggregates. Conds. of the specimens in the temp. range 400–800° are given. G. M. Kosolapoff

5661

Chemical structure of radiation-induced graft copolymers of methyl methacrylate on poly(vinyl alcohol). I. Sakurada, S. Matsuzawa, and Y. Kubota (Univ. Kyoto, Japan). *Makromol. Chem.* 69, 115–24(1963)(in English). A 0.1-mm. film of poly(vinyl alc.) (I) was dried, irradiated by γ-rays to a dose of 1×10^6 r., and held at −60°. Then 15 ml. of Me methacrylate (II) soln. (40 vol. % in MeOH) per g. of I was added, given 5 freeze-thaw cycles with liquid N, deaerated, and heated for 7 hrs. at 50° for grafting. After II homopolymer was extd. with Me_2CO, the % increase in wt. of the film, 98%, was taken as the % graft. This graft copolymer was acetylated by heating in a ratio of 1 g. to 20 ml. pyridine and 10 ml. Ac_2O for 3 hrs. at 60° and 15 hrs. at 104° and pptg. with H_2O. Successive pptns. were made from 1% C_6H_6 soln. with BuOH to give 7 fractions of graft copolymers. The remaining amt. of compd. indicated that 96% of the parent I mols. had not been grafted. Av. degrees of polymerization of the pptd. fractions were between 14,000 and 63,000. Cleavage of the backbone mol. by sapon., swelling in Me_2SO, heating for 5 hrs. at 30° with 0.004 g. HIO_4 per 0.1 g. of swollen copolymer, and re-acetylation gave no change in mol. wt., showing the presence of only 1 branch per mol. R. Bostwick

5700

Relation between stereoregularity and water resistance of poly(vinyl alcohol) (PVA). Kiyoshi Fujii, Takani Mochizuki, Junji Ukida, and Masakazu Matsumoto (Kurashiki Rayon Co., Okayama, Japan). *J. Polymer Sci.* Pt. B 1(12), 697–9(1963). Expts. on PVA samples of different syndiotacticity, subjected as films to different crystn. treatments, indicated that both the cryst. and amorphous portions should be considered as a factor in the improvement of the water resistance of PVA.
John H. Dittmar

Electrochemical properties of ionogenic membranes prepared by thermal and oxidative degradation of poly(vinyl alcohol) (PVA). T. M. Ellison and H. G. Spencer (Clemson Coll., Clemson, S. Car.). *J. Polymer Sci.* Pt. B 1(12), 707–10(1963). The electrochem. properties of PVA membranes after degradation at 175° in a stream of dry O were presented. The degradation produced an amber color in the membranes, and increased their wet strength and their brittleness when dry. The significant change in the infrared spectra of the membranes during degradation was the development of absorption in the carbonyl (~1700 cm.$^{-1}$) and alkene (~1600 cm.$^{-1}$) regions, a portion of the carbonyl absorption being due to the presence of COOH groups. The degradation apparently produced COOH groups and a more rigid membrane structure despite possible chain scission. The modifications decreased osmotic flow and sp. conductance, and increased the concn. potentials of the membranes.
John H. Dittmar

6929

Analysis of high polymers by gas chromatography of pyrolysis products. I. Identification of pyrolysis products of polymers. D. Braun. *Farbe Lack* 69, 820–7(1963). A Pt wire coil in a 10 × 100 mm. glass ampul is used for pyrolysis at 800° (20 sec.). The condensed reaction products are put through the gas chromatograph at 100° with He using a 2-in. "B"-column (Perkin-Elmer 116E). Chromatograms, peaks, and retention times of identified substances are reported. 28 references.
Konrad Parker

6990

Capillary chromatography of poly(vinyl acetate) emulsions. Sadao Hayashi, Chiyoko Nakano, and Takuhiko Motoyama (High Polymer Chem. Inds. Ltd., Osaka, Japan). *Yukagaku* 12, 501–5(1963). Poly(vinyl acetate) emulsions stabilized with soap have a considerable resistance to coagulation with a Na_2SO_4 soln. These coagulation phenomena have been easily observed by means of capillary chromatography. In the case of emulsions stabilized with nonionic soaps of the poly(ethylene oxide) type, the stabilization effect was found to increase with increase in chain length of ethylene oxide in the soap; the lauryl ether type surfactant had a better effect on the stability than the nonylphenyl ether type.
K. Kitsuta

8147

Solution and bulk properties of branched poly(vinyl acetates). I. Non-Newtonian viscosity behavior. L. M. Hobbs and V. C. Long (Univ. of Michigan, Ann Arbor). *Polymer* 4(4), 479–91 (1963); *CA* 51, 14318c. A series of linear and branched samples of the title polymer (I) having a narrow mol.-wt. distribution were prepd. and characterized by soln. viscosity, hydrolysis, and light-scattering measurements. Viscosity loss after hydrolysis and reacetylation of I was a qual. test for branching. Solns. of I having mol. wts. over 2 × 10^6 exhibited non-Newtonian flow behavior. Mol. wt. rather than structure was the major contributor to non-Newtonian behavior. The ratio of linear to branched intrinsic viscosities in samples with the same mol. wt. was insensitive to shear rate. It was therefore possible to detect branching by comparison of shear sensitivities of branched and linear fractions having the same intrinsic viscosity. Procedures for detg. intrinsic viscosity at O shear rate and shear sensitivity from soln. viscosity data are discussed.
T. W. Brooks

Colloid chemical studies of starching materials. V. Rheological properties of concentrated poly(vinyl alcohol) solutions. Masayuki Nakagaki and Takako Nishii (Osaka City Univ.). *Bull. Chem. Soc. Japan* 37(1), 60–6(1964); cf. *CA* 57, 7083f. The viscoelastic behavior of 11–12% solns. of poly(vinyl alc.) (I) was studied by using an oscillation rheometer (*CA* 55, 16079g) for dynamic measurements and a Couette-type rotation viscometer for steady-flow measurements. Thus, 4 samples of I, ranging in av. degree of polymerization (P) from 1700 to 2600, were measured at 30° for dynamic and steady-flow viscosity (η), and dynamic rigidity (G). Measurements were made 20, 60, and 110 hrs. after the prepn. of each soln. The results were analyzed by use of the Rouse theory (*CA* 57, 10956g). At low frequencies, dynamic η was almost const. for 3 samples, and G was nearly equal to zero. For these 3 samples, the relations of dynamic η and G *vs.* angular frequency (ω) did not depend on time and agreed with theory. The time and ω dependence of dynamic η and G in the 4th sample was attributed to the existence of an intermol. assocn. structure which is destroyed by increasing ω and affected by time. Steady-flow η varied with both time and velocity gradient (g) for all 4 samples, increasing with g for the low-mol.-wt. samples and decreasing with g for the high-mol.-wt. samples. For all samples, η_0/P^3 was fairly const., where η_0 is dynamic η extrapolated to $\omega = 0$.
R. Bostwick

9369

Viscosity and molecular weight of polyvinyl alcohol and its fractions. A. N. Leporskii. *Vopr. Pereliv. Krovi i Klinich. Med., Kirov Sb.* 1962, 171–5. Fractionation of poly(vinyl alc.) (I) was carried out by pptn. of individual fractions of 2% aq. soln. with the aid of an aq. Me_2CO soln. in 0.25 to 1.75 ratio. Five fractions of I were prepd. in a dry form. Viscometric detn. of the characteristic viscosity of I and its 5 fractions was made at 50° and ≦0.8% concn., The viscosity-av. mol. wt. was 28,500 for I. The mol. wt. of the 5 fractions varied in the range of 11,000–40,000. Relations of the reduced viscosity to concn. for all samples were expressed graphically by a straight line. From *Ref. Zh., Khim.* 1963, Abstr. No. 13N222.
MXRK

9372

Investigation of the intermolecular interactions in polymers and their hydrated monomers by using infrared spectra. II. Polymers. G. P. Mikhailov and A. L. Smolyanskii. *Optika i Spektroskopiya* 15(6), 766–71(1963); cf. *CA* 60, 1854c. Measurements were made of the frequencies and intensities of the $\nu_{C:O}$ infrared absorptions of poly(Me acrylate), poly(Et acrylate), poly(Bu acrylate), poly(Me methacrylate), poly(Et methacrylate), poly(Bu methacrylate), and poly(vinyl acetate) in the solid state and in C_6H_6 and $CHCl_3$ solns.
A. P. Kotloby

10803

Determination of the molecular weight of poly(vinyl acetate) by end-group analysis. G. S. Misra and V. P. Gupta (Univ. Lucknow, India). *Makromol. Chem.* 71, 110–17(1964)(in English). The polymerization of vinyl acetate by using γ,γ'-azobis(γ-cyanovaleric acid) as initiator has been studied at 80 and 90° in $HCONMe_2$ soln. The av. mol. wt. ($\bar{M}$) of the samples was detd. by viscosity detn. and end-group titrations for both fractionated and unfractionated samples. For low-mol.-wt. samples of unfractionated poly(vinyl acetate), the equation $[\eta]$ (intrinsic viscosity) = $1.46 \times 10^{-4}\bar{M}^{0.72}$ is valid. For close fractions, the relation $[\eta] = 1.08 \times 10^{-4}\bar{M}^{0.73}$ gives good correspondence. The relation between $[\eta]$ in $CHCl_3$ and in C_6H_6 is $\log [\eta]_{CHCl_3} = +0.37 + 1.26 \log [\eta]_{C_6H_6}$.
I. C. Kogon

The use of membranes permeable to the solute in the determination of molecular weights by osmometry. Fanny Boyer-Kawenoki (C.N.R.S., Bellevue, France). *Compt. Rend.* 258(1), 203–5(1964). Staverman's equation $\pi_a = S\pi_t$ (*CA* 45, 6010e) was used to relate the measured apparent osmotic pressure, π_a, as detd. with a nonselective membrane, to the theoretical pressure, π_t. S is the reflection coeff. and is given by $S = [(C_1 - C_2)/(C_1 + C_2)]_{\pi=0}$, in which C_1 and C_2 are the solute concns. in compartments 1 and 2 of the osmometer when the apparent pressure is zero. Studies were made with poly(vinylpyrrolidinone) (I) and poly(vinyl alc.) (II) at 25° with a soln.:solvent ratio of 1:2. Plots of π/C vs. C (C = concn. in g./100 ml.) gave straight lines which could be extrapolated to the limiting value of π/C as $C \to 0$. These data were used to calc. the mol. wt. according to van't Hoff's law. The apparent mol. wts. (M_a) were higher than the theoretical values (M_t). For I, $M_a = 75{,}100$, while $M_t = 23{,}000$. For II, $M_a = 32{,}400$ and $M_t = 20{,}000$. When the apparent mol. wts. were cor. by the

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reflection coeff. (M_aS), the agreement between M_a and M_t was very close for both polymers.
A. A. Hiltz

Isometric heating as a method of studying oriented amorphous solid polymers. L. A. Laius and E. V. Kuvshinskii (Acad. Sci. U.S.S.R., Moscow). *Vysokomolekul. Soedin.* 6(1), 52–7 (1964). The correlation of polymer orientation characteristics with its internal stress changes (Rudd and Andrews, *CA* **53**, 818c) was substantially extended by the use of a uniform, relatively slow increase of temp., i.e. isometric heating. Bands of poly(vinyl acetate) (I) and poly(Me methacrylate) (II) film (up to 100 μ thick), cut to 2 × 20 mm. strips, were stretched at elevated temps. The bands were prepd. from polymers of mean mol. wt. of 790,000 and 710,000 of I and II, resp., by evapn. from concd. solns. on a glass pad, and drying the film *in vacuo* for a few days at 120 and at 150° for I and II, resp. The softening temps. of dried I and II films were 44 and 120°, resp. The stretched bands were cooled with cold air and the birefringence of the oriented samples was taken. The polymer bands were then fixed vertically in 2 clamps, the upper one connected to a dynamometer, and on heating at a const. rate q (1–60°/min.) a diagram of isometric heating (*DIH*) was constructed for each expt. on the stress *vs.* the temp. coordinates. The *DIH* for the amorphous polymers showed curves with a single peak or peak plateau, and the max. stress σ_t was taken as the value of internal stress. In samples of I oriented in various conditions, the σ_t value increased continuously with the increase in birefringence $(\Delta n)^t$, irrespective of the elongation conditions (Rudd and Andrews, *loc. cit.*). The temp. of elongation T_e and the rate V_e were changed from 45 to 90° and from 0.08 to 2.58%/sec., resp. A similar relation was observed in oriented II. The shape of the *DIH* curves depended on the degree of stretch, temp., and stretch rate. In I, changes of the degree of stretch λ from 1.5 to 2.5, 3.5, and 5 at T_e and V_e const. resulted in *DIH* curves starting at the same point and max. at the same temp., but with correspondingly greater σ_t values. A decrease in V_e from 1.2 to 0.128%/sec. gave lower σ_t and a wider peak shape. An increase in T_e from 51.5° to 90° also gave lower and wider peaks, and in a case of $q = 5°$/min. isometric heating, a pronounced plateau. In II, with an increase in λ from 1.5 to 2.5, 3.25, and 3.9 (at $T_e = 105°$ and $V_e = 2.58\%$/sec.), the stresses started to increase at correspondingly lower temps., some 70–80° below the softening temp. of the initial polymer. The max. stresses in conditions of isometric heating corresponded to the stresses on structure fixation during cooling. Samples of I stretched at $T_e = 46°$, $\lambda = 6$, and $f = 16$ g., and of II stretched at 120°, 3, and 31 g., resp., showed max. stresses on *DIH*, i.e. equal to stresses on elongation (f is the const. elongating force). The stress and relaxation aspects of the *DIH* curves are discussed; it is considered that the diagrams present data on the mean orientation degree of macromol. links and reflect differences in the distribution of bonds between the macromolecules. Andrew L. Grochowski

Thermal stability of poly(vinyl alcohol). O. O. Borodina and K. E. Perepelkin. *Plasticheskie Massy* 1964(1), 7–11. The effect of NaOAc on the thermal stability of various samples of poly(vinyl alc.) was studied at 120–220°. Increasing amts. of NaOAc and increasing temps. increase the rate of color formation. Increasing amts. of NaOAc decrease the water soly. at const. time and temp. The degree of polymerization is decreased on heating in proportion to the time and temp.

E. A. Blair

Effect of intramolecular hydrogen bonds on the conformations in solution of molecules of β-diols and of poly(vinyl alcohol). Henri Buc (Ecole Super. Phys. Chim. Ind., Paris). *Ann. Chim.* (Paris) 8(7–8), 431–56(1963); cf. *CA* **60**, 10512h. The effect of inter- and intramol. interactions in a synthetic polymer, poly(vinyl alc.) (I), on its conformation was studied as a model for macromols. of biol. interest. Nuclear magnetic resonance (NMR) was used to study H bonding in aq. solns. The H_2O mols. entered into competition with the alc. groups in the formation of H bonds and modified the speed of passage from 1 configuration to another. The preferred configurations in CCl_4 soln. were not present in aq. solns. This determinative arrangement in the structure of the polyalc. disappeared progressively in the presence of certain 3rd substances (for example, SCN^-), whose activity with respect to the H bond is known. This was noted in studying the resonance of the methylene protons of *meso*-2,4-pentanediol and the sp. rotatory power of an optically active 1,3-butanediol dissolved in H_2O-KSCN solns. The introduction of these results into the statistical calcns. of the conformation allowed a prediction of the influence exerted by breaking the different types of H bond on the radius of gyration of a macromol. of I of known mol. wt. and stereoregularity to be made. In the case of atactic products, scission of the H bridges between noncontiguous hydroxyls occurred with an increase of the radius of gyration, while an inverse effect was to be expected from the rupture of more stable bonds in the β-position. These 2 phenomena could be demonstrated by studying the variation of the intrinsic viscosity of an atactic I in an aq. KSCN soln. with variable concn. of salt. These results were confirmed by measuring the intensity of light scattered by these solns. It was also shown by an infrared study that the preferential fixation of the salt probably results in the establishment of a H bond between the polyalc. and the N atom of the SCN^-. This effect is the inverse of that of an electrolyte which salts out; this type of electrolyte causes an increase in the frequency of the H bonds which are established between the alc. groups. In the latter case, the ions acting as dipoles tend to hydrate, creating local superconcns. of the org. species. These results are confirmed by a study of the NMR of the protons. The systematic utilization of aq. solns. of different electrolytes therefore allows exptl. conditions favorable to the manifestation of conformational transitions to be created by varying the state of assocn. of the solvent.

C. L. Deasy

Conductometric determination of sodium acetate in poly(vinyl alcohol). D. B. Gurvich, V. A. Balandina, and R. V. Kosmakova. *Plasticheskie Massy* 1964(2), 69–71. Unreacted NaOAc in poly(vinyl alc.) (I), prepd. by the sapon. of poly(vinyl acetate) in MeOH soln., was detd.; 4–5 g. I is dissolved in 150 ml. boiling H_2O, dild. by 120–50 ml. H_2O, and after the addn. of 5–10 ml. 0.1*N* NaCl, titrated with 0.1*N* HCl.

K. Dusek

12122

The degree of branching of poly(vinyl acetate). Hung Chou, Shui-Lin Chen, Min-Jen Chen, and Shu-Wan Chi. *Fang Chih Chi Sha* 1963(10), 18-20. The degree of branching is based on a *K* value which is defined as the ratio of $(\bar{P}_{ac}/\bar{P}_{a}) - 1$ to $\bar{P}_{ac}$, where $\bar{P}_{ac}$ and $\bar{P}_{a}$ are the viscosity av. degrees of polymerization of poly(vinyl acetate) and poly(vinyl alc.), resp. These 2 values are calcd. from the intrinsic viscosity $[\eta]$, with Me_2CO as the solvent at 30°, according to the equations: $[\eta]_{ac} = 7.04 \times 10^{-4} \bar{P}_{ac}^{0.62}$ and $[\eta]_{a} = 7.50 \times 10^{-4} \bar{P}_{a}^{0.64}$. The emulsion, bulk, soln., and suspension polymerization techniques are used to compare their effects on the degree of branching of the polymers. The *K* and *k'* (Huggins const. (*CA* 37, 19^5)) decrease in the order listed above at a conversion >80% for the first 3 techniques and above 27% for the last technique. The exptl. data obtained with a soln. technique, using 20% MeOH by wt., indicate that the *K* value increases rapidly above 60% conversion. The *K*

12176

Yellowing of poly(vinyl alcohol) on heating. Tadeusz Rosner, Zenon Joffe, and Eugeniusz Jaszczak (Politech. Szczecinska, Szczecin, Poland). *Polimery* 8(7-8), 291-3(1963). The yellowing of poly(vinyl alc.) (I) used in the manuf. of fibers was examd. with a colorimeter. The I films cast from aq. soln. were heated at 120-200° for 0.5-120 min. The effect of temp., time of heating, and salts added on the extinction of heated films was investigated. The method gives reproducible results. NaOAc accelerates the yellowing of I. The best stabilizing action was shown by 2% $ZnSO_4$. The stabilizing action is probably caused by the salt itself and not by the change of pH resulting from the addn. of amphoteric salts. Optimal concns. of stabilizers were detd.

P. Penczek

13339

Electric conductivity and conjugated double bonds in products of poly(vinyl alcohol) pyrolysis. A. Ya. Gel'fman, D. S. Bidnaya, L. V. Sigalova, M. G. Buravleva, and V. S. Koba. *Dokl. Akad. Nauk SSSR* 154(4), 894-6(1964). Powd. poly(vinyl alc.) (I) was pyrolyzed in a stream of air or an inert gas for 3 hrs. at different temps. The concn. of isolated and conjugated C:C bonds, detd. from infrared spectra, increases with increasing temp. of pyrolysis. Untreated I is only slightly cryst., but the degree of crystallinity of the products increases with increasing temp. of pyrolysis, reaching a max. value for products pyrolyzed at 200°. I pyrolyzed at 300° is completely amorphous, but I pyrolyzed at 450-800° is again cryst.; the crystallites, however, have a different structure. Samples of I pyrolyzed at 300-50° have the lowest sp. elec. cond. The resp. activation energy, *E*, generally decreases with increasing temp. of pyrolysis, except for the I treated in N; here, the max. *E* corresponds to the product pyrolyzed at 300°. Otherwise, there are only very slight differences between products treated in O or an inert gas. A phase transition occurs at 250-350°, which corresponds to the breakdown of H bonds in I and to a max. concn. of C:C bonds.

K. Dusek

13402

Thermal stabilization of vinyl polymers. N. V. Mikhailov, L. G. Tokareva, Z. N. Zhandareva, and P. A. Kirpichnikov. U.S.S.R. 159,934, June 14, 1964, Appl. Nov. 20, 1962. Vinyl polymer, e.g. poly(vinyl alc.), fibers are heat stabilized with P-contg. compds., such as the H_2O-sol. 2-cyanoisopropyl *o*-phenylene ester of phosphorus acid. From *Byul. Izobret. i Tovarnykh Znakov* 1964(2), 40.

MGCL

14624

Crystallinity of poly(vinyl alcohol) (PVA) component of poly(vinyl alcohol)-poly(vinyl chloride) (PVA-PVC) graft copolymers. Kan Shirakashi, Kinzo Ishikawa, and Keizo Miyasaka (Inst. Technol. Tokyo). *Kobunshi Kagaku* 20(223), 673-9(1963). The crystallinity of the PVA component of PVA-PVC graft copolymer prepd. from the polymerization of PVC in PVA aq. soln. was studied. The x-ray scattering curve of the PVA component was sepd. from that of graft copolymer by an at. structure factor, Compton scattering factor, and fraction of component polymer. Crystallinity of the PVA component decreases with the increase of wt. fraction of the PVC component. The half width of x-ray diffraction peak of the PVA component is much broader than that of homo- or blended PVA and influenced by no. of grafting PVC mols. per PVA mol. The change of crystallinity of the PVA component of the graft copolymer with high temp. treatment differs from that of homo- or blended PVA. From *Polymer Rept.* 1963(68), 17.

TCPM

14625

Further experiments on diffusion-controlled transitions in high polymers. K. Kanamura and M. Sugiura (Nippon Univ., Tokyo). *Kolloid-Z.* 194(2), 110-24(1964)(in English); cf. *CA* 58, 3535*b*. The temp. of diffusion relaxation (*D*) of poly(Me methacrylate) (I), polycarbonate (II), polyacrylonitrile (III), poly(vinyl chloride), and poly(vinyl acetate), esp. the rubber-like polymers with f.ps. far below room temp., and the shape of the curves of log *D* vs. 1/*T* of some high polymers capable of H-bond formation penetrated by solvents also capable of H-bond formation (e.g. nylon 6/EtOH, cellulose/EtOH, and cellulose diacetate/BuOH), and curves of high polymers penetrated by solvents only one of which can form H-bonds (e.g. I/BuOH, II/ethylene glycol, and III/$MeNO_2$) were analyzed. The curves corresponded to 4 types: (*a*) 1 intersection point and 2 linear branches; (*b*) 2 intersection points and 3 linear branches; (*c*) type (*a*), to which a downward branch is attached at higher values of 1/*T*; and (*d*) type (*b*), to which a downward branch is similarly attached. Types (*a*) and (*b*) are typical of systems in which neither the high polymer nor the solvent form H-bridges; types (*c*) and (*d*) typify those that do. Types (*a*) and (*c*) designate systems in which the polymers are lyophobic and swell only slightly; types (*b*) and (*d*) designate large swelling ability. The downward branch corresponds in both cases to desolvation of the polymers in the transition process at the higher temps.

Thomas A. Wilson

16000

Optical anisotropy of poly(vinyl acetate) molecules. III. Effect of the solvent on the internal rotation in poly(vinyl acetate) molecules. E. V. Frisman, G. A. Dyuzhev, and A. K. Dadivanyan. *Vysokomolekul. Soedin.* 6(2), 341-5(1964); cf. *CA* 58, 14127*b*. The segmental anisotropy $(\alpha_1-\alpha_2)$, dependent on the solvent used, of poly(vinyl acetate) (I) mols. was investigated by means of flow birefringence and viscosity. It was proved that a change in the long-range forces in the chain and in the dipole moment of the solvent did not affect $(\alpha_1-\alpha_2)$. Any change of $(\alpha_1-\alpha_2)$ was due to steric interactions between the side groups of the I mol., depending on the solvent. Assuming planar cis and trans configuration of the side group, a difference in polarizabilities of the monomeric I unit was calcd. Solvents with aromatic rings caused lower steric interaction between side groups in I. The temp. dependence of $(\alpha_1-\alpha_2)$ confirmed this conclusion. The solvents xylene, toluene, C_6H_6, PhCl, CCl_4, $CHCl_3$, $C_2H_2Br_4$, cyclohexanone, and $C_2H_4Cl_2$ were used.

V. Kratochvilova

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Solubilization of polyvinyl acetate. Naoya and Shuji Saito (Univ. Osaka). *Kolloid-Z.* 128, 154–8(1952).—In order to elucidate the mol. mechanism, the behavior of samples of different mol. wts. in solns. of Na dodecyl sulfate was examd. To bulk polymerized systems of degree of polymerization (D.P.) 560, 1500, and 4350 dissolved in acetone, H_2O was added gradually, and the acetone removed by evapn. and dialysis. The av. D.P. of this sol. was obtained from viscosity measurements in acetone solns. by using equations for the extrapolation of η_{sp} to zero concn. and calcn. of the D.P. given in the literature. The process of solubilization was followed by measurement of the viscosity in the polymer-soap soln. system relative to that of the soap soln. The results are exhibited in tables and graphs as functions of polymer (c_p) and soap (c_s) concns. With c_s of not more than 3%, even the systems of highest D.P. can be solubilized for all c_p-values used (less than 0.5%). Because of the size of the polymer mol., these facts exclude the customary picture of a soap micelle into which the solubilized mol. penetrates. With increasing D.P. the necessary amt. of soap increases. It varies from 0.7 soap mols. per monomer unit for the lowest to 2 for the highest D.P. Although, no final-conclusion can be reached, the following possibilities are suggested. First, there may be a polyelectrolyte mechanism. The anions of the soap are selectively adsorbed on polar sites of the polymer. The resulting electrostatic repulsions extend and solubilize the coiled mols. With increasing c_s, the presence of charged micelles again leads to coiling of the chains. This could explain the decrease of η_{sp}/c_p observed for high c_s similarly as in the case of polyelectrolytes. Alternatively, the adsorption may transform the polymer effectively into a polysoap which solubilizes itself. A second possibility is a cosolvency effect, that is, solubilization in a mixt. of two non-solvents. This is suggested by the fact that the polymer is sol. in the soap soln., whereas it is not sol. in H_2O nor in hydrocarbons.

Robert Simha

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Crystal structure of polyvinyl alcohol. Ichiro Sakurada, Keiroku Fuchino, and Noboru Okada (Kyoto Univ.). *Bull. Inst. Chem. Research, Kyoto Univ.* 23, 78–9(1950)(in English).—For explanation of the x-ray diffraction of polyvinyl alc. it is not necessary to assume a stereochem. irregularity as proposed by Bunn (*C.A.* 41, 2956*g*; 43, 16*b*). A particular irregular arrangement of mols. with OH groups alternately placed in left- and right-hand positions accounts in a satisfactory way for the diffraction pattern. It is only necessary to assume that the 2nd mol. chain in a unit cell is displaced by the 1st 1.26 A. (a length of a C atom in the zigzag chain) in the direction of fiber axis randomly upward and downward. Both displacements may occur with the same probability. Although atomic positions given by Bunn fit also for this arrangement, the following parameters give better agreement with the observed intensities: C(of CH_2) at 0.243*a*, 0.250*b*, 0.065*c*; C(of CH) at 0.293*a*, 0.750*b*, 0.217*c*; half of the O atom at 0.166*a*, 0.750*b*, 0.420*c*, and the other half at 0.466*a*, 0.750*b*, 0.480*c*. Dimensions of the unit cell are a = 7.83 A., b = 2.52 A., c = 5.53 A., β = 87. S. Kitaoka

X-ray studies on the reaction between polyvinyl alcohol and Congo red. Noboru Okada and Ichirô Sakurada (Kyoto Univ.). *Bull. Inst. Chem. Research, Kyoto Univ.* 26, 95(1951).—Polyvinyl alc. is pptd. from its aq. soln. with Congo red. In a 1.5% Congo red soln. gelatination occurred while in 3% soln. syneresis took place. Changes in X-ray diagrams from this concn. showed the strongest interference corresponding to the spacing of 4.21 A. Immersion of polyvinyl alc. films or filaments in Congo red soln. gave similar results; they became plastic and could be drawn to several times their initial length. These products showed 3 new interferences on the meridian, the spacings being 13.25, 8.80, and 6.54 A., resp. The fiber period calcd. from these spacings was 26.4 A. These spacings were assumed to belong to a complex between polyvinyl alc. and Congo red. A provisional estn. of the monoclinic unit cell of the complex was: a = 8.20 A., b = 26.4 A., c = 4.57 A., and β = 81 31′. S. Kitaoka

X-ray studies on partially acetylated polyvinyl alcohol. Kiyoshi Hirabayashi and Fumihide Fujimoto (Kyoto Univ.). *Bull. Inst. Chem. Research, Kyoto Univ.* 27, 65 (1951).—Films of 2 series of partially acetylated polyvinyl alc. (*C.A.* 46, 4272*a*) were studied with x-rays. As long as the degree of acetylation was the same there was no difference between them. At the beginning of acetylation a slight increase of the spacing A_1 (an inner weaker interference of polyvinyl alc., d = 7.33 A.) was observed. A_1 of polyvinyl alc. faded out at the degree of acetylation of about 10 mole %, while an interference corresponding nearly to R_1 interference of polyvinyl acetate appeared at about 45 mole %. The spacing of this interference gradually increased from 6.2 A. to attain finally the characteristic value of the acetate (d = 6.70–7.00 A.). The spacing of A_4 of polyvinyl alc. (the outer stronger interference) gradually decreased and finally attained the characteristic value of R_2 of the acetate (d = 3.94–4.00 A.) after passing through a max. at about 10 mole % (d = 4.65 A.). The results on the films prepd. from partially acetylated polyvinyl alc. and drawn at elevated temp. were essentially the same as those of nondrawn films. S. Kitaoka

X-ray studies on the reaction between polyvinyl alcohol and boric acid. Noboru Okada and Ichiro Sakurada (Kyoto Univ.). *Bull. Inst. Chem. Research, Kyoto Univ.* 26, 94 (1951).—A small amt. of boric acid reduces enormously the effect of heat-treatment of polyvinyl alc. fibers. This disturbing effect was studied with x-rays. In aq. soln. contg. above 3% boric acid polyvinyl alc. was not sol. and pptn. occurred. The ppt. showed no characteristic cryst. diagram of polyvinyl alc. even after complete drying or heat-treatment. With increasing concn. of boric acid, all interference rings became broader, A_1 (d = 7.98 A.) of polyvinyl alc. disappeared, and intensity of A_3 decreased while that of A_4 increased. Spacing of A_3 decreased from 4.52 to 4.26 A. while that of A_4 increased from 3.79 to 4.11 A. With 10% boric acid the ppt. gave amorphous x-ray diagram. When the films or fibers of polyvinyl alc. which had been heat treated were immersed in boric acid soln. (above 7.5%), the cryst. interferences disappeared and only amorphous ones remained. It was concluded that polyvinyl alc. reacts b as a polyalc. with boric acid to form a complex, and random cross linkages are formed between fiber mols.; this disturbs crystn. of polyvinyl alc. and reduces the effects of heat-treatment.

S. Kitaoka

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Absorption, passage, and evaporation of moisture. III. Relation between the permeability and absorption of moisture. Bunshichi Takeda. *Rept. Inst. Sci. and Technol., Univ. Tokyo* 6, 235–42(1952); cf. *C.A.* 46, 63[illegible].—Under various pressures of water vapor, both the moisture permeability and adsorption of org. films, such as bladder membrane, cellophane, cellulose acetate, polyvinyl alc., and polyvinyl acetate, were measured. Moisture permeability increases with increasing pressure of water vapor, especially in polyvinyl alc. At the same time the moisture absorption increases with vapor pressure. The increasing absorption may reduce the intermol. forces and diminish the resistance to the diffusion of water mols. IV. A relation between the moisture permeability and the thickness of the film. *Ibid.* 243–6.—Assuming that Henry's law does not always hold at the surface of the film, a relation between the moisture permeability and the thickness of the film is derived. The parameters in this formula express the characteristics of the films. Y. Morino

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Fractionation of high polymers by the solution method. O. Fuchs (Hochst Farbwerke, Frankfurt a./Main, Ger.). *Makromol. Chem.* 7, 259–70(1952)(English summary).—The previously described method (cf. *C.A.* 46, 2*d*) of fractionation by dissolving a high-polymer film was modified by using a vessel with a sintered glass disk instead of an Erlenmeyer flask. This prevented mech. entrainment of detached pieces of film during decanting, and made possible the detn. of abs. distribution curves. The validity of the method was proved: (1) by comparing the distribution curves of polyvinyl alc. and polyvinyl acetate of equal mol. wt. distribution, (2) by comparison with fractionation by pptn., (3) by fractionating two polyvinyl acetate fractions (mol. wt. 35,000 and 170,000) and their 1:1 mixt., and (4) by fractionation of the same polyvinyl acetate fraction with different pairs of solvents (MeOAc-petr. ether, MeOH-H_2O, MeOH-petr. ether). Agreement was good in all cases, except with the MeOH-petr. ether solvent pair, which formed 2 liquid layers even with small amts. of polymer. A new method for detg. the mol. wt. of polyvinyl alc. was devised, in which the intrinsic viscosity was calibrated against that of the polyvinyl acetate prepd. from it.

H. Newcombe

Note on the determination of the degree of polymerization of polyvinyl alcohol from osmotic measurements. O. Fuchs (Farbwerke Höchst, Frankfurt a./Main, Ger.). *Makromol. Chem.* 7, 271–3(1952)(English summary).—It is shown that the mol. wt. detn. of polyvinyl alc. by calibration against the corresponding polyvinyl acetate (cf. preceding abstr.) agrees with the earlier osmotic detns. of Staudinger and Warth (cf. *C.A.* 35, 2321^4), which had been questioned. H. Newcombe

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High-molecular electrolytes. III. Specific volume of the system lyophilic molecular colloid-water. Tetsuro Seiyama (Kyushu Univ., Fukuoka). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 53, 15–16(1950); cf. *C.A.* 47, 1590*g*.—The sp. vols. of sol. starch, polyvinyl alc., gelatin and Na alginate were detd. by the pycnometric method. There is no break in the sp. vol.-concn. curves ranging from sol to gel states. T. Katsurai

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Crystallinity of polyvinyl alcohol. I. Fractional extraction of heated polyvinyl alcohol. Saburo Okajima and Naomichi Takahashi (Yamagata Univ., Yonezawa). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 54, 334–6(1951).—Polyvinyl alc. powder was heated at various temps. in open as well as closed tubes and the accompanying changes in swelling and soly. have been studied. Possibility of fractional soln. has been shown by the temp. regulation of extg. water. T. Katsurai

A quantitative method for comparing "Perspex" polishes. W. M. Bielak and J. Savage. *Selected Govt. Research Repts. (Gt. Brit.)* Vol. 1, *Plastics, Rept.* No. 18, 365–82(1952).—Polymethylmethacrylate sheet was abraded by rubbing gently on a glass surface covered with 150-mesh Carborundum powder and water. The light scattering of the surface was taken as 100%. The surface was then polished by using a polishing machine with a cloth coated with the polish. The polishing-cloth disk rotated at 50 r.p.m. and the holder at 35 r.p.m. in the opposite direction. The efficiency of several polishes (not identified) in removing abrasion was measured by light scattering varied as did also the tendency of the polishes to cause light-scattering increase from new surfaces free from previous defects. H. L. Williams

4123

Thermosetting polyvinyl alcohol systems. C. F. Brown (Bethany Coll., Bethany, W.Va.). *Rubber Age* (N.Y.) 72, 211–14(1952).—The polyvinyl alc. resin was covered with alc. and the plasticizer overnight, after which the alc. was removed and the masterbatch compounded and cured. A mixt. of glycerol and triethylene glycol gave the best results, triethanolamine and Carbowax 1500 gave good results, 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol, fair results, and sorbitol, poor results. Eight parts of chloranil gave optimal cure, and optimal cure time was 15 min. at 287°F. Tensile strength increased 50 lb./sq. in. for each °C. decrease in test temp. Tensile strength was doubled by inclusion of 40 parts of reinforcing C black. Phenyl-2-naphthylamine (I) added to absorb liberated HCl yielded optimal results when 5 parts was present. An optimal formula composed of resin (50% hydrolyzed) 100, glycerol 33.3, triethylene glycol 33.3, reinforcing black 25, Pb chromate 16, I 5, and chloranil 8 gave a tensile strength of about 1200 lb./sq. in. after curing 30 min. at 287°F. Increased hydroxyl content of the resin results in difficulty in handling. H. L. Williams

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Diffusion of high polymers. I. Average diffusion constant of polydisperse system. Masao Hosono and Ichiro Sakurada (Kyoto Univ.). *Chem. High Polymers* (Japan) **8**, 361-74(1951).—Math. The diffusion const., estd. from the initial stage of diffusion at the interface of solvent and soln., is appropriate as the av. diffusion const. of a polydisperse system. **II. The method for the determination of the distribution of polydisperse system by means of diffusion experiment.** *Ibid.* 374-81.—The analysis of diffusion curves, including the case in which diffusion const. varies with concn., is discussed. T. Katsurai

Viscosity of dilute solution of polyvinyl chloride. I. Dependence of viscosity on the heating temperature. Toshiaki Kuroiwa and Kazuo Kawahara (Osaka Univ.). *J. Chem. Soc. Japan*, Pure Chem. Sect. **73**, 563-5(1952).—The effect of the heating temp. on the viscosity of the resulting solns. of polyvinyl chloride was studied for the solvents (1) tetrahydrofuran, cyclohexanone, (2) nitrobenzene, mesityl oxide, MeCOEt, (3) chlorobenzene, dichloroethane, dioxane, and tetrachloroethane. In (1) the solns. show const. viscosity independent of the heating temp., in (2) the viscosity becomes const., for the heating temp. higher than 70°, and in (3) the viscosity remains const. for the heating temp. above 80°, in this case polyvinyl chloride remains undissolved at the temp. below 55°. The results are in line with the dissolving capacity of the solvents. **II. Influence of concentration and temperature on viscosity.** *Ibid.* 565-8.—Viscosity was detd. at 20, 32, and 44° for tetrahydrofuran, and at 20, 40, and 60° for the other 8 solvents. In all cases the viscosity increases linearly with concn. at lower concn. range. The intrinsic viscosity decreases with the rise of temp. in the solvents (1) and (2). In (3), with the rise of temp. intrinsic viscosity increases uniformly in chlorobenzene; max. appear in dichloroethane and dioxane, and min. in tetrachloroethane. T. Katsurai

An evaluation of osmotic-pressure measurements using polyvinyl acetate systems. L. A. McLeod and R. McIntosh (Natl. Research Labs., Ottawa). *Can. J. Chem.* **29**, 1104-14(1951).—Detns. were made of the osmotic pressure of polyvinyl acetate in 5 solvents. The mol. wt. of the polymer was calcd. from these values and was independent of the solvent. The mol. wt. calcd. from a least-squares fit of the data gave an uncertainty of 4%. The theoretical Flory-Huggins equation of 1942 (F., *C.A.* **36**, 1229^3; H., *C.A.* **36**, 3725^2) and the Flory equation of 1949 (*C.A.* **44**, 4752*e*) gave uncertainties of about 10%. J. W. W.

Treatment of osmotic-pressure data. W. R. Krigbaum and P. J. Flory (Cornell Univ., Ithaca, N.Y.). *J. Polymer Sci.* **9**, 503-8(1952).—A critical discussion shows that the equation $\pi/c = (\pi/c)_0(1 + \Gamma_2 c + \Gamma_3 c^2)$ can be better fitted to osmotic pressure-concn. curves if Γ_3 is related semitheoretically to Γ_2, as Fox, Flory, and Bueche (cf. *C.A.* **45**, 6015*g*) have done, than if 3 independent coeffs. are used, as recommended by McLeod and McIntosh (cf. preceding abstr.) both from the standpoint of convenience and accuracy of the values of the intercept and the initial slope obtained. Replacement of the hard-sphere approximation for Γ_3 by a smaller value is indicated. Even then neglect of higher terms restricts the concn. range to less than that used by McLeod and McIntosh. If accurate values of Γ_2 are desired, the procedure of Stockmayer and Casassa (*C.A.* **47**, 4171*h*) is recommended. This requires a knowledge of the degree of coiling of the polymer mol., which can be obtained from viscosity data.

H. Newcombe

Degradation reaction of polyvinyl acetate in acetic acid solution. Masakazu Matsumoto (Kurashiki Rayon Co.). *Chem. High Polymers* (Japan) **8**, 391-5(1951).—The viscosity of an AcOH soln. of polyvinyl acetate decreases, without sapon., when a small amt. of H_2SO_4 is added. Activation energy of degradation, 18 kcal./mol. is obtained by considering that the viscosity lowering is due to the degradation of the combination of secondary polymerization of polyvinyl acetate. Insol. polyvinyl acetate is made sol. by the addn. of AcOH and H_2SO_4. T. Katsurai

The refraction of homologous polystyrenes. Kurt Ueberreiter and Gerhard Kanig (Kaiser-Wilhelm Inst. Phys. Chem. Elektrochem., Berlin-Dahlem). ***Kolloid-Z.*** **129**, 132-7(1952); cf. *C.A.* **46**, 6903*h*.—Six of the 18 purified polystyrene fractions previously described were used to det. *n* as a function of temp. over the range 20-200°. The sp

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Dichroic studies on the plastic deformation of the polyvinyl alcohol fiber. I. Preparation of isotropic fiber by spinning the molten polyvinyl alcohol. Saburo Okajima and Yasuji Kobayashi (Yamagata Univ., Yonezawa). *J. Chem. Soc. Japan*, Ind. Chem. Sect. **54**, 794-6(1951).—In order to carry out dichroic research on polyvinyl alc. filaments the conditions for spinning isotropic filaments were studied. Polyvinyl alc. powder was moistened, pressed into a hard-glass tube, heated to a molten state at 140°, and extruded in air through a nozzle under a pressure of 4 atm. The proper water contents for smooth spinning were 53.0 ± 0.5 and 65.5 ± 0.5% for the two samples whose degrees of polymerization were 1140 and 1270, resp. The filament obtained is lustrous and of circular cross section. T. Katsurai

9662

High-polymer solutions. I. Osmometer. Kinzo Ishikawa and Toru Kawai (Tokyo Inst. Technol.). *J. Chem. Soc. Japan*, Ind. Chem. Sect. **55**, 14-16(1952).—Two osmometers, a simple glass-cell osmometer of the Gee type (*C.A.* **35**, 2393^7) and a small stainless steel osmometer of the Schulz type (*C.A.* **30**, 6621^3), were constructed, and their working conditions are described. The osmotic pressure and viscosity of polyvinyl acetate subjected to the action of ultrasonics were detd. in MeOH soln. by means of the Gee-type osmometer and Ostwald's viscometer, resp., and the av. degrees of polymerization were compared. It was observed that under long treatments with ultrasonics, the viscosity av. mol. wt. approaches the no. av. mol. wt. showing that chain polymers are cut into uniform length by means of ultrasonics. T. Katsurai

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Polyvinyl alcohol as indicator in iodometry. Samuel A. Miller and Arthur Bracken (Brit. Oxygen Co., London). *J. Chem. Soc.* 1951, 1933.—Only completely deacetylated polyvinyl alc. gives a blue color with I. Polyvinyl alc. contg. 10% or more of residual OAc groups gives a crimson color; this is most sensitive at 20% residual OAc. A 1% aq. soln. of such a prepn. can be used as an indicator in I titrations. It is more stable and more sensitive than starch.
T. H. Dunkelberger

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Viscosities of concentrated polyvinyl acetate solutions in various solvents. John D. Ferry, Edward L. Foster, Geo. V. Browning, and W. M. Sawyer (Univ. of Wisconsin, Madison). *J. Colloid Sci.* 6, 377-88(1951); cf. *C.A.* 44, 8200*h*.—The viscosity of concd. solns. of polyvinyl acetates of 3 different mol. wts. (range: 62,000–840,000) in 1,2,3-trichloropropane, methyl isobutyl ketone, methyl ethyl ketone, iso-Pr_2CO, and cyclohexanone was detd. at 15–35° by the capillary and falling-ball methods. Relative η at any given vol.-concn. (C_v) was approx. the same for any solvent. Log η approached but did not equal a linear function of either (wt.-concn.)$^{1/2}$ or $(C_v)^{1/2}$. Log η was a linear function of $1/T$ over the temp. range studied. The calcd. heat of activation increased slightly with mol. wt. and approx. linearly with C_v. A nearly const. value of 10 (cc./g.)$^{1/2}$ was observed for the function $d(\log \eta)/d(C_v)^{1/2}$, and the same approx. value was observed for literature data given for other polymers and solvents. The function increased with mol. wt. but was independent of the chem. nature of either polymer or solvent.
H. K. L.

Effect of adsorption on measurements of viscosities of very dilute polymer solutions. Melvin Cutler and George E. Kimball (Columbia Univ.). *J. Polymer Sci.* 7, 445–7 (1951).—Sp. viscosities of very dil. polymer solns. were detd. in a differential viscometer described by Cox and Wolfenden (cf. *C.A.* 28, 5739^6), with an error of 1% for values as small as 4×10^{-3}. Each soln. was prepd. in the viscometer by adding a small amt. of concd. soln. to the previous soln., mixing, and withdrawing the same amt. of the mixed soln. The systems used were: polyvinyl alc. in water, polyethylene oxide in water, polystyrene in C_6H_6, polyvinyl acetate in C_6H_6, and polyacrylic acid solns. of various degrees of neutralization in water, in the presence of NaCl in various concns. A plot of the reduced viscosity against concn. showed a definite decrease at very low concns., which recent studies (cf. S. Rothman, R. Simha, and S. G. Weissberg, *C.A.* 44, 4311*a*) had failed to find. At these very low concns., a straight line obeying the equation $\eta_{sp} = A(c - b)$ was obtained. The shift from the ideal straight line through the origin suggested the hypothesis that some of the polymer had been adsorbed on the viscometer. This was confirmed by measurements on polyacrylic acid solns. in a viscometer that had previously been rinsed with dil. Na_3PO_4. The curves shifted to the left, because the neg. charged polymer mols. were repelled by the PO_4^{-3} already adsorbed.
H. Newcombe

A kinetic basis for polymer precipitation and the selective average. D. R. Morey (Eastman Kodak Co., Rochester, N.Y.). *J. Colloid Sci.* 6, 406–15(1951).—The kinetics of polymer fractionation and pptn. are analyzed in terms of a special av. mol. wt. (M_γ) defined to correspond to the av. value in pptn.: $M_\gamma = (\Sigma N_i M_i^n e^{\alpha P_\gamma \log M_i}/\Sigma N_i e^{\alpha P_\gamma \log M_i})^{1/n}$, where N_i is the no. of mols. of the i species/unit vol., M_i is the mol. wt. of the i species, α is a kinetic parameter, P is the percentage of precipitant liquid, and n is a const. with a value of 4 in the early stages and 3 in the later stages of pptn. Calcns. are made for 7 different polymers for which fractionation data have been published.
H. K. L.

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The application of precipitation-turbidity analysis to polyvinyl acetates. D. R. Morey, E. W. Taylor, and G. P. Waugh (Eastman Kodak Co., Rochester, N.Y.). *J. Colloid Sci.* 6, 470–80(1951); cf. *C.A.* 41, 5363*c*.—The turbidity curves of continuously-pptg. polymer solns. were observed for polyvinyl acetates made by soln. polymerization with Ac_2O_2 or $K_2S_2O_8$ catalysts, or by bead polymerization with Bz_2O_2 catalyst. Me_2CO was used as solvent and H_2O as precipitant. All polymers exhibited a very wide range of mol. wts. The expected linear relation between log (H_2O concn. at pptn.) and log (crit. polymer concn.) was observed over the concn. range 0.01–1 g. polymer/l. soln., but not at the lower concns. that were necessary to ppt. the very short-chain fractions. Polymer made in the presence of $K_2S_2O_8$ and H_2O required greater amts. of H_2O for pptn., owing to the slight hydrolysis that occurred during polymerization.
H. K. Livingston

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Coagulation of polyvinyl alcohol solutions with binary mixtures of salts. Tetsuro Osugi and Keiji Hashimoto. *Chem. High Polymers* 5, 193–8(1948).—Additivity of coagulation power by binary mixts. of salts, such as Na_2SO_4-$ZnSO_4$ and Na_2SO_4-$MgSO_4$, is found for pure aq. solns. of polyvinyl alc., but ion antagonism is observed for solns. contg. a considerable amt. of acetone or alc.
I. S.

The air oxidation of polyvinyl alcohol in aqueous alkaline solution. Yasuo Sone. *Chem. High Polymers* 5, 54–6 (1948).—The oxidative degradation of polyvinyl alc. in aq. NaOH was studied viscometrically.
S. Okamura

Determination of molecular weight of polyvinyl alcohol by the osmotic method. Akio Nakajima and Katsumasa Furutate. *Chem. High Polymers* 6, 460–3(1949).—Polyvinyl alc. was obtained by sapon. of com. polyvinyl acetate and fractionated. Six fractions were used for the investigation. Osmotic pressure and intrisic viscosity $[\eta]$ of the aq. soln. were measured at 30°. Between $[\eta]$ and the degree of polymerization P the following relation exists: $[\eta] = 7.50 \times 10^{-3}P^{0.64}$.
I. Sakurada

Acetalization limit of polyvinyl alcohol. Kaishi Noma, Tempei Ko, and Takahiro Tsuneda. *Chem. High Polymers* 6, 439–43(1949).—Polyvinyl alc. (I) was acetalized with diethyl chloroacetal in $C_2H_4Cl_2$ and the process repeated 3 times. The degree of acetalization (calcd. from the Cl content) was 81.5, 82.6, 85.6, and 85.8%, resp. Thus, there is a limiting degree of acetalization of I at 86%. This value agrees with Flory's theoretical value of 86.5%. In the acetalization of I with *o*-chlorobenzaldehyde or BzH, the degrees of acetalization of the products did not exceed 86%. Cf. *C.A.* 45, 2710*h*.
I. Sakurada

Depolymerization of polyvinyl acetate during deacetylation. I. Depolymerization during deacetylation in methanol solution with caustic soda. Tetsuro Osugi. *Chem. High Polymers* 5, 123–9(1948).—During deacetylation partially deacetylated samples were removed and reacetylated with Ac_2O and C_5H_5N to polyvinyl acetate. The intrinsic viscosity of the reacetylated samples was measured in acetone and the degree of polymerization calcd. from the known relation between intrinsic viscosity and mol. wt. The depolymerization takes place continuously and simultaneously with deacetylation. A discussion on the mol. structure of polyvinyl acetate [illegible]
I. S.

Osmotic and viscometric behavior of polyvinyl acetate in good and poor solvents. Akio Nakajima. *Chem. High Polymers* 6, 4[illegible]1–9(1949).—Com. polyvinyl acetate was fractionated into 9 fractions, and 5 fractions were used for the investigation. Intrinsic viscosity $[\eta]$ was detd. in C_6H_6 and acetone (good solvents) and in C_6H_6-petr. ether (7:3) (poor solvent). Osmotic pressure was measured in pure C_6H_6 and C_6H_6-petr. ether mixt. at 30°. The ratio of $[\eta]$ for the poor solvent to that for the good solvent is < 1 and decreases with increasing mol. wt. The limiting value of reduced osmotic pressure is the same for the both kinds of solvents, but the slope of the reduced osmotic pressure-

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concn. curve is different. The following relations were found between $[\eta]$ and the degree of polymerization P: $[\eta] = 7.94 \times 10^{-3}P^{0.62}$ in acetone, $[\eta] = 8.91 \times 10^{-3}P^{0.41}$ in C_6H_6. I. Sakurada

Thermal decomposition of polyvinyl acetate and polyvinyl alcohol. Kaishi Noma. *Chem. High Polymers* 5, 19[illegible]–2(1948).—When dry distd. at 250–300° polyvinyl acetate yielded only AcOH (72% of theory). When dry distd. at 250–340° polyvinyl alc. (1 mole) gave water 0.64, crotonaldehyde 0.16, and AcH 0.24 mole. It was concluded that in the thermal decompn. of these polymers the scission occurred first at the side chains and then in the main chain. I. Sakurada

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Acetylation of polyvinyl alcohol. Koji Kuroyanagi and Ichiro Sakurada. *Chem. High Polymers* (Japan) 6, 419–22 (1949).—Polyvinyl alc. was acetylated in aq. AcOH with concd. HCl at 40°. The course of the reaction did not follow the equation for a unimol. reaction or the equation for a reversible unimol. reaction. Reaction consts. decrease with progress of the reaction. K. Noma

Electrical conductivity of polyvinyl alcohol. Masao Hosono, Masakatsu Taniguchi, and Ichiro Sakurada. *Chem. High Polymers* 5, 183–9(1948).—The effects of heat treatment, water content, and various salts on the insulating value of polyvinyl alc. were measured. S. Okamura

Phenolic based adhesives. Orlando Orlandi. *Ind. vernice* (Milan) 5, 161–2(1951).—Phenol and CH_2O (used as 30–8% soln. of known acid no.) are stirred and refluxed in mol. proportions of 1 to 1.1–2.0 with alk. catalysts (NaOH, KOH, carbonates) at 60° for 0.5–3 hrs.; the product is partially dehydrated under reduced pressure, and is neutralized with weak acids (lactic) or with a mixt. of HCl and EtOH. Glycerol or glycol is used to plasticize the resins which are sol. in alc. or other org. solvents. Their properties and application are discussed. Henry A. Goldsmith

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The thermodynamics of high-polymer solutions. VI. Thermodynamics of the system polyisobutylene–cyclohexane. L. Der Minassian and M. Magat (Faculté sci., Paris). *J. chim. phys.* 48, 574–8(1951); cf. *C.A.* 44, 2332*h*.—Vapor pressures of solns. of a polyisobutylene fraction and cyclohexane were detd. in the app. of Gee and Treloar (cf. *C.A.* 36, 6371⁴), using glycerol instead of Hg in the manometer. The temp. range was 15–50°, the concn. range 30–80% of polymer, and the precision 1%. Partial molar free energy, entropy, and heat of mixing were calcd. The Flory-Huggins equation was valid, but only by a compensation of errors in the coördination no. and the heat of mixing. H. Newcombe

6426

Emulsion polymerization of vinyl acetate. I. The course of the progress of emulsion polymerization. Masaichi Matsumoto, Junji Ukida, and Hiroshi Iwasaki (Kurashiki Reyon Co., Kurashiki). *Chem. High Polymers* (Japan) 7, 390–6(1950).—The course of the progress of the emulsion polymerization of vinyl acetate can be divided into two stages. The reaction takes place in the first stage in water phase and in the second stage in polymer particles. An enormous rise of degree of polymerization of polyvinyl acetate takes place in the second stage, but the degree of polymerization of polyvinyl alcs. prepd. from these acetates is not higher than that of alcs. obtained from acetates which are formed in the first stage of polymerization. II. Molecular weight distribution of polyvinyl alcohol and acetate. Masaichi Matsumoto and Hiroshi [illegible]. [illegible]–401.—Emulsion polymer is very heterogeneous and the max. of the distribution curve was found at a degree of polymerization of about 3000, while its wt. av. degree of polymerization was about 13,600. Distribution curve of polyvinyl alc. showed two max. S. Okamura

6460

Gel elasticity. I. Nishio Hirai (Okayama Univ.). *J. Chem. Soc. Japan*, Pure Chem. Sect., 72, 8[illegible]7–[illegible] (1951).—The elasticity of agar, gelatin, potato starch, and polyvinyl alc. was detd. by statistical methods and the results are discussed in relation to gel structure. T. Katsurai

The temperature dependence of the solubility of solid

8892

Molecular weight distribution in (vinyl-type) polymers. E. J. Arlman (Koninklijke Shell-Lab., Amsterdam). *Chem. Weekblad* 48, 237–42(1952).—Expressions are reviewed for the size distribution which are based on the customary free-radical mechanism of the polymerization reaction, namely initiation, propagation, transfer and termination steps, a steady state, and low degrees of conversion. Detailed graphs of no., wt., differential curves, and integral distribution curves are presented, and the relations between no. and wt. av. mol. wt. discussed. The differences in these quantities, when termination consists of a disproportionation and combination of radicals, resp., are pointed out. They can be utilized to establish the mechanism of termination which is operative in a particular case. The inherent difficulties of an analysis of high-conversion polymers are mentioned. Robert Simha

10695

Treating polyvinyl alcohol. Société auxiliare de l'institut française du caoutchouc. Fr. [illegible]73,235, Feb. 8, 1951. Polyvinyl alc. is hardened by treating it with a polybasic acid. Polyvinyl alc. is malaxated with 10% maleic acid at 70–80° and pressed for 2 hrs. at 143° to give a hard product insol. in hot water. Polyvinyl butyral contg. 10% OH groups is mixed with a plasticizer and then malaxated with maleic acid and pressed as before. Maleic anhydride or phthalic anhydride may be used. L. A. Manning

11763

A study of plasticizer migration in vinyl compounds. James K. [illegible] (Goodall-Sanford, Inc., Reading, Mass.). *India Rubber World* 126, 646–9(1952).—A new test, said to be the first *true migration test*, is described. Weighed test-specimens are buried in a fine highly absorbent powder under moderate pressure to assure intimate contact. The powder is changed periodically and the losses of wt. of the test-specimens are detd. Suitable equipment is described. Samples with rough surfaces can be tested accurately in 1 day. Migration increases greatly with rise of temp., so temp. control is important. A temp. of 30° is recommended.

Of many powders studied, only 2 measured true migration without any disturbing influence, viz., Linde pptd. silica and hydrated silica (100-mesh analytic grade). Representative data on the tendency of some important com. plasticizers, as judged by this test, are given. Contrary to widespread belief, some polymeric plasticizers migrate. Before the test can be finally standardized, the influence of pressure, temp., moisture content of the powder, and type of powder should be studied further. C. C. Davis

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1815

Polyvinyl alcohol compositions containing corrosion inhibitor. Charles A. Porter (to Resistoflex Corp.). U.S. 2,531,700, Nov. 28, 1950. The addn. of 2-aminothiazole (I) inhibits the corrosive action of polyvinyl alc. compns. on metals. For example, 10 parts I added to a compn. composed of polyvinyl alc. 100, water 40, formamide 10, and ethanolamine.HCl 40 parts prevented the corrosion of brass. The material was still effective when used in a similar compn. contg. 4 parts NH_4Cl. H. L. Williams

2710

Acetalization of polyvinyl alcohol with palmitic aldehyde. Kaishi Noma and Takeo Sone. *Chem. High Polymers* (Japan) 4, 50–2(1947).—Polyvinyl alc. is acetalized with palmitic aldehyde and HCl, and the max. degree of acetalization (calcd. from the yield) is about 82%. This product is insol. in the usual org. solvents, but swells in benzene, CCl_4, $CHCl_3$, and C_5H_5N. The softening point is 20–30° and the sp. gr. 0.94. S. Okamura

Stearic acid and benzoic acid ester of polyvinyl alcohol. Kaishi Noma, Katsuji Nakamura, and Teizo Teramura. *Chem. High Polymers* (Japan) 4, 41–5(1947).—Esterification of polyvinyl alc. (I) with stearoyl chloride or BzCl in

2713

Viscosities of solns. of polyvinyl acetate in acetone-water mixts. (Yoshioka) 2. Diesters of aliphatic acids and thiodiglycol [plasticizing ability] (Colonge) 10. Effect of acetylenic unit on phys. properties of polyesters and polyurethans (Marvel) 10. [Resin-contg.] paint performance on cathodically protected steel (Eickhoff) 9. Cathodic protection in conjunction with paint coatings (Reichard) 9. *Patents:* Rubber plasticizers (Gregory) 30. Esters of β-hydroxycarboxylic acids [plasticizers for resinous materials] (Beears) 10. Hydroxymethyl siloxanes [for prepn. of polyurethan and alkyl-type resins] (Speier) 10. *N*-Methylol maleimide [intermediate for plasticizers] (Tawney) 10. Esters of β-alkoxy-γ-aminocrotonates [plasticizers and softeners] (Van Hook) 10. Butadiene-methylal reaction products [plasticizers] (Dermer) 10.

4094

Treating polyvinyl alcohol. A. Polgar and E. Fiorillo. Fr. 948,775, Aug. 10, 1949. Polyvinyl alc. and acetals are treated, usually in film form, with a mixt. of a solvent for polyvinyl chloride, such as cyclohexanone, chlorobenzene, or tetrahydrofuran, and HCl in water, or in the gaseous form or combined with a weak base, such as diphenylamine. The product has an increased resistance to moisture. The mixt. may be applied in any manner, e.g. by spraying or as a bath, usually for a few (10) min. only, the treatment being followed by drying. L. A. Manning

Laminating polyvinyl alcohol. Gale F. Nadeau and Clemens B. Starck (to Eastman Kodak Co.). U.S. 2,541,478, Feb. 13, 1951. Surfaces of polyvinyl alcohol, either pure or modified by polyvinyl acetate, are laminated by treatment with a 0.5–5% soln. of $Zr(NO_3)_4$. Such bonds resist delamination much better than bonds made with H_2O. Other hardening agents, such as Cr and Al salts, may be used in place of $Zr(NO_3)_4$. Wm. R. Sheridan

5058

Can eucolloids be identified by their solubility? A further
contribution to the analytical chemistry of high polymers.
Kurt Thinius (Magdeburg, Ger.). *Deut. Farben-Z.* 5,
73–81(1951); cf. *C.A.* 45, 1459*f*.—Characteristic solvents,
nonsolvents, nonsolvent pairs mutually activated to act as
d solvents, and pptg. conditions are selected to distinguish
water-sol. eucolloids (gelatin, starch, carboxymethyl-
and methyl-cellulose, polyvinyl alc., polyvinyl Me ether,
and polyvinyl pyrrolidone), cellulose ethers, (ethyl-
celluloses B and BS, propylcellulose, benzylcellulose),
cellulose esters (formate, acetates, tripropionate, aceto-
butyrate, isoheptylate [Cellit IH], stearate [Cellorit], and
nitrocelluloses of different N contents), chlorinated poly-
mers (polyvinyl chloride, chloro-rubber [Pergut], chlorin-
e ated Buna [Bunalit], and some chain polymers (polyamides,
polyurethans). Many of the data are based on earlier
studies (cf. *C.A.* 42, 8520*h*; 43, 1603*d*, 6044*d*). New data
are also presented on the distinction of nitrocellulose from
linters and from wood pulp (the former does not tolerate
addn. of ligroine to its BuOAc soln. in the same conditions in
which the latter does); on distinguishing polymers from
their tolerance towards diluents (cf. Gordijenko and Schenk,
C.A. 42, 7110*d*; 43, 4183*f*); and on distinguishing various
f degrees of substitution of sapond. polyvinyl acetates, nitro-
celluloses, ethylcelluloses, and cellulose acetates.
Henry A. Goldsmith

6444

Dielectric properties of sorbed water. I. Polarization of sorbed water in vinyl polymers. Shigehiko Kurosaki (Central Research Lab. Hitachi Ltd., Tokyo). *J. Chem. Soc. Japan*, Pure Chem. Sect., 71, 522–3(1950).—The change of dielec. const. of powd. vinyl polymers due to the adsorption of moisture was detd. by the beat method. On the assumption that water is dissolved in vinyl polymers, the sp. polarizations of sorbed water are calcd.: in polyvinyl chloride about 30, in polyvinyl alc. 8.6–7.8, in polyvinyl-formal 4.7–6.4. These values are larger than the sp.

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polarization of normal water in nonpolar solvents 3.7; this
fact suggests that the sorbed water is in the state of ioniza-
T. Katsurai
tion sorption.
Dielectric properties of water of crystallization. Kan-
ichi Kamiyoshi and Toshihiko Miyamoto. *Science Repts.*
Research Insts. Tôhoku Univ. Ser. A, 2, 370–9(1950).—The
following values of dielec. consts. were detd.: $CuSO_4.5H_2O$
6.70, $CuSO_4$ 6.70, $Na_2SO_4.10H_2O$ 5.00, Na_2SO_4 7.90, Mg-
$SO_4.7H_2O$ 5.46, $MgSO_4$ 6.67, $SrCl_2.6H_2O$ 8.52, $SrCl_2$
9.19, $BaCl_2.2H_2O$ 9.00, $BaCl_2$ 9.81, $Na_2CO_3.10H_2O$ 5.50,
and Na_2CO_3 7.14. The additivity law of molar polari-
zation held between the water of crystn. and the remain-
der of the compd. The molar polarization per H_2O of
crystn. calcd. by the Clausius-Mosotti equation was in-
variant within 5% for all compds. except $SrCl_2$. The di-
elec. const. of H_2O of crystn. was 3.75, which is nearly the
same value as that of ice, but not that of water. As the
temp. approaches the one at which the water of crystn. is
released, the dielec. const. of the water of crystn. becomes
greater. This transformation begins gradually at fairly low
temp. The temp. coeff. of the dielec. const. of the anhyd.
compds. were all pos. and no special anomalies were ob-
Henry Leidheiser, Jr.
served.

6867

Determination of the concentration of high-polymer solutions. N. Grassie (Univ. Glasgow, Scot.). *J. Polymer Sci.* 6, 643-8(1951).—A mol. still has been constructed, in which polymers can be heated while the vapor pressure of the volatiles evolved is measured with a Pirani gage. Two max. were observed, the first probably due to solvent near the surface of polymer particles, the second, which appeared at the softening point, was probably due to solvent released from within polymer particles. Between 5 and 10% of a polymethylmethacrylate (I) sample consisted of volatile products. Polystyrene (II) and polyvinyl acetate (III) were similarly investigated. In all cases the softening point was well below the decompn. temp. In the case of I, even 93 hrs.' heating in a steam oven did not remove the volatiles, but 30 min. in the still at 100° did. With II about a week in the steam oven would be necessary, but 20 min. in the still at 180° was sufficient. With III, because of its much lower softening point, overnight heating in a steam oven could be used, or 15–30 min. in the still at 170°. H. Newcombe

7374

Osmotic studies on the conversion of polyvinyl acetate to polyvinyl alcohol. Akio Nakajima (Kyoto Univ.). *Chem. High Polymers Japan* 7, 57-63(1950).—An enormous decrease of degree of polymerization is observed in the prepn. of polyvinyl alc. from polyvinyl acetate which has been obtained by mass polymerization. But neither by the conversion of polyvinyl alc. to acetate nor by the conversion of reacetylated alc. to alc. is a change of polymerization degree observed. For the relation between intrinsic viscosity and degree of polymerization, the same equation is applicable both for primary acetate and reacetylated polyvinyl alc. But the reduced osmotic pressure-*vs.*-concn. curves of the two polyvinyl acetates have distinctly different slopes.
I. Sakurada

Swelling of polyvinyl alcohol in water. W. J. Priest (Eastman Kodak Co., Rochester, N.Y.). *J. Polymer Sci.* 6, 699-710(1951).—The swelling and soly. characteristics of polyvinyl alc. and polyvinyl alc.-acetate copolymers in liquid water are studied. Swelling varies in a continuum of metastable states depending on the previous treatment of the polymer. Thus, humidification of the sample will induce a predictable change in swelling. Allen Kent

X-ray studies on the reaction of aldehydes on polyamide. Akira Okada and Keiroku Fuchino (Kyoto Univ.). *Chem. High Polymers Japan* 7, 23-8(1950).—It was found, that intramicellar swelling of polycaproamide takes place when it is immersed at room temp. in aq. solns. of HCHO, AcH, and PrCHO Aldehydes also accelerate crystn. of polyamide.
I. Sakurada

10001

Diffusion of linear polymers. II. Temperature dependence of the diffusion coefficient of vinyl polymers. I. Ya. Slonim and K. V. Chmutov. *Zhur. Fiz. Khim.* 25, 296-304(1951); cf. *C.A.* 45, 4116*i*.—With the app. described earlier (*loc. cit.*), the diffusion coeff. *D*, of vinyl polymers, was measured between 20 and 80°. The systems studied were polystyrene–ethylbenzene (I), polystyrene–Et acetate, polyvinyl acetate–Et acetate, polyvinyl alc.–water, polyisobutene–isooctane. An advantage of the app. used is that it does not limit the choice of solvent or the temp. range. Typical results for I are $D = 1.0, 1.0, 0.85$ $0.4, 0.9, 1.2 \times 10^{-7}$ sq. cm./sec. at 25, 35, 45, 61, 65, 75,° resp. The data at low temp. are reproducible after heat-treatment. The changes responsible for the min. in *D* at about 60° are thus reversible. Minima are also observed for the other systems, although some are less marked. This anomalous temp. of *D* is contrary to Einstein's law and is explained by a change of state of the mols. of solute. Polymerization is excluded; aggregation is improbable. A change of shape of the mols. suggests itself. Indeed the temp. at which *D* is min. is close to the glass temp. for each polymer. This near-equality establishes a bridge between the properties of the polymer in bulk and of its mols. in soln. and militates against the identification of polymer glass transformations with changes of the 2nd kind. The freezing-in is a mol. property assocd. with the appearance of long-range order in the polymer chain. Michel Boudart

0096

The intrinsic electric strength of polyvinyl alcohol and its temperature relation. J. D. L. Ball. *Proc. Inst. Elec. Eng.* (London) 98, Pt. I, 84-6(1951).—The intrinsic elec. strength of polyvinyl alc. films was found to be 15×10^6 v./cm. at −195°, dropping to 2×10^6 v./cm. at 80°. The value given for the elec. strength at −195° was one of the highest measured, a surprising result since the dielec. const. is so high (about 40 at room temp.) and is related to the polar nature of polyvinyl alc. At room temp. the breakdown voltage was proportional to the thickness 10–60 μ. Temp. dependence of such polymers seems to be detd. by the dipoles more than by the phys. structure. Joseph S. Smatko

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Waterproofing polyvinyl alcohol. André Polgar and Enrico Fiorillo. Fr. 937,255, Aug. 12, 1948. Polyvinyl alc. is treated with a mixt. of an esterifying agent, a condensation agent, a catalyst, and a solvent to increase its resistance to moisture. Esterifying agents preferred are acid halides, such as stearoyl or oleoyl chlorides, while as condensation agents tertiary bases, such as pyridine or PhNMe$_2$, are used. The catalysts used are the common type, such as ZnCl$_2$ or Me$_2$SO$_4$, and solvents, such as C$_6$H$_6$, CHCl$_3$, and CCl$_4$, are used. A foil of polyvinyl alc. is steeped in water 2 min., treated with 5% NaOH, dried, treated with a dioxane soln. of 10% benzoylpyridinium chloride and 3% pyridine, washed after 2 hrs. in 70% alc., and dried. Acid anhydrides may replace the acid halides. L. A. Manning

2331

Temperature dependence of the diffusion coefficient of vinyl polymers. K. V. Chmutov and I. Ya. Slonim. *Doklady Akad. Nauk S.S.S.R.* 69, 223-5(1949).—The diffusion coeff. *D* of polyvinyl acetate into AcOEt, and of emulsion polystyrene into PhEt, shows the paradoxical behavior of first decreasing with rising temp., passing through a sharp singular min. (at 37° and 62°, resp.), then increasing with further rising temp. This behavior is reversible. The same phenomenon was observed with bulk polystyrene in PhEt (min. at 85°), polyvinyl acetate in C$_6$H$_6$, and polyvinyl alc. in H$_2$O. For the latter system, *D* first rises to a max. at about 75°, then falls to a min. at about 85–90°. No min. is observed for polyisobutylene in isoöctane. The *D*(*T*) curve with a max. followed by a singular min. and subsequent rise, is at variance with Einstein's equation $D\eta/T = \text{const.}$ This newly discovered anomaly casts doubt on detns. of the mol. wt. of linear polymers from diffusion coeffs., as such detns. are often made at an arbitrarily chosen temp. The anomaly is attributed to changes of rotation of links in the polymer chains. Roughly, the exptl. temp. of the min. corresponds to the temp. of vitrification of the polymer; the absence of an observable min. in the case of polyisobutylene corresponds to its low vitrification temp. (−74°). Of the 2 possible mechanisms of vitrification advanced by Kargin and Slonimskiĭ (*C.A.* 43, 1627*i*), one due to interaction between segments of different mols., the other to an increase of the effective rigidity of the chains, the 2nd mechanism is evidently prevalent in vinyl polymers. N. Thon

2821

Electronographic study of polyvinyl alcohol films. I. G. I. Distler and Z. G. Pinsker (Acad. Sci. U.S.S.R., Moscow). *Zhur. Fiz. Khim.* 23, 1281-91(1949); cf. *C.A.* 44, 897*c*.—Unstretched polyvinyl alc. films possess 4 spacings of 4.54, 2.23, 1.70, and 1.20 A. Comparison with models having various degrees of orientation shows that the films consist of oriented patches differing in dimension and shape. These patches are nuclei for extensive structures formed on stretching. The electrons used had the wave length 0.06 A. The literature data on the spacings of other unstretched films are reviewed and an electronograph of a nylon film is recorded. I. I. Bikerman

4817

Luminescence analysis—a tool in the analysis of high polymers. K. Thinius. *Farbe u. Lack* 56, 3-9(1950).—The luminescence of many "polyplasts" (high polymers) under ultraviolet irradiation was studied for purposes of identification. The luminescence of cellulose and its derivs. was not typical enough to recognize their presence with certainty, but after dyeing them with one or more of certain suitable dyes, luminescence of characteristic colors (or its lack) was obtained by which these compds. could be distinguished. Thus *cotton linters* (bleached or kier-boiled) shone bluish purple undyed, dirty yellow with Brilliant Dianil Green G (I), but did not luminesce with Euchrysin CGHX (II), while *sulfite cellulose* (bleached or unbleached, spruce-beech), faintly blue undyed, shone strongly greenish bluish white with I and yellowish green with II; with Rhodamine 6GD (III), it shone strong yellow to orange yellow, while soda and sulfate cellulose shone a dull red brown. Nitrocelluloses, blue to bluish purple undyed, did not luminesce with I; ester-sol. types shone strongly green with Auramine G (IV), greenish yellow with Flavophosphine 4C (V), while alc.-sol. types shone green with IV and light brown with V. Cellulose acetates and cellulose tripropionate shone a faint blue to bluish purple undyed; after dyeing with III, Cellit M (58% AcOH) and Cellit F (56% AcOH) shone yellowish red to brown, while Cellit L (52% AcOH) shone intensely yellow, and Serikose (44–54% AcOH) orange; with Cotton Brown RN (VI), Cellit F shone bluish pink, Cellit L dark red; Serikose could also be differentiated with IV, Erythrosin C or N (VII), or Thioflavine S (VIII). Cellit T and Cellit TP (triesters) dyed with I shone greenish blue and bluish white with greenish areas, with VII strongly yellow and Bordeaux red, and with VI reddish gray and bluish gray, resp. Cellulose acetobutyrate (Cellit B), bluish undyed, did not luminesce with I, but shone faintly orange with III and faintly pink with VI. Cellulose nitroacetate, bluish undyed, did not luminesce with I, but shone bluish purple with VII or Eosin GGF (IX). Methylcellulose (Tyloses) had yellowish luminescence. Cellulose glycolate (Tylose MGC or AM25) did not luminesce, even when dyed. Ethylcelluloses B and BS (40% EtO) had white luminescence with bluish and yellowish streaks, resp.; dyed with I, they shone strongly bluish white and strongly blue with green streaks, and with Flavophosphin 4C they shone greenish yellow and faintly green, resp. They did not luminesce with II, III, VII, or IX, but shone strongly white with VIII and Rhodulin Yellow 6C (X). Benzylcellulose, yellowish white undyed, behaved essentially like the ethylcelluloses with the dyes mentioned. Luminescence allows distinguishing the polyamides Igamide A and B (strongly bluish white), 6A (bright white), 50 (dull cloudy blue), S5B (dull yellowish white), IC (none), and the polyurethan Igamide U (strongly blue to bluish purple); polyethylene (white) and polyisobutylene (none); polystyrenes L (faintly blue or greenish white), III and IV (strongly bluish purple), and EF (blue with white spots); polyvinyl chlorides Igelite PCU (bluish purple), Vinoflex S8 (white with blue sheen), and polyvinylidene chloride (blue); Igelite MP (dull bluish white); poly-

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chlorostyrene (white areas with blue margin), chlorinated rubber (faintly light blue), and chlorinated Buna (gray); polyvinyl alc. (dull violet), polyvinyl acetate (none or bluish white); the acrylates Acronal I (none), II (greenish), and Plexigum (bluish purple); polyacrylonitrile (dark blue or bluish white); resins from AcH (yellow), butyraldehyde (bluish purple), cyclohexanone (blue to purple); the polyvinyl alkyl ethers Igevin AZ or AD28 (dull yellowish green), DJ (yellow), J20 and A100 (none); I. G. Wax Z (bluish white); Densodrin W (none), and the polyvinyl pyrrolidone Igecoll (bluish white). Various grades of Mowital (N, NF, H, HXF, NA, O-70, and IB70) were made distinguishable by dyeing with I, III, VII, VIII, IX, and X. The dyeings were made with 1 g. of the high polymer and 5 ml. of a 0.01 to 1% dye soln. in alc. or H_2O, followed by washing out the excess. In some cases, the dyed samples differed in daylight. *Ibid.* 55-8.—No significant luminescence was obtained from films of pure hydrocellulose, nitrocellulose, cellulose acetate, or those which contain 25-100% of plasticizer (castor oil, tritolyl phosphate, Palatinol HS, or FK). Impurities introduced with the plasticizer or overheating did cause luminescence. With *Igelit PCU* (a polyvinyl chloride which luminesces), the color of the luminescence varied with the processing; 0.2% of 2-phenylindene, a stabilizer, caused a strongly bluish white luminescence; with phthalates, adipates, fatty acid esters, and Bu_3PO_4 used as plasticizers there was no luminescence, while the products shone brightly with tritolyl or trixylenyl phosphate, Mesamoll H, or Plastomoll TV; extn. of the plasticizers restored the bluish luminescence of Igelit PCU; extd. plasticizers sometimes differed in luminescence from the original, having lost or gained impurities. Among *plasticizers*, aromatic phosphates did, aliphatic phosphates and pure phthalates did not, luminesce. Luminescent were Mollit LS5 (dulling action), Elaol 2,4, and 12 (pale white or green), Plastomoll TB (yellow), Plasticizer MMA (pale green or bright bluish white), Mollit B (dull green), Igamid Plasticizers 4, 5, 7, and 11 (shades of blue or green), castor oil (faint blue or milky greenish gray white); linseed oil, ceresin, paraffin oil, and petroleum jelly also luminesce strongly. Luminescence is not a reliable analytical tool, but has limited applications, e.g. to spot deterioration under ultraviolet light in celluloids; dyes may inhibit such action of light and are therefore not reliable aids. Observation must be made on a nonluminescent glass, porcelain, or paper. H. A. G.

5188

Anisotropy in the so-called amorphous part of polyvinyl alcohol. Caroline H. MacGillavry (Univ. Amsterdam). *Rec. trav. chim.* 69, 509-14(1950)(in English).—The amorphous ring in the x-ray diffraction diagram of polyvinyl alc. fiber is most intense near the equator and weakest in the fiber direction. This fits the fringe-micelle theory of structure but differs from the results of Hermans and Weidinger with cellulose (*C.A.* 42, 7037*f*). W. W.

1950

The kinetics of degradation of macromolecular linear molecules. I. Theoretical equations. I. Sakurada, S. Okamura, and S. Kawasaki (Imperial Univ., Kioto). *J. Soc. Chem. Ind., Japan* 45, Suppl. binding, 415(1942) (in German).—When $n = 1$ in the familiar equation $[\eta] = KP^n$, the viscosity index of degradation m is defined and related to the viscosity av. mol. wt. by the equation $1/m = ([\eta]$ after degradation$)/([\eta]$ before degradation$) = (2/s^2)[s - 1 + (1/e^s)]$, where s is the av. no. of bonds broken in one original linear mol. When $n = 2$, $1/m = (1/s^2)\{6s - 12 + [(12 + 6s)/e^s]\}$. When $n = 0$, $1/m = 1$. When n is fractional, as is usually the case, m can be estd. by interpolating graphically. Experimentally detd. av. values for n are: after-chlorinated polyvinyl chloride in tetrahydrofurane $^1/_2$, polyvinyl chloride in dioxane or tetrahydrofurane $^1/_3$, polyvinyl chloride acetate in Me_2CO $^2/_3$, polyvinyl acetate in Me_2CO $^2/_3$, polyvinyl alc. in H_2O $^1/_2$, polymethylacrylate in Me_2CO $^1/_3$, polymethyl methacrylate in $CHCl_3$ or Me_2CO $^1/_2$, and polystyrene in C_6H_6 1. II. Hydrolysis of cellulose in solution. S. Okamura. *Ibid.* 416.—The velocity of degradation of cellulose in concd. H_2SO_4 and H_3PO_4 follows the law $s/t = kN$, where N is the av. degree of polymerization before degradation. In 65% H_2SO_4 at 18°, $k = 4.71 \times 10^{-4}$; in H_3PO_4, sp. gr. 1.640 at 20°, $k = 0.4 \times 10^{-4}$. III. Oxidative degradation of polyvinyl alcohol. S. Okamura and S. Kawasaki. *Ibid.* 416-17.—The viscosity of polyvinyl alc. in H_2O soln. is reduced by $KMnO_4$ or $K_2Cr_2O_7$ as a 2nd-order reaction, and one active O atom is consumed for each cleavage of a macromol. The data are presented graphically and follow the equations in Part I. IV. Molecular-weight distribution. S. Okamura. *Ibid.* 417.—The wt. fraction m_p of degradation products smaller than P (the degree of polymerization after degradation) is given by $m_p = 1 - \{1 + [1 - (P/N)]aP\}(1/e^{aP})$, where a is the extent of degradation. V. *Ibid.* 417.—Data on nitrocellulose and cellulose acetate support the equation in Part IV. H. B.

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Heat-treatment of polyvinyl alcohol. Ichiro Sakurada and Keiroku Fuchino. *Ibid.* 1077-83.—When polyvinyl alc. was once heated approx. at 200°, it became more resistant to water, especially hot water, by an increase in the intermol. tension due to dehydration by the rising temp. and the consequent constriction of the lattice space, which heightens the crystg. tendency. A minute water content helped this tendency perhaps because some OH radicals in polyvinyl alc. became free to form a new hydrous linkage. IX. **Röntgenographs of polystyrene and polyvinyl acetate at high temperatures.** Keiroku Fuchino, Masaya Tanaka, Sampei Yasui, and Ichiro Sakurada. *Ibid.* 1084-97.—At room temp. both polystyrene and polyvinyl acetate gave 2 liquid interference rings, the inner ring being due to the intermol. interference and the outer to the intramol. interference. Both seemed to be composed of zigzag chains whose axes are arranged in a hexagonal cluster system. As the temp. was raised gradually to 200°, the intramol. interference became weaker and dispersed but the interval remained unchanged, while the intermol. interference was not much weakened but the interval widened. The intermol. interval reached a max. above the softening point, widening at the rate of 1.2 A. per 100°, but after liquefaction widened further only slightly. The softening seems to be the transition from a form liquid to a typical liquid. J. G. Yoshioka

1945

The infrared spectrum of polyvinyl alcohol. Elkan R. Blout and Robert Karplus (Polaroid Corp., Cambridge, Mass.). *J. Am. Chem. Soc* 70, 862-4(1948); cf. *C.A.* 38, 916⁴; 39, 4800⁴.—Because of their possible bearing on mol. structure, data are given for the infrared spectrum of carefully purified polyvinyl alc. Measurements were made on a Perkin-Elmer infrared spectrometer, a nickel-strip bolometer, an a.-c. amplifier, and a potentiometer. The infrared spectra (700 to 4000 cm.$^{-1}$) of dried films of polyvinyl alcs. of various degrees of polymerization are displayed in graphs. Some of the absorption bands are correlated with mol. structure. W. F. Meggers

The microwave spectroscopy of paramagnetic salts; the spectrum of chromic alum. P. R. Weiss (Rutgers Univ., New Brunswick, N.J.). *Phys. Rev.* 73, 470-6 (1948); cf. *C.A.* 42, 824*a*.—Some measurements on the resonance absorption of chrome alum are analyzed for the purpose of obtaining a quant. estimate of the splitting of the lowest state of chromic ion by the elec. field in the crystal. It is found that a small cylindrical field in addn. to the large cubic field present is sufficient to account for the structure of the absorption curves and that the magnitude of the splitting is 0.15 ± .01 cm.$^{-1}$. It is pointed out that the methods used in the case of chrome alum can be applied to other similar salts such as iron alum and the hydrated gadolinium salts. L. J. E. Hofer

6157

Estimation of the degree of polymerization from the viscosity of solutions of high-molecular compounds. Ichiro Sakurada, Junjiro Matsuda, Shoichi Matsumoto, and Tsunenobu Chiba. *J. Soc. Chem. Ind. Japan* 47, 133-40(1944).—Various empirical formulas were tested and applied to polyvinyl chloride, polyvinyl acetate, and polyvinyl alc. The change in degree of polymerization in conversion from polyvinyl acetate to polyvinyl alc. is discussed. M. Kubo

Heat effect on chain-type polymers. Kisou Kanamaru, Nobutoshi Daimon, and Naoyoshi Ohno. *J. Soc. Chem. Ind. Japan* 46, 1277-82(1943). I. **Heat effect with regenerated cellulose.**—The structural change due to heating of chain-form high-mol. solids was theoretically considered, and as a typical case, the effect of heating regenerated cellulose under different conditions was examd. In a typical rubber-like elastic body in which the potential energy *U* per chain member, consequently the relaxation time, is very small, the range in temp. at which a chain member can be made to dispose itself regularly in the direction of its force field and assume the thermodynamic equil. position lies much below room temp. Heating only increases the thermal motion of the chain member and gives the effect of increasing the probability of that situation. That effect may be called the entropy effect. In the case of a chain-form high-mol. polar substance having a large *U* per mol., such range of temp. lies above ordinary temp., and the chain members that are coagulated in nonequil. condition assume stable equil. positions by heating. As a case of a typical heat effect, viscose rayon was heated for various times in air, steam, b. water, alc. vapor, b. alc., Me_2CO vapor, boiling Me_2CO, and 20% aq. soln. of each of $(NH_4)_2SO_4$, NH_4Cl, and KCl. The effect of such treatments on the strength, elongation, double refraction and polymerization degree was examd. Two types were noticed. One accompanied by a decrease of polymerization degree was shown by steam, water, and solns. of salt. In this case the strength and double refraction attained a max. and then decreased with prolonged heating, with the change in elongation the reverse. Another type not accompanied by a decrease in polymerization degree was shown by nonaq. mediums. In this case the strength and the double refraction gradually increased, reached a max., and stayed there, the elongation likewise reached a min. value. II. **Heat effect with polyvinyl alcohol.**—A similar expt. as in the preceding one was made with polyvinyl alc. fiber and vapor and liquid of ethylene dichloride, C_6H_6, xylene, resp., satd. air, soln. of $(NH_4)_2SO_4$ and air as heating media. In addn. to the properties examd. in the preceding expt., contraction of fiber during heating was examd. under the microscope. In general a typical heat effect as seen in the latter type of regenerated cellulose was observed, with the contraction during heating changing as elongation, but when $(NH_4)_2SO_4$ soln. was used as heating medium, there was observed a special phenomenon such that elongation, which decreased at the start, tended to increase after 30 min., but after reaching a max. eventually dropped, and that the rate of contraction, which increased greatly at the start, dropped markedly after 30 min., increasing again after 1-2 hrs. Such an effect is deduced to be due to the manifestation of the authors' so-called entropy effect 30 min. from the start of heating. J. Kawai

Effect of heat on chain-type polymers. III. Effect of heat on polyvinyl alcohol in salt solutions and syneresis series of ions. Kisou Kanamaru and Yasuo Kawada. *J. Soc. Chem. Ind. Japan* 47, 714-17(1944); cf. preceding abstr.—Polyvinyl alc. fiber was subjected to heat-treatment at 98° in satd. solns. of $(NH_4)_2SO_4$, Glauber salt, and NaCl. Time variation of the strength, tensile strength, Young's modulus, double refraction, swelling

6616

or contraction, and polymerization degree were studied. It was concluded that the heat effect in swelling or lyophilic state is the entropy effect accompanied by the energy effect. IV. **Thermoelastic behavior of polyvinyl alcohol in saturated salt solutions and syneresis series of ions.** *Ibid.* 717-19.—The lengths of polyvinyl alc. fibers with various wts. at their ends were measured in various satd. salt solns. at various temps. The contraction or swelling of the fiber was measured. A wt.-contraction curve was compared with the syneresis series of ions. With anions those ions at the beginning of the series with high degree of hydrogenation have a wt.-contraction curve flat along the wt. axis, whereas with cations those ions at the end of the series have the same tendency. The temp. dependence of contraction of polyvinyl alc. fiber in Glauber salt soln. was investigated with various wts. Two characteristic temps. were found. At 32° where the soly. of the salt is a max., the contraction has a sharp min. and at 73° the curve has a turning point, below which the contraction is nearly const., whereas above this temp. contraction increases. M. Kubo

Polyvinyl compounds. III. Some reactions of polyvinyl alcohol. V. V. Korshak and V. A. Zamyatina. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1946, 106–10 (in Russian); cf. *C.A.* 40, 6552^{2}.—Polyvinyl acetate (mol. wt. 16,154; *n* 187) was hydrolyzed according to Staudinger and Schwalbach (*C.A.* 25, 5138) by hot alc. KOH and according to Ushakov by alc. HCl. The polyvinyl alc. was then dialyzed and the analysis showed the presence of 1 Ac group per 75 alc. units. The mol. wt. of the alc. was 8577 (viscosity of aq. soln.), thus showing that no significant chain scission took place; this was checked by reacetylation by Ac_2O-AcOH in the presence of H_2SO_4. It was noted that absolutely dry polyvinyl alc. cannot be completely acetylated even at 60–80° or 1 month's standing; use of wetted polyvinyl alc., which was then washed thoroughly by alc. and Et_2O, however, gave rapid and complete acetylation after 1 hr. at 70°; the product was purified by soln. in benzene and evapn. Polyvinyl alc. (30 g.) in 200 ml. 30% NaOH was boiled 6–10 hrs.; an insol. modification sepd. in a lump which, after segmentation and prolonged washing in water and drying over P_2O_5, was obtained in the form of a brownish solid, insol. in water, only swelling on heating in water. The wetted material, after alc.-Et_2O washing, is readily acetylated to a similarly insol. acetate, which merely swells in the usual org. solvents, although its Ac no. is 115, i.e. very close to normal polyvinyl acetate. Oxidation of polyvinyl alc. by hot 20% HNO_3 gives only $(CO_2H)_2$, while oxidation by 30% H_2O_2-10% NaOH gave Me_2CO, confirming the 1,3-glycol structure of the normal polyvinyl alc. Polyvinyl alc. (5 g.) added to 50 g. phthalic anhydride in 150 ml. AcOH and 0.5 ml. concd. H_2SO_4, heated 1 hr. to 100°, and poured into cold water gave 7 g. polyvinyl phthalate, crumbly solid, softening at 70°, sol. in alc., AcOH, and Me_2CO.

G. M. Kosolapoff

8154

1918

Polarized infrared radiation as an aid to the structural analysis of long-chain polymers. I. A. Elliott, E. J. Ambrose, and R. B. Temple (Courtauld's Ltd., Maidenhead, Berkshire, Eng.). *J. Chem. Phys.* 16, 877–86 (1948); cf. *C.A.* 42, 2520i; *Nature* 159, 641(1947); *J. Sci. Instruments* 24, 324(1947).—An exptl. procedure is described for measuring dichroism in the infrared spectrum of oriented materials. Oriented films of polythene, polyvinyl alc., polyvinyl chloride, polyvinyl acetate, and nylon were examd. (3600–700 cm.$^{-1}$), and the species (parallel or perpendicular) of many bands was identified. The bearing of these results on current ideas concerning the structure of these polymers is discussed. A general result is that frequencies involving the motion of H atoms show rather low dichroism. On the other hand, very high dichroism was found in some frequencies in which the motion is believed to be confined to other atoms.

G. M. Petty

9075

PVA—polyvinyl alcohol. S. L. Collier. *Soap, Perfumery Cosmetics* 21, 690–1, 695(1948).—Descriptive concerning chem., film-forming, and physiol. properties, functions, and soly. A table of max. concns. of salt solns. in which polyvinyl alc. is sol. is included.

M. B. J.

9230

Thermogravitational diffusion of polymers. H. Fritzemeier and J. J. Hermans (Univ. Groningen, Netherlands). *Bull. soc. chim. Belges* 57, 130–41(1948)(in French).—Thermogravitational diffusion of methylcellulose and polyvinyl alc. in aq. soln. was negligible; that of polymethylmethacrylate (I) in acetone or toluene soln. (approx. 0.5%) was considerable. Under the conditions used no fractionation took place. The app. consisted of a vertical slit of 0.5 mm. width with a reservoir at each end; a horizontal temp. gradient of 900°/cm. was applied across the slit. The curves of concn. of I in the reservoirs against time for solns. of fractions of I of mol. wt. 4.8 × 10^4 and 15 × 10^5 checked with the curves calcd. from suitable values for the coeffs. of thermal and ordinary diffusion.

J. H. E. Herbst

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3677

The free energy, heat, and entropy of sorption of water vapor by proteins and high polymers. Malcolm Dole and A. D. McLaren (Northwestern Univ., Evanston, Ill.). *J. Am. Chem. Soc.* 69, 651–7(1947).—Equations for the integral and differential free energies and the differential net heat for the adsorption or sorption of any substance were derived in terms of the consts. of the linear, Langmuir and Brunauer, Emmett, and Teller adsorption isotherm equations. The data of Bull (*C.A.* 38, 6156[1]) were recalcd. and yield different differential free energies and differential and integral heats than those discussed by Bull but yield the same integral free energies of sorption. The av. differential heats over the first layer computed graphically are much higher than those calcd. from the B.E.T. theory (*C.A.* 32, 4037[9]) if it is assumed that a_1b_2/a_2b_1 is unity. The fraction of the polar groups assocd. with one H_2O mol. at satn. is shown to be equal to the fraction of amorphous polymer in stretched and unstretched nylon. The structural configuration of chemically similar groups must be considered. Differential and integral free energies and heats of hydration are given for cellophane, cellulose acetate, polyvinyl alc., polyvinyl butyral, and vinylidene chloride-acrylonitrile copolymer. Scott E. Wood

4021

Wetting power and the activation energy of adsorption upon a dropping-mercury cathode. Xavier Thiesse and Suzanne Belon. *Compt. rend.* 223, 794–6(1946).—The relation of the wetting power of surface-active agents to the limiting specific diln. and the activation energy necessary for the adsorption processes upon a dropping-mercury cathode was studied by polarographic measurements of O adsorption on such a cathode. The height of the maximums due to O adsorption obtained on the polarogram showed that the variation of O desorption as a function of *c*, the concn. of surface-active agent, is represented by $1-(\Delta H/H_s) = e^{-Kc}$. H_s is the height of the max. for O adsorption in a soln. of aerated H_2O contg. 50 mg. NaCl/l., ΔH is equal to $H-H_s$, where H is the height of the max. for concn. *c*, and *K*, the adsorption const. for each compd., is the vol. of soln. contg. 1 g. of wetting agent and for which $\Delta H/H_s = 1-1/e$. The variation of *K* as a function of temp. is expressed by $K = Be^{-Q/RT}$, where *Q* is the energy for the adsorption processes and *B* is the limiting specific vol. toward which *K* tends as *T* increases. Of the 7 wetting agents reported, sodium butylnaphthalenesulfonate had the lowest *Q*, equal to 3600 cal./g., and *B* equal to $10^{5.2}$ cc./g., and polyvinyl alc. (7% acetyl groups) had the highest *Q*, equal to 5200 cal./g., and *B* equal to $10^{5.5}$. Edwin M. Larsen

4382

Infrared absorption studies. XIII. Stereochemistry of the hydroxyl group in vinyl alcohols. A. M. Buswell, W. H. Rodebush, and R. McL. Whitney (Univ. Illinois, Urbana). *J. Am. Chem. Soc.* 69, 770–2(1947).—The infrared absorption curves for the region 3 μ were mapped for the compds. 2-mesityl-2-phenylvinyl alc. (I), 2,2-dimesitylvinyl alc. (II), 1,2-dimesityl-2-phenylvinyl alc. (III), trimesitylvinyl alc. (IV), and benzyl alcohol (V). The vinyl alcohols were found to show a very slight absorption peak at or near 2.76 μ and a strong absorption peak at 2.84–2.86 μ. The relative heights of these two peaks do not change as the concn. is varied and in two cases (III and IV) when the product of the concn. and cell length is held const. Thus, the possibility of assocn. is eliminated. If it is assumed that the hydroxyl group and the mesityl group are on the same side of the C—C double bond in the 2-mesityl-substituted vinyl alcs., then the coplanar configuration would permit two positions for the H of the hydroxyl. The two infrared frequencies observed were believed to correspond to these two positions. The relative heights of the two absorption peaks in the case of the various 2-mesityl-substituted alcs. are interpreted as resulting from H-bond formation between the O and the mesityl ring. It is believed that such H bonding is made possible by the accumulation of electronic charge on C atoms in the 1, 3, 5 positions on the mesityl ring as a result of hyperconjugation with the methyl groups. Harry H. Sisler

4997

The study of high-polymer structure by x-ray-diffraction methods. C. W. Bunn. *J. Chem. Soc.* 1947, 297–309.—Polystyrene and polymethyl methacrylate lack the ordered mol. structure of polythene and polyamides, which give sharp deflected beams, caused by the crystallinity of their structure. To det. the relative orientation of crystal planes, the crystals are aligned by drawing threads, and the crystal regions all have the fiber axis in common. An x-ray beam sent through such a specimen at right angles to the fiber axis produces a pattern of spots and short arcs, arranged in parallel lines. An addnl. type of orientation can be imposed by pressing or rolling the fibers. Particular crystal planes set themselves in the plane of the sheet. They then simulate single crystals. For simple types of polymers the complete stereochemistry of the mol. can be deduced from the fiber-repeat distance, which is detd. directly from the spacing of the layer lines on the diffraction photograph. The repeat distance in polyvinyl alc. is the same as in polythene (2.53 A.). Also the relative positions of OH or Cl can be estd. Whenever the fiber repeat distance for a particular polymer is the max. to be expected if the chem. structure, the bond length, and angles are known, the configuration of the mol. can be deduced. E.g., nylon 66 has a repeat distance of 17.2 A. This means a planar mol. of 7 zigzags comprising 1 chem. unit. To det. the structures of shortened chains, it is necessary to find the complete at. structure of the cryst. regions with the help of the dimensions of the unit cell. In rubber and gutta-percha, which are cis and trans isomers of polyisoprene, the repulsion between the CH_3 and adjacent CH_2 groups favors a nonplanar chain configuration. In satd. mols. the most stable configurations are those in which the bonds of linked C atoms are staggered. The "principle of staggered bonds" applied to a polymer mol. with a double bond in the chain gives a nonplanar configuration, like that actually found. To correlate mol. structure with phys. properties and to understand the configuration of the chain polymer mol. in crystals, 2 factors must be known: repulsion between substituents and possible bond orientation effects. Flexibility at the ester group of polyesters of trimethylene glycol is suggested by the change of diffraction patterns, on stretching. The theory that in polyamides the mols. are linked by H bonds, and that these are responsible for the high m.p. and high tensional stress, has been substantiated by x-ray investigation. In the early stage of drawing a sheet, orientation occurs, the H-bonded sheets becoming parallel to the direction of drawing. Only in later stages does the well-known chain orientation take place. From the study of the mol. arrangement of simple synthetic polymers deductions can be made for the more complex natural polymers (parallel features between nylon and β-keratin.). Polymers that do not crystallize (polyvinyl chloride) can have left- and right-handed groups along the chain. But when mols. carry 2 identical atoms on the same chain C atom such irregularities cannot occur, and such polymers crystallize well. W. Kitaj

6105

Fuchino. *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 39, 78–88(1941).—Fibers of polystyrene, polyvinyl acetate, and polymethyl methacrylate were röntgenographically studied. Sapond. polyvinyl acetate gives a fiber diagram identical with that of polyvinyl alc. M. Takahashi

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7156

Properties of various plastic films. Wm. H. Aiken (The Goodyear Tire & Rubber Co., Inc., Akron, O.). *Plastics* (Chicago) 7, No. 2, 34–6, 58(1947).—A review dealing with films made from cellulose nitrate, cellulose acetate, ethylcellulose, Pliofilm, nylon, polyvinyl alc., polyvinylidene chloride, polyethylene, polystyrene, polyvinylbutyral, polyvinylcarbazole, polytetrafluoroethylene, and polyvinyl chloride and vinyl chloride copolymers. Also in *Am. Paper Converter* 21, No. 7, 16–17, 23(1947).
Leopold Scheflan

7197

Structure-optical studies. I. X-ray diffraction by addition compounds of halogens with hydrophilic organic polymers. C. D. West (Polaroid Corp., Cambridge, Mass.). *J. Chem. Phys.* 15, 689(1947).—When I, Br, or IBr is incorporated in films or fibers of many hydrophilic org. polymers, such as starch, cellulose, polyvinyl alc., or nylon, the absorption coeff. of the halogen generally increases. A new well-defined strong band often appears in the visible. Pos. dichroism often occurs. In x-ray diffraction pictures of such dichroic prepns. there occurs a pair of diffuse continuous layer lines. This indicates diffraction by independent line gratings—straight chains of halogen atoms. The periodicities of the halogen chains are substantially independent of the original periodicity of the oriented org. polymer and are for I 3.10, Br 2.70, IBr 2.90 A.
G. G

7225

Heats of polymerization of some unsaturates. L. K. J. Tong and W. O. Kenyon (Eastman Kodak Co., Rochester, N.Y.). *J. Am. Chem. Soc.* 69, 2245–6(1947); cf. *C.A.* 41, 5783*a*.—Heats of polymerization (at 76.8°) were detd. (values in kcal./mole of monomeric unit) as follows: Me acrylate 18.7 ± 0.2, vinyl acetate 21.3 ± 0.2, acrylonitrile 17.3 ± 0.5, and vinylidene chloride 14.4 ± 0.5. Methods are discussed briefly.
C. J. West

Solvent separation of hydrocarbon mixtures by vapor-liquid extraction. M. R. Fenske, C. S. Carlson, and D. Quiggle (State College, Pa.). *Ind. Eng. Chem.* 39, 1322–

3150

The estimation of polyvinyl alcohols in body fluid. H. Leverne Williams (Univ. of Western Ontario, London, Can.). *Can. J. Med. Tech.* 7, 127-30(1945).—For pure solns. of polyvinyl alc. (PVA) using the Evelyn photoelec. colorimeter (for other colorimeters vols. and concns. may be worked out) place as much PVA as would correspond to 0.5 cc. of a 1% soln. in a colorimeter tube. In a second tube place 0.5 cc. of a 1% soln. of a PVA standard soln. Add water to make the final vol. 10 cc. and add 10 cc. water to a third tube; to each add 1 drop of 0.1 *N* I_2 in KI. Adjust the colorimeter with the blank tube and filter 490. Read the standard and unknown and calc. in the usual way. For serum, urine, pleural fluid, etc., mix an amt. which will contain an equiv. of 0.5 cc. of a 1% soln. PVA with double the vol. of 22.2% Na_2SO_4 soln. in a centrifuge tube. Centrifuge out the ppt., allow the tube to drain well in the inverted position, disperse the solids in 5 cc. of water and 5 cc. 10% trichloroacetic acid soln., and centrifuge. Decant the clear supernatant fluid into an Evelyn colorimeter tube. In a second tube place 0.5 cc. of a 1% PVA soln., 4.5 cc. water, and 5 cc. 10% trichloroacetic acid soln. In the third tube place 10 cc. 5% trichloroacetic acid soln. Treat as before with I_2 and read. The same grade of PVA must be used in making comparisons as the color varies with the grades of PVA. The color developed varies considerably with temp. It is simpler to develop a standard and a sample at the same temp. than to make a calibration curve at various temps. A nephelometric method is as follows: place an amt. of serum, urine, pleural fluid, etc., suspected to contain the equiv. of 0.5 cc. of a 1% PVA soln. in a colorimeter tube. Prep. a second tube contg. 0.5 cc. of a 1% PVA of the same grade and an amt. of serum, etc., contg. no PVA but with protein content near the unknown sample. A rough approximation only is necessary, for protein-free urine is obviously unnecessary. A third tube contains serum without PVA. To the tubes add water to make 2 ml., add 2 ml. of 2% gum ghatti soln. and 6 ml. of 22.2% Na_2SO_4 soln. Mix thoroughly, adjust the colorimeter with the blank using filter 540. Calc. the results in the usual way. This method is useful for all grades of PVA.

G. H. W. Lucas

4256

Plasticized polyvinyl compositions. Edward S. Yates and Robert F. Gager (to E. I. du Pont de Nemours & Co.). U.S. 2,399,456, Apr. 30, 1946. The following examples illustrate the improved properties of the polymerized vinyl alc. compns. resulting when a solid polymer of HCHO is incorporated as plasticizing agent. In example 1 the plasticizing agent is glycerol, an agent now widely used for this purpose. The characteristics of the compn. of example 1 are to be contrasted with those of example 4, where paraform alone is utilized as the plasticizing agent. In one example 100 parts of completely hydrolyzed polyvinyl alc. were mixed with 30 parts of glycerol in a mortar. The compn. was molded for 10 min. at 145° to 150° under 2500 lb. per sq. in. pressure. The

4915

Thermostabilizing flexible polyvinyl alcohol compositions. Charles Dangelmajer (to Resistoflex Corp.). U.S. 2,395,616, Feb. 26, 1946. Flexible polyvinyl alc. articles may be stabilized so as to retain their flexibility upon exposure to high temp. by incorporating in the original mixt. cupric sulfate or ferrous sulfate in concn. of 3 to 15% of the polyvinyl alc.

J. W. Barber

Curing polyvinyl alcohol and polyvinyl acetal polymers. Emil E. Novotny, Geo. K. Vogelsang, and Ernest E. Novotny (to Durite Plastics, Inc.). U.S. 2,402,075, June 11, 1946. Polyvinyl acetal and polyvinyl alc. polymers are cured by mixing them with Al stearate (1–20% by wt.) and heating the mixt. at a temp. of 275–310°F. for a period of 30 to 45 min. Cured polymers show increased resistance to heat, solvents, and water. Plasticized, cured polymers have freedom from tackiness. Suggested uses are as fabric coatings, molding compds., and lacquers

J. D. Matlack

6258

Isostatic method for determining the gas permeability of sheet materials. Donald W. Davis (Marathon Corp., Menasha, Wis.). *Paper Trade J.* 123, No. 9, 33–40 (1946).—In the isostatic method for gas permeability, the test sheet forms the partition between 2 chambers of the diffusion cell; the test gas is passed over 1 side of the sheet and a 2nd gas (sweep gas) is passed over the other side; both gases are preconditioned to the relative humidity desired in the test. If both gases are made to flow continuously over the surface of the sheet, stagnation is avoided, the permeated gases are swept out, and the partial pressure of each gas on its own side is maintained at approx. 1 atm. For CO_2 permeability, O can be used as the sweep gas, and the permeated CO_2 entrained is detd. gravimetrically by absorption in Ascarite. For other test gases, such as O or N or air, CO_2 is used as the sweep gas, which is absorbed in KOH, and the permeated test gas is detd. volumetrically. Details are given of the app. and the procedure and of the analytical methods for CO_2 and O. The max. permeation rate which can be detd. with precision, by using a single test sheet, is found to be about 1,000,000 cc. per sq. m. per 24 hrs. and thus is useful in the intermediate range of permeability. It is not adaptable for testing highly porous materials, such as bibulous and bond papers and is not sufficiently sensitive for the very low permeabilities of glass or continuous metal sheets. Most tests were carried out at 8° or 21° and at relative humidities of 0 and 75%. Data are given for the permeability of O and CO_2 through cellophane, cellulose acetate, ethylcellulose, Koroseal, vinylite, saran, nylon, parafilm (rubber-wax compn.), pliofilm, polyethylene, polystyrene, polyvinyl alc., polyvinyl butyral, rubber, butyl rubber, vistanex, greaseproof paper, glassine, sulfite paper, vegetable parchment, and Al foil. Data for the permeability of N through cellophane, cellulose acetate, parafilm, and pliofilm are also given. Varying the relative humidity between 0 and 75% has little or no effect on the gas permeability of such nonmoisture-sensitive sheets as saran, polystyrene, and polyvinyl butyral. With other materials, the gas permeability tends to decrease as the relative humidity is increased. Extremely moisture-sensitive sheets show tremendous increases in the permeability to CO_2 and O as the relative humidity is increased from 0 to 75%. In the case of parafilm it was found that increasing the temp. from 16° to 32° approx. tripled the permeability to CO_2. In general, the permeability of materials to CO_2 is higher than to O. The only reliable means of comparing different permeability methods is to make detns. with each method on the same test specimens with the same conditions of temp. and relative humidity.

C. J. West

Surface films of polymers. **II. Films of the coherent and semicrystalline type.** D. J. Crisp (Univ., Cambridge, Eng.). *J. Colloid Sci.* 1, 161–84(1946); cf. *C.A.* 40, 3299^{6}.—Surface pressure-area and surface moment-area curves for polymethyl, -ethyl, -propyl, and -butyl methacrylates spread at an air-water interface give evidence of an increasing tendency to form coherent films with decreasing mol. wt. The methacrylates are much more restricted in rotation than the corresponding acrylates. The higher interchain cohesion of the methacrylates does not lead to a trans orientation. These coherent films are characterized by hysteresis with little permanent collapse at moderately high pressures. Poly-β-ethoxyethyl methacrylate has a greater surface moment than polybutyl methacrylate at large areas, but on compression the ether group is forced away from the interface and the moment becomes identical with that of the Bu ester. Polycyclohexyl methacrylate forms an unstable film showing permanent collapse without much hysteresis. Melting was observed in polyoctadecyl methacrylate films at 20–30°. Polyalkyl methacrylate films are more expanded and fluid at the oil-water interface than at the air-water interface, because the intermol. forces parallel to the surface are greatly reduced by the oil. Polyvinyl alc., polyacrylic acid, and polymethacrylic acid on acid substrates form expanded semicryst. films. The low dipole moment of polyvinyl alc. and polyacrylic acid is ascribed to H bonding. Nylon forms very coherent semicryst. films because of bonding of the peptide link. Nylon monolayers were not affected by the injection of tannic acid beneath the film. When nylon films collapse, segments pass out of the surface layer above rather than below the main film, and this is believed to be true also of films of proteins and other polymeric substances. H. K. Livingston

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1346

Comparison of the structures of stretched linear polymers. Maurice L. Huggins. *J. Chem. Phys.* 13, 37–42 (1945).—Published x-ray data from cryst. Se and Te and from stretched amorphous S, polyethylene, polyisobutylene, polyvinyl alc., polyvinyl chloride, polyvinylidene chloride, polyoxymethylene, polyoxyethylene, polyethylene disulfide, polyethylene tetrasulfide and polyphosphonitrile chloride are compared. In most cases the exptl. identity distance in the direction of the chain axes and the expected interat. distances and interbond angles agree with the assumption that the chain atoms form a regular spiral, unidirectional in each chain and of uniform pitch. Apparent exceptions are briefly discussed. G. M. P.

2022

Osmotic pressure. II. Osmotic pressure and the lyotropic series. A. Dobry and F. Boyer. *J. chim. phys.* 40, 151–6(1943); cf. *C.A.* 34, 5334^9.—Measurements were made of the effect of salts on the osmotic pressure of aq. solns. of polyvinyl alc. The results were in agreement with the lyotropic properties of the salts. Salts having a peptizing action increased the osmotic pressure, whereas those having a pptg. action decreased it. The action of EtOH and acetone corresponded to that of salts in the middle of the lyotropic series. As the concn. of EtOH or acetone in the soln. was increased, the osmotic pressure at first increased and then decreased rapidly to zero at which point the colloid was pptd. J. R. Hill

4800

The infrared spectra of compounds of high molecular weight. H. W. Thompson and P. Torkington. *Trans. Faraday Soc.* 41, 246–60(1945).—Spectra over the range 3 to 14 μ are presented and discussed for thin films of polythene, polyisobutene, crepe rubber, hydrorubber, Buna 85, methyl rubber, polystyrene, polyvinyl acetate, poly-Me acrylate, poly-Me methacrylate, polychloroprenes (Neoprenes), polyvinyl chloride, nylon, polyvinyl alc., Novolac resin, and 3 cellulose materials (ether, acetate, and acetate butyrate). Spectra are also shown for several monomers related to the above polymers. Comparisons with the spectra of substances in different states of aggregation must be made with caution, because of the change in the vibrational spectrum of a substance when it changes its phys. state. Polarized infrared radiation to be used on samples with the oriented chains successively parallel or perpendicular to the plane of polarization of the incident radiation constitutes a promising line of attack on the structure of polymers. Victor R. Deitz

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3664

Condensation of polyvinyl alcohols with aldehydes. I. G. Farbenind. A.-G. Ger. 737,630, June 10, 1943 (Cl. 39*c*. 1). Aldehydes or aldehyde-forming compds. are caused to act on polyvinyl alcs. in an inert org. solvent and in the presence of an acid catalyst until a clear soln. is obtained.

3990

Stabilizing polyvinyl alcohol solutions. Emil Reiter and Alfred Treibs (to Consortium für Elektrochemische Industrie G. m. b. H.). Ger. 737,660, June 10, 1943 (Cl. 39*b*. 22.06). Aq. solns. of polyvinyl alcs. or of their H_2O-sol. derivs. are stabilized by an addn. of water-sol. thiocyanates.

Polyvinyl ethers. Willy O. Herrmann and Wolfram Haehnel (to Alexander Wacker Gesellschaft für Elektrochemische Industrie G. m. b. H.). Ger. 737,956, July 1, 1943 (Cl. 39*b*. 22.06). The ethers or etherlike products are obtained from polyvinyl alcs. by heating them at a temp. over 100°. The heating continues until 1 mol. of H_2O is split off for each 2 mols. of vinyl alc. present in the polyvinyl alc.

5710

Osmometry of high-polymer solutions. Apparatus. R. H. Wagner. *Ind. Eng. Chem., Anal. Ed.* 16, 520-3 (1944).—This glass static-elevation osmometer is a modification of that of Schulz (*C. A.* 30, 6621^3); it is especially useful for measurements of high-polymer solns. that tend to form a stable foam. Wrinkle-free, com. cellophane that has not been dried out, with a wet thickness of approx. 0.1 mm., makes the most satisfactory membrane. Equil. is reached, in the most extreme cases, in 8 to 24 hrs. Aq. solns. usually show an uncertainty of 2 or 3 mm. of water in the osmotic pressure; this is 10 to 20% of the total pressure in the very low-pressure region. The precision is greater with org. solvents. The app. has been used for detns. on polyvinyl alcs. with mol. wts. of 10,000 to 15,000 and on cellulose derivs. It is estd. that the error is approx. 10% at mol. wt. 70,000 and more than 50% at 225,000. T. H. Dunkelberger

4377

Vinyl alcohols. VI. 1,4-Dehydrogenation. Reynold C. Fuson and Robert E. Foster. *J. Am. Chem. Soc.* 65, 913–15(1943); cf. *C. A.* 37, 1417^3.—A remarkable property of vinyl alcs. is the ability to undergo 1,4-dehydrogenation; thus RMeC:CROH (R = mesityl) gives CH_2:CRC(:O)R (*C. A.* 36, 1601^2) and RC(OH):CROH gives RCOCRO (*C. A.* 33, 4228^9). Because it seemed probable that the ease of 1,4-dehydrogenation might depend chiefly on the firmness of attachment of the H atoms of the Me group, it was planned to replace 1 H by Ph; the resulting benzyl group would lose a H atom more readily than the Me group and hence enhance the ease of 1,4-dehydrogenation. $PhCH_2COCl$ (277 g.) and 241 g. durene in the Friedel-Crafts reaction give 332 g. of *benzyl duryl ketone* (I), m. 110–11° (m. ps. cor.). I (10 g.), 10 g. BzH, 30 cc. 10% aq. NaOH and 250 cc. EtOH, stirred 4 hrs. at room temp., give 70% of *1,2-diphenylvinyl duryl ketone* (II), PhCH:CPhC(:O)R′ (R′ = duryl), m. 150–1°; II takes up 1 mol. of H but the enol (III) [$PhCH_2$-CPh:C(OH)R′] could not be isolated; it is assumed that III is formed but is dehydrogenated immediately when exposed to the air; if the hydrogenation mixt. is allowed to stand for 48 hrs. the product is *1,2-diphenylethyl duryl ketone* (IV) [$PhCH_2$CHPhC(:O)R′], m. 106–7°; the yield is nearly quant.; reduction of II with Na in EtOH gives a mixt. of II and IV; IV also results on hydrogenation of II in AcOEt and boiling the soln. for 2 hrs. in a N atm. *Benzyl 2,4,6-triisopropylphenyl ketone*, m. 60.5–1°; *1,2-diphenylvinyl 2,4,6-triisopropylphenyl ketone*, pale yellow, m. 117–19°, 70%. *Duryl 1-phenyl-2-(p-chlorophenyl)-vinyl ketone*, pale yellow, m. 138–40°, 81%; *duryl 1-phenyl-2-(p-chlorophenyl)ethyl ketone*, m. 129–30°. *Mesityl 1-phenyl-2-(p-chlorophenyl)vinyl ketone*, pale yellow, m. 139–40°; *mesityl 1-phenyl-2-(p-chlorophenyl)ethyl ketone*, m. 148–9°. Thus, enols of the type of III ketonize readily and, like the acetylene glycols, undergo 1,4-dehydrogenation in contact with O. VII. Hindrance at the β-carbon atom. Reynold C. Fuson and Quentin F. Soper. *Ibid.* 915–17.—It is suggested that it is the steric hindrance about the β- rather than the α-C atom which is chiefly responsible for the stability of the enols such as HOCR:C(OH)R (I) and MeRC:C(OH)R (II) (R = mesityl); thus, the stability of I requires the presence of both R radicals, whereas that of II would be, to a great extent if not entirely, dependent on the hindrance offered by the β-R radical. To study this, enols have been prepd. with a 2,4,6-(iso-Pr)$_3C_6H_2$ (R′) in the α-position and a Ph group in the β-position. R′$COCH_2$Ph gives a mol. of gas in the Grignard machine, but decompn. of the reaction mixt. yielded only the ketone. MeCHPhCOCl b_3 75–6°, n_D^{32} 1.5232; with 1,3,5-(iso-Pr)$_3C_6H_3$ this yields *1-phenylethyl 2,4,6-triisopropylphenyl ketone*, m. 83–4° (m. ps. cor.); the enol is not obtained by refluxing with EtONa in EtOH for 24 hrs.; analysis in the Grignard machine showed the presence of 1 active H atom. *Ph triisopropylphenyl diketone* (III), R′COBz, bright yellow, m. 121.5–2.2°, results in 85% yield by refluxing 60 g. $PhCH_2$COR′, 30 g. SeO_2, 500 cc. dioxane and 5 cc. H_2O for 8 hrs. Catalytic reduction of III over Cu chromite (175°, 2000 lb. pressure) gives *1-phenyl-2-(2,4,6-triisopropylphenyl)ethylene glycol* (IV), R′C(OH)CH(OH)Ph, m. 133.5–4°; *diacetate*, m. 113–14°. Dehydration of IV did not yield pure products. Attempts to prep. the enediol [R′C(OH):C(OH)Ph] (V) from III by hydrogenation were unsuccessful; however the product showed the indophenol test and if the reduction is carried out in Ac_2O, HCl and $ZnCl_2$, the *diacetate* (VI), m. 161–1.5°, is formed. Hydrogenation of III in ether, followed by evapn. of the solvent, gives *2,4,6-triisopropylbenzoin* (VII), R′COCH-(OH)Ph, m. 117.5–18.5°; in the Grignard reaction VII gives nearly 2 mols. of gas; VII is also formed in the prepn. of IV and results from the hydrolysis of VI; VII is best prepd. by reduction of III with Zn and HCl in EtOH. Oxidation of VII yields III. The *acetate* of VII m. 120–20.5°. These reactions prove that the stabilizing effect of the R′ group is exerted to a greater degree on the HO group in the β- than on that in the α-position with respect to it. The instability of V shows that in stilbenediols both aryl radicals must provide hindrance similar to that furnished by the R radical; thus each of the C atoms of the enediol group, being β to an enolic HO group, must hold a radical such as R or R′ in addn. to the HO group.

4830

Plastic masses from polyvinyl compounds. Hans Orth (vested in the Alien Property Custodian). U. S. 2,312,437, March 2. Compns. suitable for elec. insulation are formed, contg. polyvinyl compds. such as polyvinyl chloride compds. and ethers of 1- and 2-hydroxymethyl-5,6,7,8-tetrahydronaphthalenes, which serve as plasticizers.

Proteinaceous plastics. Oscar Neuss. Ger. 713,039, Oct. 2, 1941 (Cl. 39c. 5). Ground, swelled horn meal is added to a soln. of urea or urea derivs., or CH_2O and urea, or CH_2O and urea derivs. The condensation is allowed to proceed without adding external heat. Acid condensation agents and fillers may be added or not. The product is dried and finished as usual.

Apparatus for treating plastic materials, as in dissolving polyvinyl esters. Fred G. Gronemeyer (to Monsanto Chemical Co.). U. S. 2,312,639, March 2. Various details of an app. suitable for use in treating a plastic material, such as polymerized vinyl acetate with a solvent, such as EtOH, MeOH, BuOH, BuOAc or a mixt. of HOAc and aq. CH_2O.

4961

Heat of polymerization of some vinyl compounds. G. Goldfinger, D. Josefowitz and H. Mark. *J. Am. Chem. Soc.* 65, 1432–3(1943).—By use of the method of adiabatic calorimetry, the heat of polymerization (cal./mol.) of styrene is 15,000, of Me methacrylate 7900 and of vinyl acetate 8000; in the 3 expts. the extent of polymerization was 35–85, 98–9 and 95%, the temp. 70–140°, 60–90° and 80°, and the time 0.5–2, 0.5 and 0.5 hr., resp.

C. J. West

cussion of the resistance to H_2SO_4 and NaOH solns. of phenolic laminates with various fillers. J. W. Barber

The electrical properties of polyvinyl acetate. T. W. Dakin. *Trans. Electrochem. Soc.* 83, 9 pp.(preprint) (1943).—Polyvinyl acetate represents, essentially a linear polymer of vinyl acetate, where the polymer is a paraffin type chain to which an acetoxy radical is attached at every other carbon atom in the chain. There are component dipole units assocd. with the ester group which may rotate independently of each other, but which together form a total dipole moment similar in magnitude to that in EtOAc whose dipole moment is 1.85 Debye units. In the solid polymer where the dielec. constant is low, the polymer chains are held rigid and cannot undergo convolutions to permit orientations of the dipoles attached to the chain in the elec. field. It might be possible for the dipoles in the acetoxy group to undergo restricted rotations (less than 360°) since it is conceivable that there is enough space in the liquid-type loose structure of the solid polymer to permit such restricted rotation. As the temp. is raised, the polymer becomes soft enough to permit convolutions of the chains themselves and the dipoles attached to them can rotate with the elec. field. This softening of the polymer at higher temps. is accompanied by an increase in the real dielec. const. with temp. and a max. in the imaginary dielec. constant, or loss factor, a region of "anomalous dispersion." C. G. F.

Manufacture of sawed Thermosit plates. M. Ya. Latash and M. V. Netshaev. *Prom. Stroitel. Material* 1941, No. 1, 64–9; *Chem. Zentr.* 1942, II, 1617.—To prep. thermal insulating plates-blast-furnace slag was run into shallow flat forms while foaming, and sawed after cooling. Karl Kammermeyer

The thermal behavior of micro- and macromolecular substances and their modification. Kurt Ueberreiter. *Kolloid-Z.* 102, 272–91(1943); cf. *C. A.* 36, 4623^4.—The article is mainly concerned with materials which are made up of a macromol. structure. Natural rubber, polyvinyl compds., styrene, tritolyl phosphate and *synthetic rubber* are especially referred to. Vol.-temp. diagrams are shown to be very helpful for describing internal softening of plastics. The various regions for the phys. condition of compds. with respect to chain length and mol. energy is diagrammatically described. The second part treats of thermal modifications of macromols. The distinction between internal and external softening is brought out. The role of filler in *vulcanization* and plasticizing is explained. Raymond H. Lambert

Introduction to the chemistry of artificial materials. XI–XIII. Wilhelm Schaefer. *Gummi-Ztg.* 55, 513–15, 565–7, 637–9(1941); cf. *C. A.* 35, 8144^9.—Natural rubber and synthetic rubbers of com. importance, products derived from cellulose, and brown and white factice are discussed. XIV–XV. *Ibid.* 55, 725–7, 793–5.—A review with special reference to the properties of factice, coumarone resins, alkyd resins and phenol plastics. XVI–XIX. *Ibid.* 868–9; 56, 10–11, 46–7, 70–1(1942).—The chemistry of phenolic resins, acetylene polymers, polyvinyl alcs., polyvinyl carbazoles, polyvinyl esters, polyvinyl acetates, and polyvinyl chloride, and applications of this last, are reviewed. XX–XXII. *Ibid.* 166–7, 178–9, 214–15.—Polybutadiene, artificial rubbers from methylbutadiene and dimethylbutadiene, mixed polymers of butadiene and styrene, mixed polymers of butadiene and acrylonitrile and Neoprene are described. Through *Chem. Zentr.* 1942, I, 113, 1943; II, 958, 2953. C. C. Davis

Symposium on adhesiveness. I. Introduction to the theory of adhesiveness. R. N. J. Saal. *Chem. Weekblad* 39, No. 8, 91(1942); *Kautschuk* 18, 109–11(1942).—A general review of nomenclature, and the basic principles of adhesion and cohesion. **II. A summary of publications on the theory of adhesiveness.** *Chem. Weekblad* 39, No. 10(1942); *Kautschuk* 18, 111–13.—The most pressing need is more data on the rheologic properties of adhesives, both before and after application. **III. Discussion.** R. Houwink, *et al.* *Ibid.* 114–15. C. C. Davis

Some hints regarding vinyl emulsions. G. Lombardo. *Materie plastiche* 7, 115(1941); *Nitrocellulose* 13, 112 (1942).—Emulsions of vinyl polymers are used as adhesives, in lacquers, artificial leathers, etc. Polyvinyl acetate is generally too hard alone and must be plasticized or contain dispersions of other polymers. Mixed polymers have greater advantages than simple mixts. of emulsions. Monomers suitable for this, in addn. to vinyl acetate and acrylic acids and their esters, are mainly vinyl chloride, vinylbenzene (styrene), acrylic acid nitrile, vinyl ether, and vinyl alc. Addn. of plasticizer has a partly favorable, partly unfavorable effect. In artificial leather there is constantly increasing use of synthetic latex, particularly emulsions of vinyl polymers, more particularly polyvinyl acetate. The otherwise generally advantageous polyacrylic esters are very expensive. E. M. Symmes

The manufacture of artificial leather. F. Fritz. *Nitrocellulose* 13, 150–2(1942).—A review. E. M. S.

Substitutes for sole leather. Wilfred Gallay. *J. Am. Leather Chem. Assoc.* 38, 250–5(1943).—A discussion of present uses and future possibilities of *rubber* and *thermoplastic resins.* J. H. Highberger

Permeability of flexible materials. L. W. Elder. *Modern Packaging* 16, No. 11, 69–72(1943).—Data are given for the air, CO_2 and vapor permeability of films made from polyvinyl alc., rubber hydrochloride, polyvinylidene chloride, glassine and of polyvinyl alc. coated on paper. The most useful information is obtained by practical storage tests, followed by internal-pressure measurements, or by chem. analysis of the gases contained in the package for air contamination. Leopold Scheflan

Dow goes down to the sea. Anon. *Fortune* 26, No. 6, 111–12, 130, 188, 190, 192, 194(1942).—The development of the Dow Chemical Company's process for the extn. of Mg from sea water is described. The growth of other Dow products, e. g., phenol, plastics, Dowtherm and styrene, is reviewed. Carolyn Kruse

New data on activated bauxite desiccants. R. G. Capell, R. C. Amero and J. W. Moore. *Chem. & Met. Eng.* 50, No. 7, 107–10(1943).—Dehydration of org. gases and liquids with an activated bauxite desiccant, Florite, is described. Equil. dryness obtainable, H_2O-adsorption capacity, regeneration and effects of pressure drop and fluid velocity are discussed. 17 references. R. G. R.

Synthetic soap from petroleum products. E. E. van Andel. *Chem. Weekblad* 39, 314–19(1942); *Chem. Zentr.* 1942, II, 1416.—The compn. and properties of German and American sulfonated detergents are discussed. M. M. Pisk

6061

Stable aqueous dispersions of polymerized alkyl methacrylates. Joseph E. Smith (to E. I. du Pont de Nemours & Co.). U. S. 2,318,429, May 4. As a dispersing agent, use is made of about 0.75% or more (based upon the wt. of the dispersion) of a partially sapond. polyvinyl acetate having a sapon. no. of 40–130 and a viscosity in a 4% aq. soln. at 20° of 10–30 centipoises.

6369

Molding polyvinyl alcohol. C. B. Hess and J. W. Criss. *Rubber Age (N. Y.)* 53, 431–3(1943).—The plasticizing, processing and molding of polyvinyl alcs. of various grades are described. C. C. Davis

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3032

Condensing polyvinyl alcohol with acetaldehyde. Ludwig Orthner and Willy Selle (to I. G. Farbenind. A.-G.). U. S. 2,143,228, Jan. 10. A soln. of the condensation product in methylene chloride is emulsified in water in the presence of Na isobutylnaphthalenesulfonate and the methylene chloride is distd. off.

3499

Etherifying polyvinyl alcohols. Henry Dreyfus. U. S. 2,[illegible], Jan. 31. By treating a polyvinyl alc. with chloroacetic acid or the like as an etherifying agent, products are obtained which may be used as *water-sol. sizes*.

3635

Precipitating colloidal substances. John E. Jones, James Y. Davies and John F. Neilson. Brit. 497,063, Jan. 2, 1939. Cellulose derivs., rubber, polymerized vinyl esters, polymerized acrylic esters, bituminous materials, starch derivs., etc., are pptd. from solns. thereof by extruding the soln. through small orifices directly into a pptg. liquid in contact with the orifices and having relative motion substantially transverse to the direction of flow of the soln. through the orifices. App. is described.

1954.

4286

The viscosity of polyvinyl acetate. I. Viscosity of acetone solutions of polyvinyl acetate. Shoichi Matsumoto. *Chem. High Polymers* 6, 176-9(1949).—The intrinsic viscosity $[\eta]$ of acetone solns. of polyvinyl acetate could be calcd. from $[\eta] = 3(\eta_r^{1/2} - 1)/c$, in which η_r is the relative viscosity and c is the concn. Up to 10%, water in the acetone has

4287

little effect. II. Viscosity of methanol solutions of polyvinyl acetate. *Ibid.* 179-81.—The following equation holds for MeOH solns.: $\log \eta_r/c =$ const. The viscosity has a max. at a water content of 15%. III. Intrinsic viscosity of polyvinyl acetate in various solvents and its relation to molecular weight. *Ibid.* 182-4.—The viscosity of polyvinyl acetate was measured in acetone, MeOH, EtOAc, AcOH, and dioxane. The relation between $[\eta]$ and degree of polymerization P is given by $[\eta] = kP^n$. For each solvent numerical values of the consts. k and n were calcd.

I. Sakurada

5603

XIV. Mechanical properties of high polymers. I. Naoyasu Sata, Masataka Okuyama, and Fumio Akao (Osaka Univ.). *J. Acoust. Soc. Japan* 8, 28-33(1952); cf. *C.A.* 46, 2830*g*.—The ultrasonic velocities and elastic consts. were measured by Bär-Walti's rotating-plate method (*Helv. Phys. Acta* 7, 658(1934)) with impulse waves of frequencies 450 kc. to 8 Mc., for solid polymers, polystyrene, polymethyl methacrylate, polyamide, polyvinyl acetate (I), and polyvinyl chloride (II). The effect of the degree of polymerization on the elastic consts. was not observed with I between 1150 and 8700. Elastic consts. decrease with increasing plasticizer contents in systems, I with dibutyl phthalate and II with dioctyl phthalate.

Hideaki Chihara

Thermally reversible gelation of linear polymer sols. I. Kenji Yokokura and Yonosuke Kobatake (Tokyo Inst. Technol.). *Busseiron Kenkyu* No. 70, 89-100(1954); cf. W. H. Stockmayer, *C.A.* 37, 1912⁷.—The gelation of a sol occurs at T_c, where mol. clusters of infinite size are formed. At T_c of a soln. of linear polymers of the degree of polymerization r, there should hold the relation $E/kT_c = -\log r - \log(rN_A/N) + 2(l - 1)\log \rho_A$ with $E = [2l(\epsilon + zw/2)]$, where k is the Boltzmann const., l is the no. of polymer mols. clustered in a micelle, ϵ and w are the energies of crystn. and of mixing, resp., N_A and N_B are the nos. of polymer and solvent mols., resp., N equals $rN_A + N_B$, z is the no. of nearest neighbors, and ρ_A is the no. of sites that the nth segment can occupy when the segments up to the

5606

Mechano-chemical systems. II. Hajime Noguchi (Aichi Gakugei Univ., Okazaki). *Busseiron Kenkyu* No. 69, 78-84(1953); cf. *C.A.* 47, 9721*c*.—Polyacrylic acid (I) cross-linked by esterification with polyvinyl alc. (II) was used as a sample of mechano-chem. systems. The relation between tension k and temp. T at a const. length of a film of I was measured between 3 and 55° when the film (about 50 × 4 × 0.02 mm.) was dipped into aq. solns. of HCl or NaOH alternately. In every case of varying concns., a relation $k = a + bT$ holds with neg. a and pos. b. Thermodynamically, $a = (\partial E/\partial l)_T$ and $b = (\partial S/\partial l)_T$ and thus the energy term is const. in the T range examd. If the energy effect arose from the elec. forces due to ionization of I, a would change with T. The ratio of the energy force to the entropy force is given by T_1/T_2, where T_1 is the temp. at which k becomes zero and T_2 is the temp. of the expt. This ratio, amounting to $^1/_3$ to $^3/_4$, is the smallest for HCl soln. followed by NaOH, carboxylic acids, and their Na salts in the ascending order. The energy effect, however, appears also in the case of pure component II and thus is not characteristic of a mechano-chem. system. The swelling of the film of I seems to be due to the entropy force arising from the osmotic effect of the counterions in the polymer (cf. Asakura, *C.A.* 47, 9721*h*). The heat of crystn. for the formation of crystallites in II may correspond to the observed energy effect with regard to I.

Hideaki Chihara

Correlation of the solubilities of gases in low-vapor-pressure liquids. G. Burrows and F. H. Preece (Metropolitan-Vickers Elec. Co. Ltd., Manchester, Engl.). *J. Appl. Chem.* (London) 3, 451-62(1953).—An analogy is drawn between the evolution of gas from a liquid and evapn. of vapor from a pure liquid. From math. analysis, it is derived that a plot of $-\log L(T/\sigma)^{1/(n+1)}$ vs. σ/T should be linear, where L is the Ostwald soly. coeff., σ the surface tension, and T the abs. temp. The gas has a neg. or pos. temp. coeff. of soly. depending on relative values for energy of cavity formation and energy of activation. To test the math. expression, the soly. of He was detd. in 3 liquids of low vapor pressure. Linear plots were obtained when the appropriate value of n was used. The theory was further applied to the solubilities of O_2 and N_2 in petroleum oils. It was also possible to calc. from the derived expressions the radii of gas mols. A plot of $-\log L$ vs. ΔH passes through zero for oils of the same group, indicating change from pos. to neg. temp. coeff. of soly.

Joseph F. Campagnolo

Diffusion of organic vapors into polyvinyl acetate. R. J. Kokes and F. A. Long (Cornell Univ., Ithaca, N.Y.). *J. Am. Chem. Soc.* 75, 6142-6(1953); cf. *C.A.* 45, 9333*e*.—The diffusion at 40° of vapors of PrCl, $CH_2:CHCH_2Cl$, $PrNH_2$, iso-$PrNH_2$, and CCl_4 into films of polyvinyl acetate (I) was studied as a function of concn. Two other vapors, PrOH and C_6H_6, were studied at 3 temps., 30°, 40°, and 50°. Diffusion coeffs. were detd. from rates of sorption and desorption of vapors by suspending carefully dried films of I, of known area, from a quartz spiral balance in an evacuated chamber; at 0 time the org. vapor, of freshly distd. and dried compds., was admitted and the rate of sorption detd. by following the wt. increase of the film as a function of time. After sorption equil. was reached, the

Plastic flow. II. Viscosity of polyvinyl alcohol-water solutions. Kenkichi Murakami (Tokyo Univ.). *Chem. High Polymers* (Japan) 9, 360–6(1952); cf. *C.A.* 47, 1126c. —The viscosity of an aq. soln. of polyvinyl alc. (8 ~ 18%) was detd. by means of an extrusion-type plastometer in the pressure range 0.402 ~ 10.000 kg./sq. cm. Distinct structural viscosity was observed. A formula was postulated

7336

giving the relation between the shearing force and rate of shear. The formula fits in the exptl. data. IV. The flow paths of viscous materials. Keikichi Arai and Kenkichi Murakami. *Ibid.* 366–71.—A 14% aq. soln. of polyvinyl alc. is first put into a glass tube. The same polyvinyl alc. soln. colored with carbon black is then put into the tube and the spreading of the colored zone was photographed. The expts. were carried out with tubes having various forms. The changes of replacement efficiency of the colorless soln. by a colored one which take place in tubes of various forms were discussed. There is no simple relation. V. Lines of viscous materials which flow through pipes. Kenkichi Murakami. *Ibid.* 371–82.—Polyvinyl alc. soln. contg. small particles of polymethyl methacrylate was forced to flow in a glass tube and the stream lines and the distribution of the velocity of flow were detd. by means of photography. The formula in II was found to hold fairly well.

T. Katsurai

7394

Behavior of a high-polymer solution. IV. Polyvinyl alcohol solution. Kinzo Ishikawa, Toru Kawai, and Yoshio Tokunaga (Tokyo Inst. Technol.). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 55, 730–9(1952); cf. *C.A.* 47, 10319a.—The osmotic pressure and intrinsic viscosities of polyvinyl alc. solns. in mixts. of H_2O and MeOH were measured. The nature of the solvents is discussed.

Katsuya Inouye

7980

Mechanism of glass formation of simple and polymeric compounds. S. N. Zhurkov and B. Ya. Levin (Phys.-Tech. Inst., Acad. Sci. U.S.S.R., Leningrad). *Khim. i Fiz.-Khim. Vysokomolekul. Soedineniĭ, Doklady 7-oĭ Konf. Vysokomolekul. Soedineniyam* 1952, 280–9.—By means of infrared spectra in the range from 1 to 2μ, the temp. dependence of the concn. of free and H-bonded hydroxyl groups is observed. In the case of phenolphthalein, glucose, phenol-HCHO resin, and polyvinyl alc. it is shown that the concn. of H-bonded hydroxyl groups is high and a const. below the glass transition temp. and that above this temp. the concn. of free hydroxyl groups increases. A plot of $\log[n^2/(1 - n)]$ vs. $1/T$, where n is the concn. of free hydroxyl groups, gives a straight line and its slope yields an activation energy of H-bond formation of 4400, 4770, and 4300 cal./mol. for phenolphthalein, glucose, and phenol-HCHO resin, resp. On the basis of the energy of H bonding of 4700 cal./mol. and from the change of dn/dt near the transition temp., the change in sp. heat capacity for glucose is calcd. as 0.2–0.25 cal./g. degree, in good agreement with other data (0.2 cal./g. degree, Parks, *et al.*, *C.A.* 24, 5210). H. D. N.

Structure of vitreous B_2O_3. H. Richter, G. Breitling, and F. Herre (Tech. Hochschule, Stuttgart, Ger.). *Naturwissenschaften* 40, 482–3(1953).—As recently found for amorphous SiO_2, x-ray dispersion spectra on B_2O_3 give atom distribution curves with distinct maxima. Curves are given for the electron unit distribution vs. r up to 10 A. The structural model for amorphous B_2O_3 is one in which BO_3 groups are arranged in B_2O_3 layers of cryst. structure at min. distance of 1.85 A. (graphitelike structure). A calcd. curve on this basis represents well the exptl. data.

B. J. C. van der Hoeven

9099

An approach to the solution of structure problems of organic chain polymers. A. Bjørnhaug, Ø. Ellefsen, and B. A. Tønnesen (Norwegian Pulp and Paper Research Inst., Skoyen). *J. Polymer Sci.* 12, 621–32(1954).—A new approach to the structural problems of unoriented samples of chain polymers makes use of a radial distribution method, with further developments, for interpreting diffuse x-ray diagrams of liquids. The principles of the technique are discussed. Exptl. distributions are calcd. for several chain polymers: polystyrene, polyvinyl acetate, polymethyl methacrylate, polyvinyl alc., polyhexamethylene adipamide, alginic acid, and regenerated cellulose. For structure interpretations a no. of the exptl. distribution curves are compared with theoretical distribution curves calcd. from the at. distances in measured out structure models, which are built up on a scale of 1 A. equal to 10 cm. by means of a set of mol. models. The results indicate that the technique may be well suited for structure investigations of unoriented samples of polymers.

Robert E. Whitfield

9789

Aging of polyvinyl gels. I. X-ray and dilatometric examinations and hardness tests. Yasuo Sone, Kiyoshi Hirabayashi, and Ichiro Sakurada (Kyoto Univ.). *Chem. High Polymers* (Japan) 10, 1–7(1953).—X-ray analysis showed that crystn. takes place in polyvinyl alc. gel because of aging. Crystn. proceeds noticeably when dehydration takes place. The decrease of vol. resulting from aging becomes 0.256%, and the stiffness of gel increases 2–3 times in 10 days. II. Variation of swelling properties in water. Influence of aging on the swelling properties of gel in water and the resistance against hot water. *Ibid.* 7–13.—The degree of swelling of polyvinyl alc. gel in water decreases owing to aging. The degree approaches a const. when temp. is kept const. The influence of temp. is greater than that of time. The velocity of the decrease of the degree of swelling increases with temp. The resistance against hot water increases suddenly at first and then gradually. T. K.

10372

Properties of plastic films. Murray C. Slone and Frank W. Reinhart (Natl. Bur. of Standards, Washington, D.C.). *Modern Plastics* 31, No. 10, 203–26, 380(1954).—Tests on 168 samples indicated a fairly wide range of properties available in com. plastic films. The investigation included tests on tensile strength, folding endurance, tear, water absorption, water-vapor permeability, sp. gr., and flammability. The films tested were cellophane, cellulose acetate, cellulose acetate butyrate, cellulose triacetate, ethylcellulose, polyethylene, polystyrene, polyester, Saran, polyvinyl alcohol, polyvinyl chloride, and polymethyl methacrylate.

R. B. Seymour

11153

av. mol. wts. is derived. VI. Determination of number- and weight-average molecular weights of polyvinyl acetate and polyvinyl alcohol by a diffusion experiment. *Ibid.* [illegible].—*D*s. were measured for mixts. of fractionated polymers of known mol. wt. The no.- and wt.-av. mol. wt. calcd. from *D* agrees fairly well with that calcd. from the ratio of mixing.

T. Katsurai

12515

The diffusion of gases through polyvinyl acetate. Patrick Meares ([illegible] Aberdeen, Scot.). *J. Am. Chem. Soc.* **76**, 3415-22(1954).—The diffusion (D), permeability (P), and soly. ($s = P/D$) coeffs. of He, Ne, A, H, and O with respect to high-mol.-wt. polyvinyl acetate (I) were obtained by measuring diffusion through thin disk membranes of I between 4 and 41° at 2-30 cm. Hg pressure on the ingoing side. The transparent membranes, of thicknesses 0.135, 0.256, and 1.332 mm., were cut from Hg-cast films, and showed no orientation in the polarizing microscope. The *diffusion cell* was described. The very low P values encountered were measured by use of a micro-Pirani gage to minimize the vol. of the outgoing side of the system. D values were detd. by the time-lag method, and P from steady-state measurements. Fick's and Henry's laws were obeyed for each gas. Plots of the logs of P, D, and s vs. $1/T$ showed 2 transitions for I. The upper occurred at about 26° for all gases, and corresponds to the usually quoted 2nd-order transition of I. The lower appeared to decrease from 18 to 15° as the mol. size of the gas increased. The heats of soln. ($\Delta H = -R(d \ln s/d(1/T))$) of the gases in I at temps. above, in, and below the transition region are given, and reasons for their magnitudes and variations with temp. are discussed. The calcd. activation energies (E) for diffusion ($D = D^0e^{-E/RT}$, where D^0 is an entropy factor) were smallest in the transition region, and larger above than below it. The results were interpreted in terms of a mol.-kinetic picture of the change in bulk structure of I in passing through the transition region. B. M. Z.

2506

Structure of vinyl polymers: the polymer from methyl vinyl ketone. C. S. Marvel and Charles L. Levesque. *J. Am. Chem. Soc.* 60, 280–4(1938).—The polymer (I) of Me vinyl ketone (II) may be a 1,5-diketone (III) ("head to tail" type), $(CH_2CHAcCH_2CHAc)_x$ or a 1,4-diketone (IV) ("head to head, tail to tail" type) $[AcCH(CH_2)_2CHAcCHAc(CH_2)_2CHAc]_x$. The following reactions favor the III structure. The I used was prepd. by warming II with a little Bz_2O_2 and was a faintly yellow, clear, tough mass, probably a linear polymer of fairly low mol. wt. I with $ZnCl_2$ in dioxane or C_5H_5N at 50–60° showed little change in properties. P_2O_5 gives a highly colored

3857

Plasticizing. British Celanese Ltd. and Wm. H. Moss. Brit. 47[illegible],638, Dec. 10, 1937. In the treatment of plasticizable compds., e. g., cellulose derivs. and synthetic resins, with plasticizers, e. g., triacetin, alkyl phthalates and tartrates, sulfonamides and alkyl and aryl phosphates, the plasticizer is distributed uniformly over the surface of particles of the compd. which are moistened with a nonsolvent for the compd. The nonsolvent is then removed from the mass by evapn. in the absence of any mech. working so that the original phys. state of the compd. is substantially unchanged. Solns. of solid plasticizers in volatile solvents may be used. Pigments, dyes and fillers may be added, e. g., before the damping with the nonsolvent.

Synthetic resins. Siemens-Schuckertwerke A.-G. Fr. 821,8[illegible], Dec. 15, 1937. Org. compds. contg. 1 or more aromatic groups and 1 or more aliphatic groups the chain of which contains more than 10 C atoms are used as plasticizers for resins made from polyvinyl compds., particularly polyvinyl chloride which may be subsequently chlorinated. Examples of plasticizers are tetradecyl benzoate, benzyl stearate, diphenylamides or dibenzylamides of stearic, palmitic or oleic acid, or dicetyl phthalate. These may be used along with aromatic hydrocarbons of high mol. wt. or chlorinated aromatic hydrocarbons, e. g., chlorobiphenyl or the reaction product of $C_6H_5CH_2Cl$ on $C_{10}H_8$.

3858

Polyvinyl acetal resins. Kodak Ltd. Brit. 477,446, Dec. 29, 1937. Resins contg. not more than 12% of OH groups, calcd. as polyvinyl alc., and not more than 10% of ester groups, calcd. as polyvinyl ester, are prepd. by treating a partially or completely hydrolyzed polyvinyl ester (other than the formate), or polyvinyl alc., in the presence of an acid acetalysis catalyst with CH_2O and AcH in monomeric or polymeric form, either simultaneously or successively, at above 30°, the proportion of aldehydes in the reaction mixt. being such that the acetal portion of the resin contains about 15–25% by mols. of formaldehyde acetal. When polyvinyl alc. is used as starting material, it may be suspended in a resin solvent, e. g., isopropyl or other alc., C_6H_6, heptane, there being then added the aldehyde mixt. with the catalyst, which may be strong acid, e. g., H_2SO_4. The resin may be sepd. by pptn. or steam-distn., which may be followed by repptn. and washing. Alternatively, a polyvinyl ester may be used as starting material and the reaction conducted in the presence of a deësterifying agent. The resins may be plasticized; they may be pressed into blocks and skived to laminae suitable for use in the production of safety glass or made into films by coating a soln. of the resin in a noncorrosive solvent onto a glass or metal plate or a revolving drum, evapg., stripping and curing by heating with warm air. Among examples, polyvinyl acetate 100, paraacetaldehyde 34 and $(CH_2O)_x$ 6.8 parts are dissolved in EtOH and AcOEt and warmed for 144 or 161 hrs. at 40° in the presence of H_2SO_4 to yield a resin sol. in Me_2CO and having a OH content of 6.4 or 9.6% and acetate content of 4.0 or 4.1%, the acetal portion contg. 19.7 or 18.5% of formaldehyde acetal.

4361

The chemical identification of artificial resins used in lacquers and varnishes. H. Wagner and Herm. Schirmer. *Farben-Ztg.* 43, 131–3, 157–8(1938).—A rigorous identification is not always possible. *Coumarone resin.*—The dry distillate gives an orange Storch-Morawski test. If colophony interferes by giving a purple color, a milky purple fluorescence under ultraviolet light indicates the presence of coumarone resin. *Aldehyde resins.*—After first sepg. the resin from saponifiable material and nitrocellulose, dry distn. produces a suffocating odor resembling that of HOAc. *Ketone resin.*—(Cyclohexanone resin). The isolated unsaponifiable resin is detected by the color reaction with diphenylamine sulfate soln. and by a wine-red Storch-Morawski test. *Urea-formaldehyde resins.*—After removal of solvents, the sample on refluxing with concd. KOH or NaOH gives NH_3, or with 20% H_2SO_4 it gives CH_2O. *Phenol resins.*—After removal of solvents, alkali fusion liberates phenol, which forms red dyes on coupling with diazotized *p*-nitroaniline or with Fast Red Salt 3 GL. *Phthalate resins.*—(Glyptals, alkyds, etc.). Dry distn. produces phthalic anhydride crystals and the suffocating odor of decomposing glycerol. The phthalate radical can also be detected by the resorcinol test or as K phthalate (cf. *C. A.* 31, 7271^4). *Colophony-maleic acid resins.*—Attempts at detecting the maleate radical by sapon. and pptn. with $Ba(OH)_2$ gave uncertain results. The Storch-Morawski test gives a wine-red color rapidly going to brown. However, cyclohexanone resin gives a similar test and ester gum gives a violet color which masks the wine-red color. *Vinyl type of resin.*—Dry distn. yields condensates having characteristic fluorescence under ultraviolet light. Such distillate is sol. in concd. caustic soln. only if derived from polyacrylic resins. Polyvinyl esters saponify to polyvinyl alc., which shows a large increase in viscosity when its soln. in a little hot water is treated with cold satd. borax soln. *Chlorinated rubber.*—Fusion with a mixt. of K_2CO_3 and Na_2CO_3 produces a typical odor and converts the Cl into ionizable form readily detectable with $AgNO_3$. Chlorinated diphenyl and vinyl chloride resins also give chloride ion but not the typical odor. *Nitrocellulose.*—The nitrocellulose is first pptd. with benzine, then redissolved and finally poured as a layer on a 1% soln. of diphenylamine sulfate. A blue ring is formed. *Cellulose acetate.*—Heating with dil. H_2SO_4 gives an odor of HOAc. *Cellulose ethers.*—Simple tests have not been developed. Benzylcellulose on heating gives an odor of BzH. Tabulations of Storch-Morawski tests and results of examn. of resins, etc., under ultraviolet light are given.

J. W. Perry

4939

Structure of vinyl polymers. II. Polyvinyl alcohol. C. S. Marvel and C. E. Denoon, Jr. *J. Am. Chem. Soc.* 60, 1045–51(1938); cf. *C. A.* 32, 2506^a.—Present evidence in the literature indicate that polyvinyl alc. (I) contains both 1,2- and 1,3-glycol units (cf. Staudinger, *C. A.* 21, 1271; 22, 215; Herrmann and Haehnel, *C. A.* 22, 214). HNO_3 gives $(CO_2H)_2$. I is not oxidized by HIO_4; 2,3-butanediol (II) is completely oxidized in 15 min., while 2,4-pentanediol (III) is unaffected in 13 hrs.; thus I does not contain 1,2-glycol units. CrO_3 oxidation of I followed by alk. hydrolysis produces Me_2CO and AcOH, which is definite evidence for the 1,3-glycol structure in I. Both I and III show absorption max. in the neighborhood of 2750 A., whereas II does not absorb in the ultraviolet. I and H_3BO_3 give an insol. ppt., which is not a definite compd. but is apparently formed by some random cross-linking of the linear polymeric chain through complex formation; the Na and Ca salts are gelatinous. Heating I and $(CO_2Et)_2$ at 140–60° for 2.5 hrs. gives an insol. ppt.; about 8% of the HO groups in I are esterified (sapon. no.); by treating the ester with $ClCH_2COCl$ a compd. results in which about 75% of the HO groups are still present. There appears to be no reaction between the Na salt of I and $(COCl)_2$. I and Br in cold H_2O give the *compd.* $(C_4H_5O_2Br)_n$ (IV); no further reaction occurred in dioxane; for each C_4 unit of I 4 atoms of Br are taken up; 3 are converted to bromide ions and the 4th is introduced into I as org. Br; the presence of 1 HO group is evidenced by the prepn. of an *acetate*, $(C_6H_7O_3Br)_n$; the Br in IV may be replaced by treating a dioxane soln. with p-$O_2NC_6H_4CO_2Ag$. Heating IV with H_2O for 14 hrs. at 100° removes only 5% of the Br; H_2O in dioxane at room temp. removed 16% of the Br in 2 days; heating gives a charred black mass. Bubbling Cl through I in H_2O for 48 hrs. gives the *compd.* $(C_4H_6O_2Cl)_n$. X-ray photographs of I are given; the well-defined interferences in the pattern are such as would be expected for a regular structure in I rather than for a random arrangement of 1,2- and 1,3-glycol units. C. J. West

5107

Mixed polyvinyl resins. Howard W. Matheson and George O. Morrison (to Shawinigan Chemicals Ltd.). U. S. 2,116,635, May 10. A polyvinyl ester such as the acetate, water and an aldehyde such as acetaldehyde are caused to react with hydrolysis of the ester and condensation of the hydrolysis product with the aldehyde and the reaction product is subsequently caused to react with a different aldehyde such as paraformaldehyde with further hydrolysis and condensation, the reactions being carried out in the presence of an acid catalyst such as H_2SO_4 and until the total hydrolysis is at least 66%. The resulting products are suitable for molding, making films, etc.

b) Hidrólisis

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J. L. Goffart

[redacted] Japan Synthetic Chemical Indu[redacted] Japan [illegible].712 '64), Nov. 4, Appl. Dec. 21, 1962; 2 pp. [redacted] stream of an inert gas (N), [redacted] by cooling. Iwao Shimada

[redacted] Romania Ministry o[redacted] Alexandru Lupu and Maria Opris). Brit. 993,893 (Cl. C 08f), June 2, 1965, Appl. Aug. 1, 1962; 2 pp. Poly(vinyl alc.) with >70% [redacted] crystn. was prepd. by [redacted] stereoisomerism-controlling medium (Me_2CO or MeCOEt) and hydrolysis of the poly(vinyl acetate). Thus, vinyl acetate 500, Me_2CO 500 parts, and azodiisobutyronitrile 0.3% were heated to give the acetate. Then, 200 parts of the acetate, 1060 parts MeOH, and 2–7% NaOH were heated. The poly(vinyl alc. obtained had an intrinsic viscosity of 32 and was 75% cryst.

L. Tetzloff

6376

Extraction of acetic acid from the hydrolysate. A. E. Akopyan and R. Kh. Bostandzhyan (Branch Arm. Sci.-Res. Chem. Inst., Erevan). *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* 17(6), 693-8(1964)(Russ). The extn. of AcOH was tested with different solvents. AcOH 10, poly(vinyl alc.) 14, and H_2O 76% were treated with ethyl acetate, diisopropyl ether, Bu_3PO_4, or with a mixt. contg. BuOH 66, C_6H_6 31, and H_2O 3%. The best solvent for the extn. of AcOH from the hydrolysate is diisopropyl ether (I). By changing the temp. from 20 to 50°, the distribution coeff. of AcOH between aq. soln. of poly(vinyl alc.) and I decreases by a factor of 1.2. An increase of the AcOH content in the initial soln. of poly(vinyl alc.) from 10 to 45% leads to an increase of the distribution coeff. by a factor of 3. The presence of poly(vinyl alc.) did not affect the equil. of the system H_2O–AcOH–I. Ethyl acetate can be used as a solvent also, but only in the presence of HCl. M. Charmandarian

10089

Poly(vinyl alcohol). A. F. Nikolaev and L. P. Vishnevetskaya. U.S.S.R. 170,679 (Cl. C 08f), April 23, 1965, Appl. July 8, 1963. Poly(vinyl alc.) (I) is prepd. according to U.S.S.R. 157,106 (*CA* 60, 5663f). To improve the quality of I, powd. I, which contains β-hydroxyethylacetamide and monoethanolamine as impurities, is extd. with distd. H_2O until all impurities are removed. From *Byul. Izobret. i Tovarnykh Znakov* 1965(9), 70.

MHCL

A new method of producing grafted poly(vinyl alcohol) fibers. A. M. Maksimov, Ya. A. Kharit, L. A. Vol'f, and A. I. Meos (S. M. Kirov Inst. Textile and Light Ind., Leningrad). *Zh. Prikl. Khim.* 38(7), 1638–9(1965)(Russ). In the treatment of poly(vinyl alc.) (I) fibers, films, and fabrics with dialdehydes to render them resistant to water, introduction of free aldehyde groups into the macromols. took place in addn. to the main reaction of cross-linking. The aldehyde groups in the polymer that became insol. in water could be used as active centers for graft copolymerization. After freshly formed I fibers had been acetalized with maleic dialdehyde for 1.5 hr. at 55°, washed, and extd., they were treated with a 1.5% H_2O_2 soln. for 30 min. to convert the aldehyde groups into hydroperoxide groups. The fibers were then treated with an acrylic acid soln. in the presence of a ferrous salt. Graft copolymerization in this manner precluded formation of homopolymer. The fibers obtained had cation-exchange properties; their static ion-exchange capacity was 2.0–2.5 mg.-equiv./g. Acrylonitrile and other vinyl monomers were grafted onto the fibers, films, and fabrics in a similar manner. To obtain products with a higher ion-exchange capacity, I polymer materials with a higher content of

10121

Modification of poly(vinyl alcohol) and poly(vinyl alcohol) fibers by diene synthesis. Yu. K. Kirilenko, L. A. Vol'f, A. I. Meos, and V. V. Girdyuk (S. M. Kirov Inst. Textile and Light Ind., Leningrad). *Zh. Prikl. Khim.* 38(7), 1638(1965) (Russ). On dehydration of poly(vinyl alc.) and poly(vinyl alc.) fibers, dienophilic compds. were added to the double bonds thus formed. By the addn. of maleic anhydride, a cation exchanger with a static capacity ≤6 mg.-equiv./g. could be synthesized. Addn. of other dienophilic compds. (*p*-benzoquinone, acrylonitrile, acrylic acid, acrolein, cyanocarbonic ester, etc.) makes it possible to obtain poly(vinyl alc.) and poly(vinyl alc.) fibers with a variety of new properties. The method is promising from the standpoint of synthesis from poly(vinyl alc.) of modified polymers with ion-exchange properties, improved water resistance, stability to the action of light, and thermal stability. GZJR

11728

[redacted] dimethylacetamide. Kwan C. Tsou ([illegible] Co.). [illegible] 91.3), July 27, 1965, Appl. Sept. 13, 1962; 2 pp. [illegible] dissolved in 300 [redacted] MeOH in a pr[illegible] cooled to 0°; 100 parts Me_2NH was added and the mixt. [redacted] 40° and 30 psi., at which time the reaction had terminated. The poly(vinyl alc.) (29 parts) was removed

11729

by filtration and washed 3 times with MeOH. [redacted] as a white powder and [redacted] lyzed. It was ash free. ~~After removal of the poly(vinyl alc.)~~ from the reaction mixt., the MeOH was removed by distn. and 30 parts dimethylacetamide was obtained. Ramona Mayer

Poly(vinyl acetate) and poly(vinyl alcohol). Kiyokazu Imai (to Kurashiki Rayon Co., Ltd.). U.S. 3,193,542 (Cl. 260–91.3), July 6, 1965; Japan. Appl. May 25, 1960; 3 pp. Poly-[redacted] alc.) (I) of a desired degree of low swelling in H_2O [redacted] greater crystallinity is produced from poly(vinyl acetate) (II) prepd. by polymerization of vinyl acetate in the presence of a azo nitrile catalyst in combination with H_3BO_3, the latter [redacted] to greatly increase the rate of polymerization. [redacted] 90-g. charge consisting of vinyl acetate 59.99, MeOH 35, H_3BO_3 5, and $[Me_2C(CN)N:]_2$ 0.01% was sealed in a tube and polymerized at 60° for 21 hrs. to give II in 76% conversion. The II was freed of H_3BO_3 by washing with boiling water and converted into I by alk. sapon. The clouding characteristics of the hydrous Me_2SO soln. of the I obtained showed this I to be superior to that obtained from II prepd. without H_3BO_3. K. J. Durant

15007

[redacted]. A. G. Sayadyan. U.S.S.R. 171,561 (Cl. C 08f), May 26, 1965, Appl. Jan. 18, 1963. [redacted] of poly(vinyl acetate) with a mineral acid while heating. To obtain a colorless, thermally stable polymer, the hydrolysis [redacted] or [redacted] From *Byul. Izobret. i Tovarnykh Znakov* 1965(11), 77.

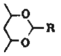
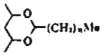
MHCL

5353

Highly crystalline poly(vinyl alcohols). Kurashiki Rayon Co., Ltd. (by Kiyoshi Fujii, Saburo Imoto, Junji Ukida, and Masakazu Matsumoto). Japan. 9854('65), May 29, Appl. Sept. 3, 1959; 2 pp. Copolymerization of vinyl formate (I) with <10% vinyl acetate (II) [illegible], followed by hydrolysis, gave the title polymers. Polymerization without II caused gelatinization in the reaction mixt., while addn. of >10% II reduced the crystallinity as indicated by increased swelling of the film in H_2O. Thus, a mixt. of 100 parts I and 0.1 part azodiisobutyronitrile was kept at 30° for 24 hrs. under N together with 0, 1, 2, 3, and 5% II to give 68.1, 62.8, 63.2, 58.5, and 51.7% polymer, resp., and hydrolysis of these of polymers gave poly(vinyl alc.) with the following properties (degree of swelling and d.p. given): 1.48, 1.30, 1.36, 1.34, and 1.31; 910, 899, 908, 911, and 901, resp. c

Ikuo Matsumoto

Basic acetals of poly(vinyl alcohol). Sankyo Co., Ltd. (by Nobuyoshi Sampei). Japan 10,593('65), May 28, Appl. July 14, 1961; 3 pp. The title compds., contg. 2 acetal groups of the general formulas I and II, where R is dialkylaminophenyl, dialkylaminoalkyl, quinolinyl, pyridinyl, or piperidinyl, *n* is 0–4, are sol. in gastric juice and org. solvents, insol. in H_2O, and are

d  (I)  (II)

useful for coating drugs. Thus, 4.4 g. poly(vinyl alc.), 50 cc. H_2O–MeOH (1:1), 0.5 cc. 10% aq. HCl, and 1.44 g. n-C_3H_7CHO, were stirred at 60° for 1 hr., cooled, and poured into H_2O to give an acetal ppt. The ppt. was dissolved in 50 cc. H_2O–MeOH (1:1), 1.2 g. 6-quinolinylcarboxaldehyde, and 4 cc. 10% aq. HCl were added at 60° for 2 hrs., the mixt. cooled, and poured into dil. aq. NaOH to give a white, rubberlike product. This product was washed with H_2O, dissolved in 50 cc. MeOH, dild. with H_2O, the ppt. washed with H_2O, and dried *in vacuo* to give 4.8 g. of acetalized compd.

Junichiro Sugano

658

The synthesis of water-soluble salicylals of poly(vinyl alcohol). S. N. Ushakov, E. M. Lavrent'eva, and L. I. Petrova. *Vysokomolekul. Soedin., Khim. Svoistva i Modifikatsiya Polimerov, Sb. Statei* 1964, 282-4. Poly(vinyl alc.) (I) in 10% aq. soln. (pH 6) was treated with concd. HCl to pH 2, and salicylaldehyde (II) was added at I:II molar ratios varying from 100:3 to 100:10. The reaction temps. varied between 20 and 60°, and the reaction times from 1 to 10 hrs. The resulting salicylals were pptd. by the addn. of Me_2CO and were subsequently vacuum dried to const. wt. Virtually all II was consumed in acetal formation, about 4-8 hrs. being required for completion of the reaction. Viscosity measurement showed that the polymer chain length was essentially unaffected by salicylal formation.

C. H. Fuchsman

1803

Heat stabilization of poly(vinyl alcohol) with phosphoric acid. Joseph G. Martins (to Shawinigan Resins Corp.). U.S. 3,156,667 (Cl. 260-45.7), Nov. 10, 1964, Appl. Mar. 5, 1962; 3 pp. A poly(vinyl alc.) with high resistance to color-producing thermal degradation is achieved by neutralization of vinyl ester polymer hydrolyzates with H_3PO_4. A MeOH soln. of a poly(vinyl acetate) resin (453 g.) was mixed at 47° with 13 ml. 3.9% NaOH in MeOH. The mixt. was agitated for 2 min. A gel structure appeared after 9.5 min. The gel was finely chopped and, after 28 min., was steeped in 400 ml. MeOH contg. 0.45 ml. 85% H_3PO_4. After a few minutes stirring, the resin was drained, washed 5 times with 300-ml. portions of MeOH, and dried in an air oven at 70°. The resinous product was heated to 145° for 45 min. and was sol. in H_2O and negligibly colored. The poly(vinyl alc.) thus produced had a viscosity of 9 cp. as a 4% soln. in H_2O at 20° and contained 34.6% poly(vinyl acetate) as measured by sapon. The polymers which can benefit from this invention are partially to completely hydrolyzed poly(vinyl ester) homopolymers and copolymers. These compds. should have $\geqq 20\%$ of their ester groups hydrolyzed and have a mol. wt. of 1200-125,000. Useful hydrolyzed homopolymers are those of vinyl acetate, propionate, butyrate, hexoate, and benzoate. Useful hydrolyzed copolymers include those of vinyl acetate, propionate, butyrate, hexoate, stearate, chloride, and bromide. The lower-alkyl esters of acrylic, methacrylic, and crotonic acids and ethylenic monomers such as ethylene, propylene, and isobutylene are also included. The H_2O-sol. poly(vinyl alcs.) may contain 0-45% unhydrolyzed ester groups and may have a viscosity of 3-65 cp. as a 4% soln. in H_2O at 20°. The preferred org. liquids for carrying out the H_3PO_4 neutralization of poly(vinyl alc.) and the washing of the neutralized resin are essentially those in which the hydrolysis may be done, such as MeOAc, EtOH, MeOH, EtOAc, and Me_2CO.

W. D. Barrow

2527

[redacted] Tamotsu Eguchi and Hideo Itō (Rayon Kabushiki Kaisha, Kurashiki, Japan). *Denki Kagaku* 29(2), 97-101(1961)(Japan). Purification of crude NaOAc which is a by-product of poly(vinyl alc.) production, was studied for its use as the reactant for electrolytic HOAc formation. This NaOAc soln. contains org. impurities (probably aldehyde resins). Activated C is effective to remove small amts. of the org. impurities, and the process follows Freundlich's adsorption equation. However, the use of activated C is not economical when large amts. of the org. impurities are present. Recrystn. methods yielding 45-50% NaOAc give pure enough reactant. Continuous dialysis of the liquor follows the Lane equation, and gives pure NaOAc soln. of 1/3 the concn. of the original liquor, with about 90% recovery. An economical purification procedure consisting of combined steps of the above 3 methods is described.

GKJY

4134 | 4135

Poly(vinyl alcohols) from acetaldehyde. [illegible] Electrochemische Industrie G.m.b.H. Fr. 1,365,127 (Cl. C 08*f*), June 26, 1964; Ger. Appl. Aug. 4, 1962; 2 pp. AcH is treated with 0.001-1 mole alkali metal or alkali metal amide in a solvent that is inert to the alkali metal, in the absence of air and H_2O, and the products are hydrolyzed to give the title polymers. Thus, 0.55 g. K is slowly added at 20° to a soln. of 8.8 g. AcH in 50 ml. tetrahydrofuran (I). The mixt. is agitated 2 hrs. and I is evapd. *in vacuo*. The residue is taken up in H_2O, the mixt. is filtered, and the filtrate is neutralized with an acid ion exchanger and concd. *in vacuo* to give 4.32 g. oil. The oil is digested with ether and the ether-insol. fraction is dried *in vacuo* to give 3.05 g. poly(vinyl alc.).

BDPF

Effects of sodium chloride on acetalization of poly(vinyl alcohol) in water. Ichiro Sakurada (Univ. Kyoto, Japan), Yasuyoshi Sakaguchi, and Shuji Yoshida. *Kobunshi Kagaku* 21 (234), 620-4(1964). Poly(vinyl alc.) (I) and some low-mol.-wt. polyhydric alcs. were acetalized with various aldehydes (AcH, EtCHO, and PrCHO) in H_2O, by using acid catalysts (HCl, $MeSO_3H$, and toluenesulfonic acid), and the effects of addn. of NaCl on the initial rate of the reactions were investigated. NaCl (0-0.7*M*) generally accelerates acetalization of polyhydric alcs., and the order of the acceleration effect is: I > pentaerythritol > 1,3-butanediol > 1,3-propanediol. By the addn. of 0.7*M* NaCl, the acetalization rate of I becomes about twice as large as the original one. The acceleration effect is nearly independent of the reaction temp. (5-70°) in the case of I, but increases with decreasing reaction temp. in the cases of the other alcs. For any alc., the acceleration effect is nearly independent of the concn. (50-200 meq./l.) of the alc. and the type and concn. (*N*/200 and *N*/10) of the catalysts. Hydrolysis of EtOAc under similar conditions is accelerated only slightly by the addn. of NaCl.

Eiichi Wada

5360

Partially saponified poly(vinyl esters). Hans Dexheimer, Otto Fuchs, Michael Lederer, and Werner Schmieder (to Farbwerke Hoechst A.-G.). U.S. 3,156,678 (Cl. 260-89.1), Nov. 10, 1964; Ger. Appl. Aug. 18, 1960; 5 pp. An alk. catalyst is stirred with a poly(vinyl ester) (I) in a solvent mixt. consisting of an alc., the ester (II) of the alc., and the acid portion of I. A ratio of II to the alc. of 50:1 to 2.5:1 is maintained. Thus, 10 parts of poly(vinyl alc.) having a reduced sp. viscosity of 0.41 was dissolved in a mixt. of 48.7 parts MeOAc and 6.8 parts MeOH. The temp. of the soln. was adjusted to 23° and a soln. of 0.1 part NaOH in 0.79 part MeOH was added. A max. viscosity was reached after 20-min. stirring. After 3 hrs., the reaction was terminated. The poly(vinyl acetate) contained 28.1% residual acetyl groups. The product was converted to an aq. soln. by steam distn. or isolated by evapn.

D. K. Hayes

6582

Saponification of poly(vinyl acetates) prepared by various procedures. Ichiro Sakurada (Univ. Kyoto, Japan), Yasu-

6591

3 pp. The title compd. was sepd. from its tetrachloroethane (I) soln. by feeding the soln. into an agitated mixt. of 1 vol. I and 0.3–0.35 vol. MeOH at 18°, simultaneously adding MeOH alone or with I to maintain the vol. ratio. After filtration, the finely divided powder was washed with MeOH and dried. L. Tetzloff

Vinyl polymers and copolymers. Sicedison Societa per Azioni (by Gianni Benetta and Gennaro Cinque). Belg. 637,626, March 20, 1964; Ital. Appl. Sept. 20, 1962; 13 pp. Vinyl halides, such as vinyl chloride (I), are polymerized or copolymerized with another vinyl monomer in aq. suspension in the presence of a mixt. of (*1*) a mixt. of standard primary and secondary suspension agents and (*2*) a surfactant, such as a C_{1-18} alkanol, C_{1-18} aliphatic acid, or low-mol.-wt. poly(methylsiloxane), to give porous products with uniform dimensions. Thus, I is polymerized in the presence of 0.1% (of H_2O) maleic anhydride–vinyl acetate (II) copolymer (H_2O-sol.), 0.2% (of I) allyl alc. (III)–II copolymer contg. 14% III, and 0.07% (of I) isooctyl alc. to give a product, porosity 0.460 ml./g., 0.01 ml./g. for the control. BDPF

Poly(vinyl alcohols) from metal vinylates. Consortium fuer Elektrochemische Industrie G.m.b.H. Fr. 1,361,830 (Cl. C08f), May 22, 1964; Ger. Appl. July 10, 1962; 3 pp. Metal vinylates are catalytically polymerized and the resulting polymers are hydrolyzed to poly(vinyl alcs.) of the general formula CH_2:$CHOMeX_n$, where Me is the metal, X is an anion, and *n* is zero or a value depending on the valence of Me and X. Useful metals are Na, K, and esp. Li. Org. solvents which are inert to the vinylates are used, e.g. AcH, acetone, C_6H_6, or Et_2O. Soln. concns. are 3–10% and polymerization can be effected at temps. as high at 150°, but under reduced pressure from 20 to 100°. Thus, 0.05 g. azodiisobutyronitrile is added to a soln. of 1.6 g. vinyllithium in 50 cc. abs. ether and heated in a sealed tube under N for 17 hrs. at ~60°. The nearly colorless polyvinylate seps. quant. and is then dissolved in 20 cc. H_2O. The soln. is passed over an acidic cation-exchange column, e.g. 40 cc. Dowex 50, and is thoroughly water washed. Evapn. of the aq. soln. gives 0.6 g. of a yellowish, resinous product (45% yield). A nearly colorless, filterable substance obtained by ether pptn. of an iso-PrOH soln. has a poly(vinyl alc.) ir spectrum. David Goland

6640

Granular poly(vinyl alcohol). Rhone-Poulenc S. A. (by Marc Galuzet). Fr. 1,367,378 (Cl. C 08f), July 24, 1964, Appl. April 11, 1963; 5 pp. Poly(vinyl acetate) is hydrolyzed in MeOH in the presence of MeONa. The resulting gel is extruded through a plate, with perforations of appropriate size, and dried to obtain granules. R. D. Witman

7896

Condensation products of poly(vinyl alcohol) with carbonyl compounds. Sekisui Chemical Co., Ltd. (by Eiichi Yamamoto, Yoshiichi Matsuura, and Tadashi Hasegawa). Japan. 17,064('64), Aug. 18, Appl. Mar. 6, 1962; 3 pp. The title compds. are prepd. by using ion-exchange resin (H-type). Thus, a soln. of 100 g. poly(vinyl alc.) (d.p. 1000) in 1000 cc. H_2O is warmed at 40° for 2 hrs. with 16 g. butyraldehyde and 50 g. Diaion SK No. 1 resin, and the product sieved (50-mesh) to give a poly(vinylbutyral) soln. (degree of butyralation 20 mole %) in 98% yield. Hiroshi Kataoka

Poly(vinyl alcohol). Romania, Ministry of Petroleum and Chemical Industry (by Johannes Brandsch, Ioan Gunesch, Gheorghe Ciobanoglu, and Ion Birsan). Belg. 639,011, April 22, 1964; Rom. Appl. Oct. 22, 1962; 6 pp. Poly(vinyl acetate) (100 kg.) in suspension was stirred at 54–60° with 100–150 kg. MeOH and 20–50 kg. MeOAc until the mixt. became homogeneous. The rate of sapon. was followed by dissolving ~0.2 g. dry sample in 20 ml. water, adding 2 drops of 0.1 N [illegible] soln.

Abstracts

9260

and 5 ml. satd. H_3BO_3 soln., and comparing the color produced with that of standard. The sapon. stopped by itself 1–2 hrs. after adding MeONa, giving poly(vinyl alc.) (I) with a sapon. no. 110 ± 10. After adding 5 l. water or 300 ml. AcOH dild. with 5 l. distd. water, the solvent was recovered. The duration of the process was 8–12 hrs. The partially hydrolyzed I (degree of hydrolysis 83 ± 2%) can be used as colloid protector. N. A. Abraham

10613

Improved poly(vinyl alcohol). Air Reduction Co., Inc. (by Harold D. Smyser and Ora L. Wheeler). Fr. 1,360,102 (Cl. C 08f), April 30, 1964; U.S. Appl. June 11, 1962; 10 pp. Completely hydrolyzed poly(vinyl alc.) (I) is treated at 95–105° with superheated steam at 135–53°. The product retains less H_2O on washing and drying. A concd. pourable paste (up to 30% I) can thus be formed in cold H_2O. James B. Normington

13263

A new route to stereoregular poly(vinyl alcohols). S. Murahashi, S. Nozakura, and M. Sumi (Univ. Osaka, Japan). *J. Polymer Sci.* Pt. B 3(4), 245–9(1965)(Eng). Syndiotactic and isotactic poly(vinyl alc.) (I) are prepd. by cationic polymerization of CH_2:$CHOSiMe_3$ (II) followed by alcoholysis. Moisture in the air readily hydrolyzes II to I. Stereoregularity of I can be measured by measuring the ratio of the optical d. of the ir absorptions at 916 and 849 cm.$^{-1}$, this ratio having been 0.25–0.3 for conventional atactic, <0.25 for isotactic, >0.3 for syndiotactic I. Polymerization of II was at −78° under N atm. for 3 hrs., by injecting an initiator soln. (5 mole % of $SnCl_4$ or Et_2AlCl) with a hypodermic syringe into a mixt. of toluene, hexane, or CH_2Cl_2 solvent, and 3 ml. monomer. After polymerization a large amt. of MeOH was introduced to stop the reaction and to alcoholyze the polymer, which was completed in about 30 min.; conversion 16.3–100%, d.p. (calcd. for CH_2:CHOH) 52–948. The latter was calcd. using the formula, $\log \bar{P}_A = 1.5625 \times \log([\eta] \times 10^4)/7.50)$, where $\bar{P}_A$ is the d.p. and $[\eta]$ is the intrinsic viscosity in dl./g. in H_2O at 30°. $TiCl_4$, VCl_4, and BF_3 initiators were also effective, but $BF_3.OEt_2$ was not. Ir spectra were recorded with films cast from a 1% aq. soln. of I and dried at 30°. I obtained with less polar solvents is largely isotactic, but with polar solvents highly syndiotactic. The CH_2Cl_2–$SnCl_4$ system gave a highly syndiotactic polymer. T. E. Muller

13272

Partially saponified poly(vinyl acetate). Hitachi, Ltd. (by Mitsuo Tsukui). Japan. 24,710('64), Nov. 4, Appl. Oct. 8, 1962; 2 pp. Sapon. degrees of poly(vinyl acetate) (I) can be controlled easily and with high reproducibility by carrying out the sapon. in a 10–20% aq. acetone soln. Thus, to 40 g. I dissolved in 800 ml. of a 15% aq. soln. of acetone was added 120 ml. of 0.5*N* NaOH soln. in MeOH under stirring at 20°. Upon stirring for addnl. 4 min., the reaction mass became a gel. An aliquot was taken, washed with warm water, and dried. This sequence was repeated 8 times. Sapon. degrees were between 34.8 and 42.0. Iwao Shimada

13324

Production of poly(vinyl alcohol) for use as an emulsifier in the production of poly(vinyl acetate) latexes. F. Gregor and E. Pavlacka. *Chem. Prumysl* 15(1), 36–7(1965)(Slo). Poly(vinyl acetate) was converted to poly(vinyl alc.) (I) by methanolysis catalyzed by H_2SO_4. The amt. of bound S was detd. as a function of the acid concn. and the reaction time. In the production of poly(vinyl acetate) latexes, the best results were obtained by using I contg. 0.36–0.45% bound S and 1–2% residual Ac groups. H. Morawetz

744

[redacted]ht. Consortium fuer Elektroch[redacted] Industrie G.m.b.H. Brit. 950,220 (Cl. C 08f), Feb. 19, 1964; Ger. Appl. Nov. 21, 1960; 3 pp. [illegible] soln. of poly(vinyl alc.) (I) having a viscosity of 120 centipoises at 20° is prepd. thus: 500 g. vinyl acetate and 600 g. water contg. 0.3 g. carboxymethyl cellulose and [illegible] g. [illegible] were mixed and heated to 60°. At 60°, a 0.2% aq. [illegible] soln. was added dropwise and the temp. rose to reflux. The reaction was regulated by the rate of addn., and the polymerization was terminated when the temp. fell from reflux to 60°. The resulting polymer was converted to I either with 1% NaOMe in MeOH or [redacted] in MeOH to give clear, colorless solns. Kenneth A. Kun

Poly([redacted] alcohol). Ryunosuke Naito and Saburo Yamane (to Kurashiki Rayon Co., Ltd.). U.S. 3,124,562 (Cl. 260–91.3), Mar. 10, 1964; Japan Appl. Apr. 23, 1959; 3 pp. Poly(vinyl alc.) (I) having a low degree of polymerization (DP 100 to 1500 monomer units per polymer mol.) can be polymerized in the lab. by modifying the conditions of polymerization and by degradation by using oxidizers suspended in aq. solns.; however, these methods are not suitable from an industrial point of view. Poly(vinyl esters), e.g. poly(vinyl formate) [redacted] (II), and poly(vinyl butyrate) [redacted] of oxidizing [redacted] periodic acid (III), periodates, [redacted] hypochlorites. [redacted] 5 parts of II (DP 1450) [redacted] of a 5% aq. soln. of NaOH in which 0.045 part III [redacted] The soln. was sapond. at 40° by adding 2 [redacted] soda having a concn. of 200 g./l. [redacted] I was sepd. by filtration, washed with a small amt. [redacted] and dried. [redacted] DP of 580, showed no discoloration after drying for 5 hrs., and was satisfactorily sol. in [redacted] by the [redacted] used. Lloyd E. Cockerham

791

High-viscosity poly(vinyl alcohol). Shawinigan Chemicals Ltd. [redacted] Can. 679,581 Feb. 4, 1964, Appl. July 21, 1962; 14 pp. Very-high-mol.-wt. poly(vinyl alc.) of intrinsic viscosity after reacetylation of 1.7–3.2 dl./g., as detd. in acetone at 20°, is obtained on hydrolysis of radiation-polymerized poly(vinyl acetate). Vinyl acetate is purified by distn. to an ultraviolet absorption of <0.5 at 265 μ and, after purging with N to eliminate O, is emulsified with 0.5% of a radiation-resistant emulsifier, such as stearoylaminopropyldimethyl-β-hydroxyethylammonium di-H phosphate (Cationic SP) or 1 of the products described in Brit. 819,451 (*CA* 54, 10396*d*) to preferably 30–5% solids. The polymerization can be carried to 85% conversion or above at a total dose of 1.20–2.32 × 10^6 r. by using ^{60}Co or its equiv. and takes place at 0–15°. The dose rate is immaterial. Hydrolysis of the product gives a highly H_2O-resistant poly(vinyl alc.) which is useful as a thickening agent or a protective colloid. Manfred Luttinger

2016

[redacted] Kozo Fujii and Yasuji Oyanagi (to Kurashiki Rayon Co., Ltd.). U.S. 3,096,298, (Cl. 260–29.6), July 2, 1963, Appl. Mar. 26, 1959; 2 pp. [redacted] are given improved [redacted] vinyl ester by using an alk. catalyst. [redacted] g. vinyl acetate with an org. peroxide or azodiisobutyronitrile or a small amt. of MeOH is sealed in a 25-cc. capsule and heated for 10 hrs. at 140–60° to give poly(vinyl acetate), which is purified by pptn. and then sapond. by alcoholysis by using an alk. catalyst giving completely sapond. I. [redacted] by washing with MeOH, and the I is [redacted] under reduced pressure at 65°. Upon standing at 60° after dissolving in [redacted] H₂O soln. to double its [redacted] F. S. Stewart

2029

Alkoxylated poly(vinyl alcohol) and alkoxylated amide compositions. Philip L. Gordon (to Borden Co.). U.S. 3,129,196 (Cl. 260–32.6), Apr. 14, 1964, Appl. May 12, 1961; 2 pp. Alkoxylated poly(vinyl alc.) plasticized with alkoxylated fatty acid amides produces films that withstand high temps. during heat sealing and exhibit good clarity. Thus, into a pressure reactor was charged 100 parts of poly(vinyl alc.) (I), having a viscosity of 30 cp., representing 98% hydrolyzed poly(vinyl acetate) in the form of a fine powder 95% by wt. of which passed through 140 mesh. Then 11 parts *N*-diethanol-substituted stearamide alkoxylated with 20 moles ethylene oxide was added to 1 mole of the amide and approx. 1.3 parts 26% aq. NH_4OH. With agitation at 70–5°C., 36 parts ethylene oxide was

3202

Stereoregularity of poly(vinyl alcohol). Kiyoshi Fujii, [illegible] Mochizuki, Saburo Imoto, Junji Ukida, and Masakazu Matsumoto (Kurashiki Rayon Co., Okayama, Japan). *J. Polymer Sci.* Pt. A 2(5), 2327–47(1964). Free-radical polymerization of vinyl formate at temps. near −78° gave poly(vinyl formate) (I) of high syndiotacticity; at 60°, the polymer was completely amorphous. I was converted to syndiotactic poly(vinyl alc.) (II). Both atactic and syndiotactic II can be crystd. by heat treatment. Vinyl *tert*-Bu ether polymerized by Lewis acids at −50° or −78° gave isotactic poly(vinyl *tert*-Bu ether) (III), which could be cleaved to the poorly crystallizable highly isotactic II. It is suspected that the latter polymer contains intramol. H-bonds which inhibit crystn. Isotactic I was prepd. by formylation of isotactic II. In cryst. isotactic I, the main chain is in the shape of a 3_1 helix, while in cryst. syndiotactic I, the main chain is zigzag. Atactic I cannot be appreciably crystd. The relation between tacticity on the one hand and crystallinity and crystallizability on the other, which varies from polymer to polymer, is discussed for I, II, III, poly(vinyl acetate) (IV) and poly(vinyl trifluoroacetate) (V). IV and V of known tacticities were prepd. from syndiotactic I and isotactic III via known reactions; atactic IV and V were prepd. directly from the monomers. The infrared spectra and x-ray patterns of all polymers are discussed as their preparative interrelations. William A. Swarts

16180

Continuous hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol). Lupu Alexandru, Florica Bataciu, and Istvan Balint. *Plasticheskie Massy* 1964(9), 6–8; cf. *CA* 57, 16857*h*. [redacted] hydrolysis of [redacted] (I) to spinnable poly(vinyl alc.) (II) was developed and the dependence of the process on some parameters studied. A 25–35% soln. of I in MeOH was charged into a mixer at a controlled rate by means of a gear pump. A NaOH soln. in MeOH (prepd. by diln. [redacted] aq. soln. with MeOH) was charged into the mixer by [redacted] same pump at a rate [redacted] and to obtain [redacted] 25% I concn. in [redacted] NaOH soln. passed into the reactor through the central tube of a mixer ending with a rotating nozzle, which sprayed the NaOH soln. on the film of the soln. of I formed in a throttling device. Thus, efficient mixing necessary for complete and uniform hydrolysis of I was secured. The reactor was of a tube type with parallel cylindrical cavities connected along their length and with 2 parallel stirrers. The stirrers had inclined blades partially penetrating the other cavity and rotating at a rate of 70–200 r.p.m. in opposite directions, thus moving the reaction mixt. in a translational and returning movement and cleaning the walls of the reactor. The hydrolyzate passed from the reactor through a worm conveyor into a centrifuge from which II passed for washing and drying and the filtrate for regeneration. Before the beginning of the continuous process, the reactor was filled with the NaOH soln. and heated to 40° by means of a heating jacket. The resulting II was in the form of white granules that did not require bleaching. The dimensions of the granules decreased with diln. of the soln. and even powder could be obtained. Changes in the concn. of I in the reactor from 15 to 25%, in the reaction time from 10 to 40 min., in the concn. of NaOH from 1.80 to 4.00%, and in the rate of introduction of I from 2920 to 13,000 g./hr. did not greatly influence the degree of hydrolysis (92.1–9.8%), but at 10 min. reaction time, 25% concn. of I in the reactor, and a rate of introduction of I of 19,500 g./hr., it was 81.7%. At 25% concn. of I in the reactor the degree of hydrolysis was noticeably lower (81.7–98.7%), while at concns. of 15–21%, it was >99.2% and good spinnable II was obtained in a yield of 0.4 kg./hr. M. Kalfus

Maximum conversions in acetalization of poly(vinyl alcohol) with aldehydes containing sulfonic acid groups. Ichiro Sakurada (Univ. Kyoto, Japan), Yasuyoshi Sakaguchi, and Yasuhiro Omura. *Kobunshi Kagaku* 21(233), 561-7(1964). Poly(vinyl alc.) was acetalized with aldehyde sulfonic acids, such as β-sulfobutyraldehyde, *o*-sulfobenzaldehyde, or 2,4-disulfobenzaldehyde, in soln. The max. conversions are generally much less than the calcd. values obtained by using Flory's theory (*CA* 33, 6286^9), and are dependent on the steric configurations of the polymer and the compns. of the reaction mixt. Steric hindrance and (or) electrostatic effects are apparently caused by acetals introduced into the polymer chains. Statistical calcns. are given for max. conversions. Eiichi Wada

16187

Poly(vinyl alcohol) protective colloids. Badische Anilin- & Soda-Fabrik A.-G. (by Wolfgang Sliwka and Manfred Gellrich). Ger. 1,178,593 (Cl. C 08f), Sept. 24, 1964, Appl. Dec. 15, 1961; 2 pp. Modified poly(vinyl alcs.) (I) are prepd. by sapon. of a vinyl ester mixt. contg. a cyclic carbonate, e.g., 5-methylene-4,4-dialkyl-1,3-dioxalan-2-one. For example, a mixt. contg. vinyl acetate 2375, 5-methylene-4,4-dimethyl-1,3-dioxalan-2-one 125, and azodiisobutyronitrile 2.5 parts by wt. was added to 3000 parts by wt. 0.17% aq. poly(vinyl alc.) (*K* value 60). The stirred mixt. was heated 3 hrs. at 65° and 1-2 hrs. at 92° until refluxing stopped, and the polymer obtained (II) was filtered, washed with H_2O, and dried at 40°. II (600 parts by wt.) was dissolved in 700 parts by wt. MeOH, 420 parts by wt. methanolic NaOMe was added during 2 hrs., and the mixt. was held 5 hrs. at this temp. The product was washed with MeOH and dried at 40° to give I, sapon. no. 53, and viscosity 24 cp. in 40% aq. soln. I are useful as protective colloids in emulsion polymerization, and the presence of as little as 3% I permits the prepn. of homogeneous polymer mixts. without the use of other emulsifying agents. F. N. Standen

Poly(vinyl alcohol). Monsanto Co. (by Roland J. Kern). Belg. 636,139, Feb. 13, 1964; U.S. Appl. Aug. 13, 1962; 22 pp. Dil. acid hydrolysis of poly(vinyl alkyl ethers) (I) gave poly(vinyl alcs.) (II). I must contain tertiary C_{4-16} alkyl groups, or benzyl radicals, or substituted benzyl radicals. Thus, 1.5 g. poly(vinyl *tert*-Bu ether) (III) was dissolved in 25 ml. iso-BuOH, and the soln. boiled. After the addn. of 3 ml. iso-BuOH-HCl-H_2O (1:1:1 by vol.), the mixt. was boiled for an addnl. 5 min., then allowed to cool and the II recovered. A blend of equal wts. III and poly(vinyl iso-Bu ether) (IV) similarly treated gave II and unchanged IV. II are stereospecific if the starting polymer was stereospecific. Lewis J. Young

3231

Karol Butkiewicz

Purifying poly(vinyl alcohol). Kurashiki Rayon Co., Ltd. Brit. 933,104 (Cl. C 08b), Aug. 8, 1963; Japan. Appl. Dec. [illegible] 1958; 4 pp. Poly(vinyl alcohol) (I) prepd. by sapon. is purified by a 4-step process. Thus, I is washed with MeOH, sepd. from the MeOH in a centrifuge, and dissolved in H_2O, and residual MeOH removed in a stripping tower to give an aq. soln. of [illegible]

Herbert B. Rickert

4537

Poly(vinyl alcohol) for fiber production. Zaklady Chemiczne "Oswiecim" (by Maria Tokarzewska, Jadwiga Jablonska, Halina Pietkiewicz, and Jan Mitus). Pol. 47,799, Dec. 6, 1963, Appl. Feb. 27, 1962; 3 pp. Linear poly(vinyl acetate (I) is obtained by the method described. Thus, 100 parts by wt. vinyl acetate (>99% purity and contg. aldehydes and AcOH in amts. of <0.01%) was introduced into 36.3 parts pure MeOH and 0.15 part 2,2'-azobis(2-methylpropionitrile) (II). The amt. of MeOH used in the polymerization process was 20-30% by vol. The amts. of II (0.05–0.15%) depended on the reaction temp., which may be varied within the range 50–60°. The soln. was refluxed at the b.p., and the degree of monomer condensation was controlled. Polymerization was carried out in an inert gas (N or CO_2). When condensation was 55% complete, the mixt. was introduced into the rectifying column, and the unused vinyl acetate was removed in a continuous process by azeotropic distn. with MeOH to obtain a soln. contg. ~1% monomer. Condensation should be ≦55%, because otherwise a linear structure of the polym will not be obtained. A polymer contg. <1% of monomer and having a polymerization degree of 1760 was obtained in MeOH soln. The changes in polymerization temp. and amt. of II (within the above mentioned ranges) make it possible to obtain polymers having polymerization degrees of 1200-2400 and a linear structure. Next, 10 parts by wt. of I per 90 parts of MeOH (I was also used in concns. of 10–20%) was mixed with 0.93 part of a 45% NaOH soln. per 100 parts of MeOH soln. of I (NaOH was used in amts. of 0.1–0.2 mole within reference to acetate). Sapon. was carried out with stirring at 35° for 12 min. The poly(vinyl alc.) obtained was centrifuged, washed with MeOH, and dried. A white powder (bulk d. 0.3) was obtained, and the degree of hydrolysis was 99.5%. In another case, 3 l. of MeOH soln. of I (20 parts I per 80 parts MeOH) was sapond. in 2 stages in a Werner-Pfleiderer mixer. The 1st stage was carried out at 17° for 40 min., and 0.02 mole of a 45% soln. of NaOH per 1 mole of (I) was used. Next, another 0.18 mole of NaOH soln. was added, and this 2nd stage of sapon. was carried out at 35° for 20 min. Small flakes of poly(vinyl alc.) were obtained, washed with MeOH, and dried. The degree of condensation was 99.5%.

Karol Butkiewicz

Stereoregular poly(vinyl alcohol). Clifford A. Neros and Nelson V. Seeger (to Diamond Alkali Co.). U.S. 3,141,003 (Cl. 260-2.5), July 14, 1964, Appl. May 26, 1960; 5 pp. The compn. consists essentially of a soln. of H_2O contg. 2-20% stereoregular poly(vinyl alc.) (I) which is insol. in H_2O at 100°C. I was prepd. by polymerizing a vinyl chloro- or vinyl fluoroacetate in the presence of 0.01-1% of a peroxide catalyst at 25–80°, hydrolyzing, and neutralizing the resultant I which is insol. in boiling H_2O and most solvents or combinations of solvents. For example, a 5% mixt. of I and H_2O is agitated for 30 min., transferred to a pressurized vessel, and heated to 250°F. under 15 lb./in.^{2} for 30 min. I completely dissolved. This soln. may be cooled to 85–110°C. The I soln. is cast on a glass plate and allowed to dry 48 hrs. at 73°C. and a relative humidity (R.H.) of 50%. The film is stripped from the plate and contitioned for 3 days at 73°C. and a R.H. of 50%. The film when tested had a tensile strength of 1×10^4–1.2×10^4 lb./in.^{2} and a tensile modulus of 316,700, 5×10^4 lb./in.^{2} James R. Jones

Polystyrene. N. S. Tsvetkov and E. S. Beletskaya. U.S.S.R. 162,966, May 27, 1964, Appl. Apr. 13, 1963. Polystyrene of increased mol. wt. is prepd. by mass or suspension polymerization of styrene at 65–80° in the presence of polymeric peroxides of

8440

C_{7-10} dicarboxylic acids, e.g. sebacic acid, as initiators. From *Byul. Izobret. i Tovarnykh Znakov* 1964(11), 48. MHCL

Continuous washing of highly viscous organic polymers. Wacker-Chemie G.m.b.H. (by Eduard Bergmeister, Heribert Schwarz, Rupprecht Fritzweiler, and Hans Wimmer). Ger. 1,168,641 (Cl. C 08f), Apr. 23, 1964, Appl. Dec. 30, 1959; 4 pp. After completion of polymerization, the crude mixt. is fed by means of a heated gear pump via a perforated disk or nozzles into a chamber where it is mixed with hot water entering at right angles to the direction of flow at a pressure of 5–30 atm. The mixt. is fed into a conical, fluted emulsifier rotating at 2800 r.p.m. and more H_2O is added. The mixt. then passes to a sepn. vessel arranged so that good phase sepn. is obtained.

Francis W. Wood

728

Water-insoluble poly(vinyl alcohols). Societe Anon. "Verre et Vitrification" (by Jacques L. A. See). Fr. 1,336,756 (Cl. C 08f), Sept. 6, 1963, Appl. July 18, 1962; 7 pp. A method is described for making poly(vinyl alc.) resins, plastisols, and semi-finished products insol. in H_2O at 50-80°. Poly(vinyl alc.) of 78-98% esterification or sapon. is treated with aq. furfural catalyzed with concd. HCl or H_2SO and then dried in air at 100°. For each 1% less than complete esterification or sapon., 10 g. furfural and 5 g. of acid is added per 100 g. of poly(vinyl alc.) and 12.5 g. H_2O is used per 10 g. of aldehyde. When used to treat a plastisol, the H_2O and acid replace an equal amt. of solvent. Thus, to treat 100 g. poly(vinyl alc.) of 80% sapon., 200 g. furfural, 100 g. acid, and 250 g. H_2O are used.

Florence R. Phillips

Plasticized hydroxyalkylated poly(vinyl alcohols). John N. Milne (to E. I. du Pont de Nemours & Co.). U.S. 3,106,543 (Cl. 260-45.5), Oct. 8, 1963, Appl. Apr. 12, 1960; 3 pp. Hydroxyethylated poly(vinyl alc.) I is used to plasticize untreated I. Films cast from the resulting compns. retain their high flexibility, low brittleness, and good elongation over a wide range of relative humidities. An alkylene oxide, preferably ethylene oxide, reacts with an aq. soln. of I to produce hydroxyethylated I. The resulting compn., believed to consist of hydroxyethylated I together with ethylene glycol and polyethylene glycols, is used to plasticize untreated I and may itself be used as self-plasticized modified I. The reaction may be carried out over a wide range of temps. (10-150°) and pressures (1-50 atm.) The final compn. contains 5-50% by wt. of chem. combined ethylene oxide based on the wt. of I used. The films gave good results when used to package the detergent Tide upon exposure to atms. of 0 and 100% humidity.

Mark Plunguian

3105

Dehydration of poly(vinyl alcohol). E. N. Rostovskii and I. E. De-Millo. *Zh. Prikl. Khim.* 36(8), 1821-4(1963). A sample of 0.0856 g. 98.3% poly(vinyl alc.) was heated with 0.5 g. CaH_2 in dry pyridine at 117° for 5.5 hrs. or until evolution of H ceased. Under these conditions, dehydration was practically complete.

Florance Williams Beers

Cobalt catalysts for preparing syndiotactic 1,2-polybutadiene. Ermanno Susa (Soc. Montecatini, Novara, Italy). *J. Polymer Sci.* Pt. C 1963(4), 399-410. Stereospecific polymerization of butadiene (I) with catalyst contg. trialkylaluminum (II) or a mixt. of II and dialkylaluminum halide and mixts. and derivs. of Co and other metals of Group VIII was obtained. Highly pure syndiotactic 1,2-poly-I, and 1,4-*cis*-poly-I were prepd. The reaction conditions directing the polymerization in one or in the other stereoisomeric polymer were compared. Results of x-ray analysis and infrared spectroscopy are reported. These expts. confirm the exceptional selectivity of Co catalysts in obtaining stereoisomeric polymers of I.

Myra T. Willard

Isotactic poly(vinyl alcohol). Shunsuke Murahashi, Heimei Yuki, Takezo Sano, Utami Yonemura, Hiroyuki Tadokoro, and Yozo Chatani (Univ. Osaka, Japan). *J. Polymer Sci.* 62(174), S77-S81(1962). The title compd. (I) was prepd. by debenzylation of isotactic poly(vinyl benzyl ether) (II). $CH_2:CHOCH_2Ph$ was purified by distn. from $LiAlH_4$, and polymerized with BF_3 at −78° in *n*-heptane-MePh mixt. The Me_2CO-insol. fraction was repptd. from MePh and MeOH to give II. A quant. yield of I was obtained when II was treated with HBr in MePh at room temp. I was considered to be isotactic since the infrared spectra of I and atactic poly(vinyl acetate) differ in various detailed features, and since the parent polymer of I was confirmed by x-ray diffraction to possess an isotactic structure. The mol. arrangement of I is discussed.

A. Foxton

Relation between the degree of polymerization of poly(vinyl [illegible]) and its method of preparation. Tadeusz Rosner, Z[illegible]a Pintowska, and Joanna Kosmider. *Zeszyty Nauk. Politech. Szczecin. Chem.* No. 3, 63-81(1961). The dependence of the [illegible] degree of polymerization (D.P.) of poly(vinyl alc.) as a function of conditions of alk. or acidic alcoholysis of poly(vinyl acetate) was detd. During the initial [illegible] hrs. of reaction, a decrease in the [illegible] D.P. was observed; the av. D.P. increased in the next [illegible]

3110

hrs. [illegible] D.P. was much higher than in the case of the alk. reaction. The av. D.P. of poly(vinyl acetate) was detd. from the intrinsic viscosity $[\eta]$ by the equation $[\eta] = 1.76 \times 10^{-4} + M^{(0.66)}$, where M is the mol. wt. The av. D.P. of poly(vinyl alc.) was calcd. from the formula $[\eta] = (-0.00779 + 0.01992\alpha - 0.0115\alpha^2)M^{(0.64 - 0.2\alpha + 0.34\alpha^2)}$ where α = acetate content expressed as fraction of unity. M was then converted to av. D.P. by using the relation $D.P._{av.} = M(86-42\alpha)$. Alk. and acidic alcoholyses were both carried out in anhyd. MeOH, in the presence of NaOH and H_2SO_4, resp.

E. Wieckowski

4276

Poly(vinyl alcohol). Romania, Ministry of Petroleum and Chemical Industry (by Alexandru Lupu and Maria Opris). Fr. 1,334,037 (Cl. C 08f), Aug. 2, 1963, Appl. Aug. 7, 1962; 4 pp. Poly(vinyl alc.) (I) with [illegible] crystallinity can be obtained by the alcoholysis of poly(vinyl acetate) (II) prepd. by polymerization in a ketone. Thus, 200 parts $AcOCH:CH_2$, [illegible] Me_2CO, and 0.1-0.7% [illegible] were refluxed with agitation to produce II, of which [illegible] parts was added to 1000 parts MeOH (or MeOAc [illegible]) 2.7% NaOH. Refluxing with agitation was then continued to completion. The I thus obtained had a [illegible]rystallinity [illegible] 75% ([illegible] an [illegible] solid) and [illegible]ty of 32. The substitution [illegible] MeCOEt for [illegible] provided a I [illegible] of 15.

Herbert Schwartz

5663

Paul P. Birnhaum

Poly(vinyl alcohol). A. F. Nikolaev, S. N. Ushakov, L. P. Vishnevetskaya, and E. V. Lebedeva. U.S.S.R. 157,106, Sept. 25, 1963, Appl. June 15, 1962. Poly(vinyl alc.) is prepd. by aminolysis of poly(vinyl acetate) with monoethanolamine (I). To accelerate the process, an excess amt. of I is used. From *Byul. Izobret. i Tovarnykh Znakov* 1963(17), 66.

MDCL

Copolymers of vinyl alcohol. S. N. Ushakov and E. F. Panarin. U.S.S.R. 157,105, Sept. 25, 1963, Appl. Apr. 23, 1962. In the prepn. of copolymers of vinyl alc. with hydrazides of unsatd. carboxylic acids (I), copolymers of complex vinyl esters with esters of I are heated with an excess of $N_2H_4.H_2O$. From *Byul. Izobret. i Tovarnykh Znakov* 1963(17), 65.

MDCL

Graft copolymers. Z. A. Rogovin and R. M. Livshits. U.S.S.R. 157,108, Sept. 25, 1963, Appl. Dec. 22, 1961. The above copolymers are obtained by polymerization of H_2O-sol. vinyl monomers in the presence of a polymer having groups with reducing properties (CHO, NH_2, C:O) and oxidizing agents. In order to widen the choice of oxidizing agents, compds. of V(V) are used. From *Byul. Izobret. i Tovarnykh Znakov* 1963(17), 66.

MDCL

6947

Hydrolysis of poly(vinyl acetate) of various tacticities. Kiyoshi Fujii, Junji Ukida, and Masakazu Matsumoto (Kurashiki Rayon Co., Okayama, Japan). *J. Polymer Sci.* Pt. B 1(12), 687-91(1963). The initial hydrolysis rate const., K_0, at 30° of poly(vinyl acetate) (I) of various tacticities was: isotactic I 0.07, stereoblock I 0.13, conventional and syndiotactic I 0.07 mole/l./min. The rate of hydrolysis was relatively insensitive to the tacticity of the polymer as compared with the rate of hydrolysis of poly(vinyl acetal). The effect of the tactic structure on the rate becomes noticeable only when isotactic sequences longer than some crit. lengths are present in I samples.

John H. Dittmar

Schotten-Baumann esterification of poly(vinyl alcohol). I. Minoru Tsuda (Govt. Chem. Ind. Res. Inst., Tokyo). *Makromol. Chem.* **72**, 174-82(1964)(in English). The Schotten-Baumann method for the esterification of poly(vinyl alc.) (I) by cinnamoyl chloride (II) is discussed in the light of its reaction mechanism and the use of various org. solvents, alkalies, and detergents. II, dissolved in a mixt. of PhMe and MeCOEt, is

14628

added to the aq. mixt. of I and NaOH or KOH at low temp. to yield poly(vinyl cinnamate), which is dissolved in the org. layer. Weak alkalies have no effect, suggesting that the ionization of the OH groups of I plays an important role in the esterification. The addn. of surface-active agents lowers the yield since the esterification of semi-esterified I in the later stages of the reaction proceeds in the org. solvent layer and the detergents aid only in the hydrolysis of the chloride. II. *Ibid.* 183-90. A reaction mechanism for the Scotten-Baumann esterification of I to poly(vinyl cinnamate) is proposed and the apparent activation energy is calcd. a 10.4 kcal./mole.

G. V. Aseff

16003

Poly(vinyl alcohol). Mitsuhishi Chemical Industries Co., Ltd. (by Seizo Okamura and Toshinobu Higashimura). Japan. 7136('63), May 27, Appl. Jan. 14, 1961; 1 p. Poly(vinyl alc.) is prepd. from poly(vinyl *tert*-butyl ether) (I) by cleavage of the ether linkage by a H halide. The reaction takes place in soln. or in a swollen state of I. Thus, a mixt. of 30 parts vinyl *tert*-Bu ether (II) and 70 parts *n*-C_6H_{14} was cooled to −78°. After the addn. of $BF_3.Et_2O$ (0.07 millimole for II), the mixt. was stirred for 00 min. in the absence of air. I (5 g.) thus obtained was dissolved in 40 cc. $CHCl_3$. After the addn. of 10 cc. AcOH, anhyd. HBr was introduced for 10 min. at 0° and the mixt. was let stand for 1 hr. A solid product (2.1 g.) was obtained. It was sol. in hot water and insol. in acetone; its intrinsic viscosity in H_2O at 30° was 0.91.

Yo Miyagi

16041

Synthetic poly(vinyl alcohol) fibers. Kurashiki Rayon Co., Ltd. (by Akio Mitamura, Kenji Akabane, Norimoto Kawai, Osamu Morimoto, Naoo Ashikaga, and Kenichi Tanabe). Japan. 912('64), Feb. 3, Appl. Jan. 27, 1961; 6 pp. Poly(vinyl acetate) obtained by photopolymerization at −40° is sapond., and the resulting poly(vinyl alc.) (degree of polymerization 1700 on the av.) is dissolved in H_2O with 3.0% 4,5-dihydroxyimidazoline. The soln. is spun into Na_2SO_4 soln. (420 g./l.) kept at 45°, the fibers are stretched 100% by use of rollers, dried, then stretched to their max. length with heating at 240° 5 sec., and heated in 245° air with 15% shrinkage to give fibers of 10.5 g./denier tenacity and 12.5% elongation, softening at 120° in H_2O. The use of cyclic ethylenethiourea, cyclic propylenethiourea, cyclic ethyleneurea, and thiourea instead of 4,5-dihydroxyimidazoline also gave similar products.

Hiroshi Kataoka

2203

Partially saponified product from polyvinyl acetate. Shohei Masuda and Yoshikazu Takamatsu (to Sekisui Chemical Industries Co.). Japan. 6893('54), Oct. 23. Polyvinyl acetate of mol. wt. 2800 (50 g.) in 450 g. 90% MeOH and 100 g. hexane was sapond. at 40° with 1.16 g. NaOH to give a white powder contg. 83% polyvinyl alc. K. Kitsuta

6086

Standard drying method of a high polymer. I. Historical, standard method, and apparatus. Hiroshi Miyabe and Yasushi Yano (Waseda Univ., Tokyo). *Chem. High Polymers* (Japan) 11, 455–9(1954).—Drying methods of high polymers proposed by several authors are summarized. For the purpose of studying the standard drying method, a drier is constructed which consists of a spring balance in a oil bath, a vapor trap, a H_2SO_4 reservoir, and a vacuum pump. The temp. of the spring is kept const. by a water jacket. II. Drying process of polyvinyl alc. by strong heat-treatment. *Ibid.* 459–64.—Changes in wt. and water-sorption ability due to vacuum drying (10^{-4} mm. Hg) are measured from 150° down to room temp. for 3 kinds of polyvinyl alc., i.e., unpurified polyvinyl acetal fiber (I), polyvinyl alc. fiber (II), and purified polyvinyl alc. fiber. The wt. decrease of II is larger than that of I. The results are considered in connection with the second-order transition temp. Eiichi Wada

9785

Poly(vinyl alcohol). John E. Bristol and Walton B. Tanner (to E. I. du Pont de Nemours & Co.). U.S. 2,734,048, Feb. 7, 1956. A continuous method of producing a substantially completely hydrolyzed poly(vinyl alc.) (I consists of feeding a soln. of poly(vinyl acetate) (II) in MeOH into a heated vessel contg. 0.2–0.5% MeONa so as to maintain unreacted II at 0.2–0.5%, distg. off most of the MeOAc formed, and sepg. I as a 25% slurry. J. T. B.

Poly(vinyl alcohol). Setsuo Yoshioka, *et al.* (to Nippon Synthetic Chemical Industries Co.). Japan. 8445('54) Dec. 21. Sapon. of an emulsion of poly(vinyl acetate with mineral acid is effected by adding 5–10% of a water-sol solvent, such as MeOH or a partly sol. solvent, e.g. Me_2CO K. Kitsuta

13504

Poly(vinyl alcohol) and its water-soluble derivatives. Farbwerke Hoechst A.-G. vorm. Meister Lucius & Brüning (Werner Starck, inventor). Ger. 874,664, Apr. 27, 1953 (Cl. 39*c*, 25_{01}). Aq. emulsions of poly(vinyl esters) or copolymers of vinyl esters are sapond. with a small amt. of an inorg. acid in the presence of a low-boiling alc. (MeOH or EtOH) and possibly of substances, such as aldehydes, capable of reacting with the OH radicals of the poly(vinyl alc.). The carboxylic esters formed as a by-product are constantly removed by distn. to give solns. of poly(vinyl alc.) (I) or its water-sol. derivs. Thus, a glass vessel equipped with a fractionation column was filled with 400 g. of a 50% poly(vinyl acetate) emulsion prepd. with a 5% I soln. as an emulsifying agent. A mixt. of 100 g. MeOH and 8 g. concd. H_2SO_4 was added with stirring and the mixt. heated with agitation at 85–90°. AcOMe (II) began to distil off after about 2 hrs. and the emulsion gradually changed to a clear soln. After 10 hrs., a 200 g. distillate composed of 75% II and 25% MeOH was recovered. The distn. was continued for 1 hr. without fractionation. A pale-yellow, clear I soln. remained. It was suitable, after diln. with water, as an emulsifying agent in the manuf. of poly(vinyl acetate) emulsions. G. Stargard

Light- and heat-stable condensation products of poly(vinyl alcohol). Farbwerke Hoechst A.-G. vorm. Meister Lucius & Brüning (Hans J. Hahn and Fritz Winkler, inventors). Ger. 888,008, Aug. 27, 1953 (Cl. 39*c*, 25_{01}). Poly(vinyl alc.) (I) or its derivs. are condensed with aliphatic aldehydes in the presence of a small amt. of a substituted aldehyde contg. a functional radical, e.g. OH, NO_2, S, or NRR′ (R and R′ = H or alkyl); a heterocyclic aldehyde contg. N or S in the heterocyclic nucleus; or of a mixt. of such aldehydes to give light- and heat-stable condensation products. Thus concd. HCl 66, butyraldehyde (II) 63, and $3\text{-}H_2NC_6H_4CHO$ (III) 1 part were added at 0° with agitation to 1000 parts of a 10% aq. I soln. in EtOH. Stirring was continued for 2 hrs. at 0° and the mixt. heated for 3 hrs. at 25°. The ppt. (IV) was washed free of acid, treated with aq. NaOH to neutralize acids, and dried. The pale-yellow powd. IV recovered was particularly suitable for the manuf. of *lacquers*. Heating IV at 140° caused almost no change in color and no sintering, whereas a condensation product prepd. in the absence of III and tested similarly gave a molten, brown glassy mass after 1 hr. of heat-treatment. A product obtained by condensing poly(vinyl acetate) 240 in MeOH 360 with II 84 in the presence of concd. H_2SO_4 12 and $(EtO)_2CHCH_2S_2CH_2CH(OEt)_2$ (V) 0.12 part mixed with a softener, e.g. di-Bu phthalate, gave a light- and heat-stable foil useful as interlayer in the manuf. of safety glass. Salicylaldehyde, *o*-, *m*-, or *p*-nitrobenzaldehyde, 3-nitro-4-methylthiobenzaldehyde, 4-thiocyanobenzaldehyde, 4-methylthiobenzaldehyde, *β*-methylthiopropionaldehyde, *β*-methylthiobutyraldehyde, *α*-thiophenecarboxaldehyde diethyl acetal, piperidinoacetaldehyde, *o*-quinolinecarboxaldehyde, or *α*-thiophenecarboxaldehyde can be used instead of III or V. Ger. 906,754 (Fritz Winkler and Hans J. Hahn; to same assignee), Mar. 18, 1954. Light- and heat-stable condensation products from I or its derivs. and aliphatic aldehydes can also be obtained by adding substituted aldehydes to the finished acetals. Thus, a soln. of *m*-nitrobenzaldehyde 1 in MeOH 40 was dropped with agitation into a suspension of poly(vinylbutyral) 100 in water 400 parts. The product was a white powder stable on heating for 2 hrs. at 135°. G. Stargard

Formals of poly(vinyl alcohol) containing acetyl radicals. Wacker-Chemie G. m. b. H. (Josef Heckmaier and Hugo Zoebelein, inventors). Ger. 891,144, Sept. 24, 1953 (Cl. 39*c*, 25_{01}). The prepn. of the above by treating Ac-contg. poly(vinyl alcs.) with HCHO in the presence of acids is improved by use of a mixt. of dil. HCl and glacial AcOH (I) capable of dissolving poly(vinyl alc.) or its Ac-contg. derivs. The content of Ac radicals in the formals is raised by increasing the amt. of I in the acid mixt. and decreased by increasing the HCl. Thus, poly(vinyl alc.) (II) 1000, sapon. no. 127, was mixed with I 400, 36% HCl 140, and 40% HCHO 1000 g. The mixt. contained about 7% HCl and about 40% AcOH based on the aq. phase. The mixt. was gradually heated to 65° and the reaction completed after 2 hrs. The fine flocculent product isolated by pptn. with water consisted of poly(vinyl acetal) (III) 79.6, poly(vinyl acetate) (IV) 11.7, and II 8.7%. Similarly, an acetal contg. III 87.8, IV 2.2, and II 10.0% was obtained by dissolving II (sapon no. 150) 100 in a mixt. of water 410 and I 60, adding 36% HCl 600 and 40% HCHO 125 kg., and heating the mixt. for 2 hrs. at 85°. G. Stargard

Poly(vinyl alcohols). Farbwerke Hoechst A.-G. vorm. Meister Lucius & Brüning (Hans J. Hahn, inventor). Ger. 895,980, Nov. 9, 1953 (Cl. 39*c*, 25_{01}). Pearl-shaped poly(vinyl ester) beads obtained by polymerization of vinyl esters (I) in the presence of poly(vinyl alc.) (II) as a dispersing agent are, after removal of unpolymerized I, sapond. with org. or inorg. acids in an aq. suspension in the presence of alcs. The carboxylic esters formed as by-products are simultaneously stripped off. Thus, 1000 kg. $AcOCH:CH_2$ contg. 350 g. *o*-toluoyl peroxide was added in 1.5 hrs. with agitation to a mixt. of 1000 l. distd. H_2O, 4 kg. highly viscous II, and 2.5 kg. Ac_2O heated to 70°. The polymerization was completed in about 2.5 hrs. Unreacted monomers were removed by steam distn. The residue was dild. with 1000 l. distd. H_2O, mixed with 30 kg. H_2SO_4, dissolved in 1000 kg. MeOH, and refluxed until the sapond. poly(vinyl acetate) was sol. in the water-MeOH mixt. (about 1.5 hrs.). The AcOMe formed was slowly removed by distn. After about 5 hrs. the sapon. was 99% complete. Excess MeOH was then removed by distn. G. Stargard

Plastic loom picker from poly(vinyl alcohol) and a metal stearate. John W. Baymiller (to Armstrong Cork Co.). U.S. 2,750,348, June 12, 1956. Serviceable loom pickers which are unaffected by normal service conditions of temp., humidity, and shock are molded from compns. contg. poly(vinyl alc.) and a Zn or alk. earth stearate which have been heated with mastication in air at 280–340°F. prior to molding. Thus, poly(vinyl alc.) 100, TiO_2 5, and Mg stearate 2 parts were mixed for 0.5 hr. Water (50 parts) was added with continued mixing, and the mass allowed to stand overnight. Glycerol (60 parts) was mixed in and, after standing overnight, the mixt. was heat-treated on a mill at 330–40°F. for 8–10 min. The cooled mixt. was then pulverized to obtain a molding powder suitable for manuf. of loom pickers. H. N. Dyer

Poly(vinyl esters). Farbenfabriken Bayer A.-G. (Max Coenen and Karl Hamann, inventors). Ger. 887.123, *a* Aug. 20, 1953 (Cl. 39*c*, 25_{01}). Diketene (I) treated with OH-contg. vinyl polymers, e.g. poly(vinyl alc.) (II) or its partly esterified, etherified or acetalized derivs., or sapond. copolymers from poly(vinyl acetate), poly(vinyl chloride), or polyacrylic esters, gives acetoacetic esters of II suitable for the manuf. of shaped articles. The reaction is carried out in the presence of the usual solvents or swelling agents, e.g. MeCl, CH_2Cl_2, $CHCl_3$, CCl_4, PhCl, 1,2-$Cl_2C_6H_4$, Me_2CO, MeCOEt, cyclohexanone, or methylcyclohexanone. Thus, 40 parts *b* I was added with stirring to 40 parts of a soln. of a sapond. 80:20 $CH_2:CHCl/AcOCH:CH_2$ copolymer (OH content about 3%) in 400 parts PhCl, heated to 100–20°, the mixt. boiled 1 hr., excess I and PhCl removed by distn. *in vacuo*, and the residue kneaded with an equal vol. of MeOH to give 42 parts of a crumbly mass which hardened after drying. G. Stargard

Poly(vinyl acetals). Farbwerke Hoechst A.-G. vorm Meister Lucius & Brüning (Adolf Weihe and Fritz Herrlein, *c* inventors). Ger. 891,745, Oct. 1, 1953 (Cl. 39*c*, 25_{01}) Poly(vinyl acetals) with an improved water resistance and a high rate of acetalization are obtained by acetalization of the sapon. products of org. poly(vinyl esters) (I) or of copolymers of I and unsatd. carboxylic acids or their esters. The materials are treated with aldehydes or cyclic ketones in dil. mineral acids at <12°, preferably 0–4°. I can be preacetalized with an insufficient amt. of a higher-mol. aldehyde or a cyclic ketone and the acetalization can be completed with *d* an excess of a lower-mol. aldehyde. Thus, 3.2 l. 10% methanolic NaOH was triturated with a homogenized mixt. of 40 kg. poly(vinyl acetate), *k* value 75, and 60 kg. MeOH until the mixt. became water-sol. Excess MeOH and AcOMe formed as by-products were removed by centrifugation. The resulting poly(vinyl alc.) (II) was added with agitation to 268 l. water. The II soln. was filtered, cooled to 0°, treated with 15 kg. AcH, and cooled to 0°. Cooled 18% HCl (50 kg.) was added with stirring after 0.5 hr., the temp. *e* of the mixt. being thus increased to 4–5°. The poly(vinyl acetal) formed began to ppt. after approx. 1.5 hrs. and agitation was continued for 2 hrs. The solid product was filtered off, triturated repeatedly in 1.5 hrs. with 500 l. water until it was free of acid, heated for 5 hrs. at 40–50° with 300 l. 0.2% NH_4OH, isolated once more by centrifuging, and dried at 40° in an air stream. A loose, white polymer (rate of acetalization 82%) sol. in C_6H_6, AcOEt, C_6H_6-EtOH mixts. etc., was recovered. II can be similarly *f* acetalized with isobutyraldehyde and AcH added successively, or with cyclohexanone or methoxybutyraldehyde. A 90:10 $AcOCH:CH_2$/Me maleinate copolymer can be acetalized similarly with AcH. Ger. 904,592, Feb. 22, 1954. More uniform and granular poly(vinyl acetals) are obtained if the acetalization mixts. are heated after completion of the process at >20°. Thus, poly(vinyl alc.) (prepd. by sapon. of 258 kg. of a highly viscous poly(vinyl acetate) with 7 l. 20% methanolic NaOH) was dissolved in 1480 l. water at 80–90°. The soln. was filtered and the filtrate cooled at *g* 0°, triturated with 71 kg. cyclohexanone, and 360 kg. 18% HCl added after 15 min. The mixt. was maintained for 2 hrs. at 4° with agitation and 97.5 kg. AcH was added, resulting in a temp. rise to 7°. The mixt. was cooled to 4°, held 1 hr., and after another hr. heated 0.5 hr. to 40° and agitated for 1 hr. at this temp., unreacted AcH being removed by distn. The mixt. was dild. with 1200 l. water, cooled to 15°, and the pptd. fine-grained poly(vinyl acetal) worked up as specified above. G. Stargard

h **Polymerization of vinyl esters in aqueous emulsions.** Farbwerke Hoechst A.-G. vorm. Meister Lucius & Brüning (Werner Langbein and Werner Starck, inventors). Ger. 894,450, Oct. 26, 1953 (Cl. 39*c*, 25_{01}). Polymerization of vinyl esters in aq. media in the presence of poly(vinyl alc.) (I) or its water-sol. deriv. by means of an oxidation-reduction system contg. H_2O_2 and a Fe compd. gives polymers of a high *k* value. Thus, 0.165 part 40°Bé. $NaHSO_3$ liquor and an amt. of Mohr's salt sufficient to adjust the Fe content of *i* the total mixt. to 0.003% was added to 25 parts of a 5% poly(vinyl alc.) soln. (viscosity about 100 centipoises, pH 6.3) which had been evacuated at 60° to expel the O present. $AcOCH:CH_2$ (25 parts) was added and 1.5 parts 1% H_2O_2 was gradually dropped in at the b.p. Heating the mixt. for

0.5 hr. gave a poly(vinyl acetate) emulsion, *k* value 110. G. Stargard

Solution of poly(vinyl alcohol) in water. Tetsuro Osugi, *et al.* (to Kurashiki Rayon Co.). Japan. 991('55), Feb. 17. Poly(vinyl alc.) (20 g.) and 80 g. water were heated for 3 min. at 70° in a metal container by passage of a 100-v. a.c. through the mixt. The container was used as one electrode and the other electrode was located in the center of the container. When external heating was used, 60 min. at 83° was required for complete soln. K. Kitsuta

Poly(vinyl alcohol). Kiyoshi Shibata, *et al.* (to Morimata Co.). Japan. 1246('55), Feb. 24. An alc. soln. 100 contg. poly(vinyl acetate) (mol. wt. 15,000) 30 parts was treated with 1/6 of its equiv. of 50% NaOH, sapond. by heating at 30–60°, and the ppt. filtered. The ppt. was let stand for 30 min. at room temp. in several vols. of alc. and 0.1% of its wt. of NaOH and the soln. drained off to give poly(vinyl alc.) (mol. wt. 2500) of 99.99% purity and contg. <0.1% NaOH. K. Kitsuta

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Polyvinyl alcohol. Clemens Bondy and Kurt Reiser (to Revertex Ltd.). Brit. 749,458, May 23, 1956. Polyvinyl esters were alcoholyzed with low mol. wt. aliphatic alcs. in such a manner that the formed *polyvinyl alcohol* (I) pptd. from soln. in the form of fine particles. *Polyvinyl acetate* (41 kg.) was dissolved in 41 kg. MeOH and 3.2 kg. MeOAc and treated with 6.8 kg. 10% methanolic NaOH and 46 kg. high-boiling aliphatic hydrocarbon (Risella Oil 33), contg. 110 g. stearic acid. After 1 hr. of mixing the soln. was neutralized with 195 ml. HOAc and allowed to sep. The upper oil layer was drawn off and the solid I sepd. from any remaining solvent and washed with several portions of freshly distd. solvent. William C. York

14323

A purified poly(vinyl alcohol). John E. O. Mayne, Henry Watson, and Ralph M. Levine (to Vinyl Products Ltd.). Brit. 766,565, Jan. 23, 1957. Poly(vinyl esters), more or less completely hydrolyzed to poly(vinyl alc.) emulsions (cf. Brit. 655,734, *C.A.* 46, 3900*b*), can be purified by the addn. of alcs. or ketones to cause pptn. of the polymer. If a small amt. of such org. solvent is added, a "crit. gel" is formed. This is more mannageable and may be extruded into excess solvent which ppts. the poly(vinyl alc.) as a thread. The product may even be obtained as a fine powder by the use of equal parts of emulsion and acetone to give a "hypercrit. gel." This was extruded into acetone at a temp. <60°. The wt. of solvent used is 8–12 times that of the polymer, but recovery is good. The purified polymer may have 3% residual acid. It is useful as an emulsifying agent for the further polymerization of vinyl acetate. N. M. Foote

Poly(vinyl alcohol). Norsk Hydro-Elektrisk Kvaelstofaktieselskab. Brit. 774,729, May 15, 1957. See Norw. 85,683 (*C.A.* 50, 7504*f*). John T. Barr

Poly(vinyl alcohol) derivatives. Massimo Baer (to Monsanto Chemical Co.). U.S. 2,796,413, June 18, 1957. A process is described for the prepn. of poly(vinyl alc.) derivs. contg. ester groups and carboxylic acid groups and, if desired, OH groups. Thus, by heating a soln. of 100 parts of 75% hydrolyzed poly(vinyl acetate) and 135 parts maleic anhydride (I) in 1200 parts anhyd. di-Me formamide for 2 hrs. at 80° and pouring into benzene pptd. a product, sol. in water and MeOH and in a mixt. of 75 parts acetone and 25 parts water. By titration, it was found that approx. 40% of the available OH groups were combined with the I. The product therefore contained about 25% acetate groups, about 30% maleic acid groups, and about 45% OH groups, calcd. on the OH groups in poly(vinyl alc.). These products are useful as soil conditioners, destaticizers, textile-finishing agents, and may be cross-linked to provide a thermoset product. They may be cast into films or molded by conventional methods. J. T. Barr

15177

Aqueous dispersions of poly(vinyl acetate). Lonza Elektrizitätswerke und Chemische Fabriken A.-G. Swiss 315,329, Sept. 29, 1956 (Cl. 41). The following substances are used: [illegible] g. water, 300 g. 10% aq. poly(vinyl alc.) soln., 16 g. AcH (in 20 cc. water), 0.2 g. Na formaldehydesulfoxylate (in 50 cc. water), 650 g. vinyl acetate monomer, and 2.5 cc. 30% H_2O_2 (of which 2 cc. is dissolved in the monomer and an addnl. 0.5 cc. is added with the first portion). The water and poly(vinyl alc.) in a reaction vessel are swept out with H, heated at 65–70° with agitation, and the residual gas is allowed to escape. From a separate vessel, all of the formaldehyde-sulfoxylate and the AcH are added and then 60 cc. of vinyl acetate monomer is added along with 0.5 cc. of addnl. 30% H_2O_2. On continued heating at 68–70° for 30–40 min., the pressure reaches 0.8–1 atm. to start the reaction. When the pressure stabilizes at 0.5 atm., the reaction is terminated by the addn. of another 60 cc. monomer. Heating and observation of pressure are continued as before. In this way all the monomer and H_2O_2 are added over a period of 2 hrs., with a total reaction time of 7 hrs. On cooling, a dispersion is obtained of 60 poise viscosity, of 54% solids (51% poly(vinyl alc.)), 1.8–2 μ diam. particles, and pH 4.2. The suspension is spread on a glass plate and dried in air for 12 hrs. to give a glossy, transparent film which would not come off by rubbing with a wet brush. On prolonged immersion in water the film sepd. but retained its homogeneity. A similar dispersion made in the absence of AcH and dried on a glass plate as a transparent film sepd. by rubbing with a wet brush or by prolonged immersion in water. In general, the improved resistance to moisture was obtained by the presence of only 20–30% AcH, based on the vinyl monomer at the beginning of the reaction. Similar results were obtained with film plasticized with 25% [on poly(vinyl acetate)] of dibutyl phthalate. The poly(vinyl alc.), used as protective colloid, contained 38% vinyl acetate groups and had a viscosity of 25 centipoises in 5% aq. soln. at 20°. Mark Plunguian

Improved polymeric sulfonyl chlorides. Bela Gaspar. Brit. 776,044, June 5, 1957. Polymeric sulfonyl chlorides treated with dye-forming compds. in *photographic colloids* produce colors which are fast to diffusion. Such sulfonyl chlorides are made by introducing SO_2Cl groups into polymers contg. recurring aromatic rings, such as polystyrene (I). Thus, 25 parts by wt. Dow Resin PS-1 (I of mol. wt. 6000) in 80 parts by vol. $MeCHCl_2$ (II) was added to 120 parts by vol. $HOSO_2Cl$ (III) during 2 hrs. at 0° and stirred for 3 hrs. to form a homogeneous soln. The addn. of 700 parts by vol. of II pptd. a poly(styrenesulfonyl chloride) which was washed 3 times each with 250 parts by vol. II. The nearly colorless solid residue was sol. in aq. NaOH, acetone, and $HCONMe_2$, but insol. in C_6H_6. It had an equiv. wt. of 215 indicating 95% chlorosulfonation. Similarly, Dow Resin PS-2 (I of mol. wt. 9000) as well as a copolymer of styrene and diethyl maleate are chlorosulfonated. Satd. aliphatic hydrocarbons or their chlorinated derivs. may be substituted for II. The large excess of III acts as a solvent for the sulfonyl chlorides during the reaction. E. D. Witman

Modified poly(vinyl alcohol). I. Solubility and swelling of vinyl and allyl alcohol copolymer films in water. Gisaku Takahashi and Ichiro Sakurada (Kyoto Univ.). *Kobunshi Kagaku* **13**, 449–54(1956).—Copolymers (I) of vinyl alc. and allyl alc. are prepd. by sapon. of copolymers of vinyl acetate (II) and allyl acetate (III). The initial concn. ratios II:III are 98:2, 95:5, 90:10, and 80:20. The soly. and swelling property of films in water at 30, 50, and 80° are measured after heating them at 100, 120, 140, 160, 180, and 200°. I films dissolve and swell more easily than do II films, e.g., I film containing 5% of allyl alc. is completely sol. in water at 30° after heating at 30°, whereas for II only 4.7% of the sample is dissolved. **II. Solubility and swelling of vinyl and isopropenyl alcohol copolymer films in water.** *Ibid.* 497–501. —Copolymers (I) of vinyl alc. and isopropenyl alc. are prepd. by the sapon. of copolymers of vinyl acetate (II) and isopropenyl acetate (III). Initial concn. ratios II:III are 98:2, 95:5, 90:10, and 80:20. The soly. and swelling property of I films in water at 30 and 50° are measured after

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heating at 100, 120, 140, 160, and 180°. Properties of I films are similar to those of the films of copolymers of vinyl alc. and allyl alc. I films are more easily sol. and swellable in water than are ordinary poly(vinyl alc.) films. **III. Stability of vinyl and allyl alcohol copolymer solution.** *Ibid.* 502–6.—Copolymers of vinyl alc. and allyl alc. (1.3 and 5 mole %) are prepd. by sapon. of copolymers of vinyl acetate and allyl acetate. Viscosities of the aq. solns. (5, 10, and 15 g./100 cc.) are measured after standing at 15, 10, 5, and 0°, and are compared with that of poly(vinyl alc.). These solns. are very stable, and their viscosity increase on standing is very small compared with those of poly(vinyl alc.) solns. E. W.

18702

High-purity poly(vinyl alcohol) or partially deacetylated poly(vinyl acetate). Seizo Murakami (to Dai Nippon Spinning Co.). Japan. 7447('55), Oct. 15. High-purity poly(vinyl alc.) or partially deacetylated poly(vinyl acetate) was prepd. by the sapon. of poly(vinyl acetate) with the addn. of an aq. soln. of NH_3 or NH_3 gas to a MeOH or EtOH soln. of poly(vinyl acetate). Thus, 3.0 g. poly(vinyl acetate) was dissolved in 30 ml. MeOH and sapond. by the addn. of 9.0 ml. of about 20% com. liquid NH_3 at about 20° for 48 hrs.
S. Inokawa

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Hollow particles for low-density products. Franklin Veatch and Ralph W. Burhans (to Standard Oil Co. (Ohio)). U.S. 2,797,201, June 25, 1957. Discrete, hollow, spherical particles substantially free from holes and resistant to shrinkage are formed when water solns. of PhOH-HCHO resins, poly(vinyl alc.), or SiO$_2$ are spray dried in the presence of 0.1–1.0% of such latent gas formers as (NH$_4$)$_2$CO$_3$, NH$_4$NO$_2$, or dinitrosopentamethylenetetramine; materials such as *p*-hydroxyphenylazide, CO$_2$, or MeCl prevent hole formation, but not shrinkage. Particles range up to 100 μ in size, have a bulk d. of 0.1–0.2 g./cc., and approx. 97% of them float on naphtha after 24 hrs. Solid sheets, blocks, or shaped masses of varying d. are prepd. by molding PhOH-HCHO "Microballoons" with rubber cement, aq. Na silicate, aq. rubber latex, Vinsol resin powder, portland cement, or gypsum powder. The products are useful as ***thermal insulation***, as ***fillers*** in manuf. of ***molded articles***, ***linoleum***, and ***floor tile***, and as aggregates in ***concrete*** and ***plaster***. E. L. London

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The preparation of poly(vinyl alcohol) by alcoholysis of poly(vinyl acetate) in the presence of a polyacid catalyst. II. The lifetime of the cationite catalysts and regeneration possibilities. I. P. Losev, O. Ya. Fedotova, and G. N. Freidlin (Plant "Polyvinyl acetate," Erevan). *Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki* 11, No. 1, 31–6 (1958); cf. *C.A.* 52, 12529*i*.—Kationite MSF-3 showed an initial capacity of 310 mg. KOH per g. After reaction with its fourfold wt. of poly(vinyl acetate) (PVA) in 32% soln. at 63° for 24 hrs. (68% conversion) it was 274 mg. KOH/g., and this converted 20% PVA under the same conditions, 215.6 mg. KOH/g. capacity being left. Another exp. with 25% PVA soln. and 10% of its wt. MSF-3 at 63° yielded the following conversion rates within 24 hrs.: fresh 33.3%; fresh, but treated with 2*N* HCl and water 1.1%; fresh, but washed with 20 times the wt. water 4.6%; the same but MeOH 12.2%; used, then treated with 2*N* HCl and water 5.8%. A third alcoholysis for 24 hrs. at 63° and 32% concn. of 16 g. PVA resulted in these conversion %: 4 g. fresh MSF-3: 81.3–84.5; methanolic ext. of 4 g. MSF-3: 70.0–73.5; the residue extd. with addnl. 120 ml. MeOH: 13.8. Other brands of catalysts yielded analogous results. The active matter is also water sol. The alk. ext. of MSF-3, washed with ether, supposedly low-mol. sulfonic acids, contained: C 18.16; H 0.95; S 22.1%. K. Bloss

21225

Acetal resins. VII. Hydrolysis of poly(vinyl acetate) with sulfuric acid and acetalization of its hydrolyzed products. Keinosuke Yoshida (Osaka Municipal Tech. Research.). *Osaka Shiritsu Kogyo Kenkyusho Hokoku* 13, 26–32 (1951); cf. *C.A.* 44, 2273*b*.—The optimum concn. of H$_2$SO$_4$, was detd. from the studies of the sapon. velocity, viscosity, and color of the reaction products at room temp. The most effective concn. of H$_2$SO$_4$ for the sapon. of poly(vinyl acetate) was 50–5%. The acetal resin was derived from the hydrolyzed soln. by the reaction with paraldehyde in different conditions; the acetalyzed resin was sol., especially in cold water. S content of the sol. resin was detd. by the Asbóth method, and it was detected that the poly(vinyl alc.) derived from the hydrolysis in 50–5% H$_2$SO$_4$ had been esterified. **VIII. Hydrolysis of poly(vinyl acetate) by mixed acids and acetalization of its hydrolyzed products.** *Ibid.* 33–8.—The effects of the ratio of 20% HCl and 50–5% H$_2$SO$_4$ on the velocity and degree of sapon. and polymerization were studied. The max. degree of sapon. was obtained in hydrolysis with 1:1 mixed acid ratio. The reaction of this hydrolyzed soln. with paraldehyde under different conditions was investigated. The derived resins were sol. in cold water and insol. in hot water. K. Kudo

Recent developments of the diisocyanate-polyaddition-process (polyurethans). Otto Bayer. *Farbe u. Lack* 64, 235–41(1958).—A review. Konrad Parker

21246

Molded poly(vinyl alcohol) product having water-resistant properties. Masahide Yazawa, Toshio Ozawa, Keizo Ueda, and Yoshio Tsuchihira (to Kanegafuchi Spinning Co.). Japan. 798('58), Feb. 12. A 10% aq. soln. of poly(vinyl alc.) (degree of polymerization 1400 and 95% sapond.) is treated with 0.5% KMnO$_4$ and 0.1% H$_2$SO$_4$, heated 1 hr. at 90°, Na$_2$S$_2$O$_3$ added until no more coloration of MnO$_4^-$, cooled, the soln. filtered, the filtrate mixed with an equal vol. of 15% aq. soln. of poly(vinyl alc.) with degree of polymerization 1600, the mixt. is poured on a glass plate and dried, the film is immersed for 30 min. in a soln. contg. 10% H$_2$SO$_4$, and 5% (NH$_4$)$_2$SO$_4$ to obtain a film insol. to boiling H$_2$O. Cf. *C.A.* 52, 14187*c*, 16752*i*.
K. Kitsuta

Poly(vinyl alcohol) of low degree of polymerization. Iku Inoue, Kanejiro Iwai, and Nobuji Sakata (to Sekisui Chemical Co.). Japan. 4744('58), June 17. Vinyl acetate monomer (100 g.) is dissolved in 66.7 g. azeotropic mixt. of MeOH-MeCOEt and polymerized with the addn. of 0.16 g. acetyl peroxide for 22 hrs. to give poly(vinyl acetate) having a degree of polymerization of 350. This is dild. with 176 g. azeotropic mixt. of MeOH-MeCOEt and 48.4 g. MeOH to make 25% soln., warmed at 35° with the addn. of NaOH soln. for 20–30 sec., and the mass pptd. is purified as usual to give a colorless powder of poly(vinyl alc.) having a degree of polymerization of 260. Hiroshi Kataoka

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Polyvinyl alcohol. Lonza Elektrizitätswerke und Chemische Fabriken A.-G. Brit. 797,127, June 25, 1958. An improved process for the prepn. of poly(vinyl alc.) (I) by alcoholysis of poly(vinyl acetate) at low temps. is claimed. For example, 40 kg. aq. soln. contg. 2 kg. I and 0.1 kg. 30% H_2O_2 was stirred with 60 kg. vinyl acetate at 60–80° and 220 kg. MeOH was added to the dispersion. After cooling to 0°, a soln. of 1.2 kg. NaOH in 20 kg. MeOH and 2 kg. H_2O was added and the mass stirred for 5 hrs. at 0°; 50 kg. H_2O was added and MeOAc and MeOH were distilled off. Diln. with H_2O gave a 10% soln. of I which was freed of Na^+ by treatment with Amberlite IR-120 at 50°. The I contained 15% vinyl acetate groups. A. B. Ross

Polymerization with oxidation-reduction catalysts. "Montecatini" Società generale per l'industria mineraria e chimica. Brit. 797,953, July 9, 1958. Acrylonitrile (I) and its copolymers contg. at least 50% I are polymerized in the presence of an oxidizing agent and a compd. (II) contg. a H atom in α-position to a :C:S group. Examples of II are thioöxalacetic acid (III); *N,N'*-diphenylthiourea; dimethylthiuram sulfide; diethyldithiocarbamic acid, and EtO(CS)SH. II acts as a reducing and chain transfer agent. High yields of stabilized polymer are obtained. Thus, 6 parts 30-vol. H_2O_2 and 20 parts CH_2:CHCN were added to 200 parts of an aq. soln. contg. 0.162 part NaOH and 0.3 part III at 50°. After 1 hr., a 96% yield of polyacrylonitrile was obtained (mol. wt. 60,000). R. G. S., Jr.

Cross-linked poly(vinyl alcohol). General Electric Co. Brit. 798,146, July 16, 1958. The title product is prepd. by subjecting an ester of poly(vinyl alc.) (PVA) to high-energy irradiation and deacylating the product. While dry PVA is degraded by irradiation, the esters yield cross-linked products. High-energy electron irradiation (50,000–20,000,000 e.v.) is preferred, but γ-rays, x-rays, and protons can be used. Thus, 195 parts granular poly(vinyl acetate) was irradiated in a N atm. with 2×10^7 roentgens. The poly-

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Poly(vinyl alcohol) from poly(vinyl esters). Norris Turnbull (to E. I. du Pont de Nemours & Co.). U.S. 2,850,489, Sept. 2, 1958. Poly(vinyl esters) are treated with H_2SO_4 prior to alk. hydrolysis in the presence of an alkali metal alcoholate to produce poly(vinyl alc.) (PVA) of improved color. Thus, 4000 g. high-viscosity poly(vinyl acetate) was mixed with 66.5 cc. 1% H_2SO_4 at 60° for 2 hrs. and was then cooled to room temp. This acid-treated PVA soln. was then subjected to alcoholysis in 3 vessels arranged in series. The 1st vessel served as the main reactor in which alcoholysis largely took place. In the 2nd vessel, alcoholysis was carried to desired degree. The overflow from this vessel then entered the 3rd vessel for neutralization of the catalyst with AcOH. The H_2SO_4-treated polymer was added to a stirred catalyst soln. of 500 cc. MeOH and 10 cc. 10% NaOMe at 56° during 9 hrs. Addnl. NaOMe in MeOH was added to maintain the NaOMe concn. at 0.19–0.21%. After 2 hrs., the mixt. flowed to the 2nd vessel and, after 4 hrs., to the 3rd vessel. The PVA was filtered off and dried. The color of the PVA powder was 6.6% yellow as compared with 12–14% yellow for PVA made from untreated polymer. Using the American Public Health Assocn. Index (APHA), the 10% aq. soln. prepd. from treated PVA had a 150 APHA color as compared with 250 for sols. of the untreated product. Roy C. Laible

Poly(vinyl alcohol). Ichiro Sakurada and Gisaku Takahashi (to Nippon Chemical Fibers Research Institute). Japan. 3047('58), Apr. 23. Poly(vinyl acetate) (20 g.) contg. some unpolymerized CH_2:CHOAc in 80 g. MeOH and 0.2 ml. of 20% H_2SO_4 are heated for 30 min. at 60°, and then sapond. with 2 ml. of 50% NaOH to obtain a pure white poly(vinyl alc.) contg. only 0.2 mole % of residual AcO group. K. Kitsuta

Depolymerized poly(vinyl alcohol). Ichiro Sakurada and Gisaku Takahashi (to Nippon Chemical Fibers Research Institute, Inc.). Japan. 3048('58), Apr. 23. Powd. poly(vinyl alc.) (I) (8 g.) with a degree of polymerization of 1210

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and contg. 8.4% H_2O is suspended in 500 ml. MeOH contg. HIO_4 (3.3 mole % of I) and heated 3 hrs. at 30°. The product is filtered and washed with MeOH to give a quant. yield of I with a degree of polymerization of 220 and sol. in H_2O. K. Kitsuta

4821

Stable poly(vinyl alcohol). Kozo Fujii and Yasuji Oyama, (to Kurashiki Rayon Co.). Japan. 9794('58), Nov. 12. Vinyl acetate (15 g.) is placed in a 25-cc. ampul and heated in an autoclave with MeOH at 140° for 10 hrs. The resulting poly(vinyl acetate) is purified by repptn. and sapond. with alkali. The resulting poly(vinyl alc.) is washed with MeOH and dried at 65° *in vacuo* for 24 hrs. to give a stable product. Hiroshi Kataoka

5754

Poly(vinyl alcohol). John C. Lukman and Orville G. Lowe (to Celanese Corp. of America). U.S. 2,862,916, Dec. 2, 1958. Poly(vinyl alc.) (I) is pptd. by the alcoholysis of poly(vinyl acetate) (II) in the presence of an alk. alcoholysis catalyst and a basic nitrogenous compd. that will react with aldehydes to form a colorless product. Thus, 40 parts II (25 centipoises viscosity grade) is dissolved in 360 parts denatured EtOH (2B) (contg. approx. 50 p.p.m. AcH) by heating and stirring at 60–78°. There is then added with stirring at 60° 0.4 part anhyd. H_2NNH_2 and 0.4

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part NaOH as a soln. contg. 0.0147 g. NaOH/ml. EtOH. The soln. gels in 2.5 min., and the gel is broken by stirring and the addn. of 40 parts anhyd. EtOH. After 45 min. the mixt. is made neutral to phenolphthalein with AcOH. The pptd. I, after having been washed with EtOH (2B) and dried at 60° is colorless. Hyman Iserson

16598

Poly(vinyl alcohol). Lonza Elektrizitätswerke und Chemische Fabriken Akt.-Ges. Swiss 334,652, Jan. 31, 1959 (Cl. 41). H_2O-sol. poly(vinyl alc.) having less than 30% vinyl acetate groups is prepd. by treating a dispersion of 40–60% poly(vinyl acetate) in 60–40% H_2O with a lower aliphatic alc. and <2.5% alkali hydroxide at not higher than 5°. Mary Jo B. Carlson

Poly(vinyl alcohol). Wacker Chemie G. m. b. H. (Josef Heckmaier, and Eduard Bergmeister, inventors). Ger. 963,194, May 2, 1957 (Cl. 39*c*, 25_{01}). Poly(vinyl alc.) (I) is obtained as fine powder by sapon. of poly(vinyl acetate) (II), which is added in fine grains of <3 mm. diam. to a stirred alc. soln. of alkali heated to at least 35° contg. 2–5% H_2O. Thus, 10 g. II (1 mm. grain size) was added to a soln. of 1.7 g. NaOH in 100 cc. MeOH and 2 g. H_2O heated to 40°. The resulting I had a sapon. value of 1.7. R. W. Rosner

18546

Pure poly(vinyl alcohol). Consortium für elektrochemische Industrie G. m. b. H. (Hans Anselm and Heinz Winkler, inventors). Ger. 1,001,821, Jan. 31, 1957 (Cl. 39*c*, 25_{01}). Addn. to Ger. 964,443. Carboxylic esters of poly(vinyl alc.) (I) are sapond. with H_2O and acidic catalysts in the presence of a higher-boiling solvent which exts. the carboxylic acid formed. The countercurrent extn. is accelerated by vibrations at 50–100 cycles/sec. at an amplitude of 0.3–3 mm., no emulsion is formed. A vertical countercurrent extn. column with vibrating perforated disks is described. In an example, a soln. of I (viscosity at 60° 6840, at 20° 35,000 cp.) was extd. at 60°. The extn. agent consisted of butanone 66, C_6H_6 31, and H_2O 3%. J. Klar

20890

Symposium on synthetic water-soluble resins and gums: Poly(vinyl alcohol), a versatile synthetic polymer. C. P. Argana (E. I. du Pont de Nemours & Co., Wilmington, Del.). *Chem. Specialties Mfrs. Assoc., Proc., 45th Midyr. Meeting, May* 1959, 148–50, discussion 150–1.—See *C.A.* 53, 18516*i*. Polyacrylic and polymethacrylic acids, salts and derivatives. Geo. L. Brown, Joseph Johnson, and Henry Schneider (Rohm & Haas Co., Philadelphia, Pa.). *Ibid.* 151–2.—Methods of prepn. and properties and applications of the polymers are discussed. Poly(vinylpyrrolidone). Properties and applications of a versatile polymer. Julian L. Azorlosa (Gen. Aniline & Film Corp., Easton, Pa.). *Ibid.* 154–7, discussion 157.—See *C.A.* 53, 18389*c*. Nonionic water-soluble resins. M. T. Ivison and S. G. Sellers (Union Carbide Corp., New York, N.Y.). *Ibid.* 157–8, discussion 158. Manuf., properties, and applications are discussed. Ned E. Jaffa

20915

Pure poly(vinyl alcohol). Consortium für elektrochemische Industrie G. m. b. H. (Hans Anselm and Jürgen Smidt, inventors). Ger. 964,443, May 23, 1057 (Cl. 39*c*, 25_{01}). An improvement is described in the method of sapong. carboxylic esters of poly(vinyl alc.) (I), esp. of poly(vinyl acetate) or poly(vinyl formate), in aq. solns. with use of acid sapon. catalysts, e.g. mineral or strong org. acids ($HClO_4$, HCl, or oxalic acid). The new method is characterized by its way of removing the by-products: carboxylic acids formed during the sapon. reaction are removed by extn. with a proper solvent at 80–100°. This purification stage is started when about 90% of the ester has been sapond. and it is continuously performed until at least 99% of the ester is converted into I and at least 95% of the formed carboxylic acids are removed. Examples of suitable extn. solvents comprize the group consisting of isopropyl ether, 2-butanone, 2-pentanone, methyl isobutyl ketone, isophorone, and tributyl phosphate. Those parts of the extn. solvents that are dissolved or emulsified in the I-soln. during the extn. stage are removed therefrom by distn. or extn. with C_4H_9OH. The acid catalysts are removed from the I-soln. partially together with the extd. carboxylic acids, while the rest may be removed either by dialysis or by extn. with C_4H_9OH or by pptn. of I with CH_3OH or $(CH_3)_2CO$ and subsequent washing. The new method gives aq. solns. of I of 99% purity. H. Sontag

18540

Hydroxyethyl ethers of poly(vinyl alcohol). O. M. Klimova, I. P. Nikiforova, and L. N. Vinokurova. *Trudy Leningrad. Tekhnol. Inst. im. Lensoveta* 44, 31-9(1958).—NaOH (0.5 mole in 20% soln.) was added to a 10% aq. poly(vinyl alc.) soln.; the mixt. was cooled to 2-3°; and 4-8 moles $(CH_2)_2O$ was added. After 1 day, fractional pptn. with 1:1 EtOH-Me_2CO gave materials contg. 12-65 wt. % of hydroxyethyl groups. The hygroscopicity, softening temp., the swelling in a C_6H_6-gasoline mixt., and the breaking strength decrease. The plasticity and elongation increase with increasing substitution. The products are more rapidly acetylated or benzylated than the original. The acetates and benzyl ethers have still lower softening temps. John Howe Scott

Influence of initiator concentration on molecular weight of poly(vinyl acetate). František Gregor and Magdalena Sírová (Výzk. úst. acetylénovej chém., Nováky, Czech.). *Chem. průmysl* 9, 325-6(1959).—The polymerization of vinyl acetate (I) was studied at the b.p. of the mixt. I + H_2O with Bz_2O_2 as initiator. The mol. wt. (*M*) and some properties of the resulting polymer are detd. by the concn. of Bz_2O_2 from 0.10 to 2.0 wt. % Bz_2O_2, *M* ranges from 200 to 33 × 10^3, resp. J. Šebenda

Mechanism of shear degradation of vinyl polymers in dilute solution by high speed stirring. William R. Johnson,

21864

Water-soluble poly(vinyl alcohols). Farbwerke Hoechst Akt.-Ges. vorm. Meister Lucius & Brüning (by Werner Langbein). Ger. 1,038,756, Sept. 11, 1958 (Cl. 39*c*). Vinyl esters of lower fatty acids, e.g. vinyl acetate (I) or vinyl propionate, are polymerized in the usual manner with addn. of 0.1–10, preferably 0.2–5% vinyl ethers, contg., besides the vinyl groups, an aliphatic hydrocarbon residue with at least 6 C atoms. The polymers obtained are hydrolyzed giving poly(vinyl alcs.), the 4% aq. soln. of which has a viscosity of >100 cp. For example, I 995 was mixed with vinyl octadecyl ether 5 and dissolved in MeOAc 550 parts by wt. After adding 8.5 parts by wt. dilauroyl peroxide, the mixt. was heated to the b.p. for about 20 hrs. until the monomer content had decreased to <1%. MeOH (5700 parts) was then added and the mixt. stirred for homogenizing. Sapon. occurred in 5 hrs. at the b.p. with a mixt. of 3500 parts MeOH and 75 parts 20% methanolic NaOH. After cooling, the liquid was removed and the poly(vinyl alc.) obtained was washed with MeOH and dried at 40°. The viscosity of the 4% aq. soln. was about 5000 cp. I. Sch.

21865

Partially acylated poly(vinyl alcohol). Consortium für elektrochemische Industrie G. m. b. H. (by Hans Anselm, Jürgen Smidt, and Heinz Winkler). Ger. 1,038,281, Sept. 4, 1958 (Cl. 39*c*). Uniform or mixed carboxylic acid esters of poly(vinyl alc.) (I), esp. poly(vinyl acetate) (II), are sapond. with heating and in the presence of H_2O and acid catalysts to give a substance contg. 10–30 mole % acyl residues. The catalyst then is removed or inactivated and the carboxylic acid is extd. with an org. solvent immiscible with H_2O. For example, 40 g. H_2SO_4 and 40 g. butylnaphthalenesulfonic acid were dissolved in 2.93 l. H_2O and 5 kg. pearl-like II. In an autoclave, the mixt. was heated to 110° with stirring. After about 8 hrs., a sapon. degree of 75% was reached. After cooling to 90°, a soln. of 40 g. NaOH in 4810 g. H_2O was added with stirring. At 60°, 99.2% of the resulted AcOH was extd. with a mixt. of 82 parts EtOAc and 18 parts C_6H_6 by vol. and recovered by distn. After distg. off the dissolved extg. medium, a 28% aq. soln. of I contg. 25 mole % Ac groups and small amts. of AcOH and Na_2SO_4 was obtained. I. Sch.

21866

Improving poly(vinyl alcohol) resins. Kutoku Tomonari, Kenichi Shinohara, Ayao Amemiya, and Terubumi Dano. Japan. 9277('59), Oct. 13. The insoly. of molded poly(vinyl alc.), such as powders, films, and filaments, in hot H_2O is improved by irradiation with γ-rays from Co^{60}. Other high-energy particles may be used. Toshio Fukazawa

2195

Alcoholysis of poly(vinyl acetate). James M. Snyder (to E. I. du Pont de Nemours & Co.). U.S. 2,950,271, Aug. 23, 1960. To obtain poly(vinyl alc.) (I) as a finely divided solid by alcoholysis of poly(vinyl acetate) (II), it is necessary to break down the gel that forms during the reaction. At the conventional alcoholysis temps. (30–60°), large power inputs are required. However, by conducting the alcoholysis with 30–60% by wt. solns. of II in alc. and in the presence of alk. alcoholysis catalysts at 90–100°, the gel can be broken down by conventional agitator equipment at power inputs as low as 10 horsepower/1000 gal. of polymer soln. charge. I. I. Bezman

Poly(vinyl alcohol). Wacker-Chemie G. m. b. H. (by Josef Heckmaier and Eduard Bergmeister). Ger. 1,042,237, Oct. 30, 1958 (Cl. 39*c*). Monomeric vinyl esters or their mixts. with other polymerizable compds. are polymerized by bead polymerization to give a cross-linked product. A useful cross-linking agent is 0.1–2% of an unsatd. aliphatic ester with at least 2 double bonds in the mol., e.g. a dicarboxylic acid divinyl ester. The cross-linked product is insol. in alc. It is suspended in alc. and alcoholized in the presence of 0.5–2% of an alk. catalyst. For example, 30 parts of a bead polymer of a particle size of <1 mm., prepd. from 99.5% vinyl acetate and 0.5% vinyl crotonate, was suspended in a closed vessel in a soln. of 1 part NaOH in 100 parts MeOH. The bead polymer swelled, after 7 min. coagulation occurred, and after 25 min. the product became H_2O-sol. It was filtered after 3 hrs. and then dried. I. Sch.

6934

Poly(vinyl alcohol). Farbwerke Hoechst Akt.-Ges. (by Werner Lehmann and Alfred Kühlkamp). Ger. 1,065,176, Sept. 10, 1959 (Cl. 39*c*). A solid, filterable poly(vinyl alc.) (I) is prepd. by ester interchange of poly(vinyl esters) with alcs. in the presence of H_2O and acid catalysts. Thus, a mixt. of BuOH 300, poly(vinyl acetate) 200, H_2O 100, and H_2SO_4 8 g. was heated to 66° with vigorous stirring. After 3.75 hrs., the I sepd. After 7.25 hrs., the I contained <1.5% Ac groups, was easily filterable, and was completely sol. in H_2O. Irwin A. Pearl

7920

Poly(vinyl alcohol) resin plasticized with ethyl acid phthalate. Irving Poesel (to Cambridge Industries Co.). U.S. 2,963,461, Dec. 6, 1960. The softness, flexibility, water-resistance, and impermeability of fully hydrolyzed poly(vinyl alc.) (I) is improved by plasticization with a H_2O-insol. acid ester of an org. polybasic acid. Dispersions of the I and plasticizer are cleared by the addn. of 28% NH_4OH which solubilizes the acid esters. Thus, 2227 lb. of phthalic anhydride and 761 lb. of 87.7% EtOH were mixed and allowed to stand for several days to form a mixt. of the acid esters. Then 5 lb. of this acid ester mixt. was added to 100 lb. of a 10% aq. soln. of completely hydrolyzed I resin. The milky dispersion was cleared by the addn. of 28% NH_4OH. Films cast from the soln. were soft, clear, glossy, flexible, and tough. John H. Dittmar

9936

Syndiotactic poly(vinyl alcohol). Howard C. Haas and Albert S. Makas (Polaroid Corp., Cambridge, Mass.). *J. Polymer Sci.* 46, 524–8(1960).—Solns. of syndiotactic poly(vinyl alc.) (I) were prepd. by dissolving poly(vinyl trifluoroacetate) in diethylenetriamine (II). The viscosity of dil. solns. of I in II was observed over a period of 444 days at room temp. Considerable decrease in viscosity occurred, and $[\eta]$ approached a limiting value of 1.9. It was shown that this result was due to degradation of the chain. The reaction proceeded until all the links unstable to alkali were consumed. Several com. samples of I gave a similar degradation. Millard Maienthal

10975

Resaponified poly(vinyl alcohol). Mitsubishi Rayon Co., Ltd. (by Hidenari Suyama and Masao Ishii). Japan. 11,691–2('60), Aug. 22. A mixt. of 1 part vinyl acetate and 2.5 parts partially sapond. poly(vinyl alc.) was polymerized at 60° for 5 hrs. in the presence of 0.3% Bz_2O_2. The resulting poly(vinyl acetate) (10 parts) was sapond. with a methanolic soln. of NaOH at 40° to give poly(vinyl alc.) (I), degree of polymerization of 1200. The I obtained was pulverized, soaked in 10 vols. of 0.5% methanolic NaOH at 40° for 2 hrs., and centrifuged. The resulting resapond. poly(vinyl alc.) was heated at 70° for 2 hrs. The product was pulverized, soaked in 10 vols. of 0.6% H_2SO_4 at 20° for 1 hr., filtered, and washed with H_2O to give poly(vinyl alc.) (II) contg. 0.027% sulfate. II was dry-spun, elongated 700%, and heated at 220° to give fibers resistant to boiling H_2O. Hiroshi Kataoka

Cold-stable poly(vinyl acetate) dispersions. Lonza Elektrizitätswerke Chemische Fabriken Akt.-Ges. (by Paul Wicht). Swiss 346,028, June 15, 1960 (Cl. 39*c*). Aq. dispersions of poly(vinyl acetate) are prepd. contg. up to 25% o-$C_6H_4(CO_2Bu)_2$ (I) (based on the solids content) and undamaged after cooling to −20°. The crit. factors in the polymerization are an addn. of the $AcOCH{:}CH_2$ (II) in at least 4 portions, each after conversion of the preceding portion, and the absence of alkali metal and alk. earth metal ions. Thus, 75 g. II, 520 g. 5% aq. poly(vinyl alc.) (purified by passing through a cation-exchange column), 0.01 g. $FeSO_4$, 1.5 g. 30% aq. H_2O_2, and 80 g. deionized H_2O were mixed at 50° in a closed vessel. The mixt. was stirred and heated to 65–70° until the pressure reached a max. and diminished. Then 75 g. II was introduced, and the procedure was repeated until 600 g. II had been polymerized. The product contained 51.9% solids and had a pH of 3.1, an av. particle diam. of 2 μ, and a viscosity of 40 poises.

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room temp. and extruded to produce reinforced I with a lower coeff. of friction and improved compressive yield and extrusion characteristics. Thus, 190 g. naphtha-Vistanex soln. (1 part polyisobutylene plus 16 parts by wt. of V.M.P. naphtha) was added as a lubricant to a homogeneous blend of 810 g. cold-ground I (Teflon TE3086) and 0.81 g. BN, and mixed for 2 min. The mixt. was screened, reblended, and stored for 16 hrs. at room temp. before use. Preforms of the material were made at 10–50 lb./sq. in. and extruded in a ram-type extruder. There were no defects or flaws at the preform junction points. James H. Modeen

Insoluble poly(vinyl alcohol). S. N. Ushakov. U.S.S.R. 134,868, Jan. 10, 1961. An insol. poly(vinyl alc.) powder is obtained by emulsion polymerization of vinyl acetate with a diallyl acetal, e.g., diallyl formal, diallyl ethylal, diallyl butyral, etc., or with methylenebiscrotonamide, as well as with other tetrafunctional monomers. The polymerization is followed by alcoholysis in a heterogeneous medium by treating the polymer in anhyd. MeOH or EtOH in the presence of an alk. catalyst. The emulsion polymerization is carried out in the presence of H_2O-sol. initiators, emulsifiers, and other ingredients necessary for the production of powd. poly(vinyl alc.). M. Hoseh

Saponification of low-molecular weight esters as the model of poly(vinyl acetate). Ichiro Sakurada, Yasuyoshi Sakaguchi, and Michio Kagau (Univ., Kyoto). *Kobunshi Kagaku* 17, 87–94(1960).—To study the mechanism of sapon. of poly(vinyl acetate) (I), ethylene glycol diacetate, 1,2- and 1,3-propyleneglycol diacetate, 1,3- and 2,3-butyleneglycol diacetate, and triacetin were chosen as models. Sapon. rates of these compds. were measured in water or 75:25 acetone-water in the presence of NaOH or HCl as the catalyst. In the preceding reaction, the apparent rate const. *k* changed a little in water, but increased considerably in acetone-water mixt. The increase of *k* was greater for NaOH than HCl catalyst, for the esters in which the distance between two ester groups was shorter, and for secondary esters than primary ones. This behavior was similar to that of I. The

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Poly(vinyl acetate) and poly(vinyl alcohol). Kurashiki Rayon Co. Ltd. Brit. [illegible], Apr. 26, 1962; Japan Appl. Aug. 7, 1959; 4 pp. Poly(vinyl acetate) (I) with a degree of polymerization of <1000 is prepd. by polymerizing vinyl acetate (II) continuously in a 45% alc. soln. of I and adding the reactants at the same rate as the polymerization reaction mixt. is removed. Thus, MeOH 200, II 170, and 2,2'-azobisisobutyronitrile (III) 0.3 part were polymerized at 70°. A soln. of III 0.25 in II 630 was continuously added to maintain the soln. compn. of MeOH 200, II 160, and I (80% conversion) 640 parts. The compn. of the soln. was held const. during polymerization, and MeOH 200, II 800, and III 0.32 parts added continuously at the rate of 50 l./hr. The compn. of the material in the reaction vessel and that being removed were the same.
John H. Dittmar

Removal of water from organic chemicals. Robert C

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Binning, Joseph F. Jennings, and Eugene C. Martin (to Standard Oil Co. (Indiana)). U.S. 3,035,060, May 15, 1962, Appl. June 18, 1957; 6 pp. Water can be effectively removed from a water-org. chem. mixt. by using a permeation membrane of hydrolyzed poly(vinyl acetate) in which at least 98% of the Ac groups have been removed by hydrolysis. This membrane is very stable toward water, and its stability may be further improved by curing it at >100° in the absence of O. The membrane may also be used over long periods of time without losing any of its selectivity. For example, when using a new hydrolyzed poly(vinyl acetate) membrane, the initial permeate contained 93% water, and after 2600 hrs. of continuous use, the permeate contained 91.5% water. This method may be used to remove water from compds. contg. one or more atoms of O, S, halogen, N, or P. It is esp. applicable to aq. solns. of EtOH and iso-PrOH, dioxane, pyridine, *sec*-BuOH, and acrylonitrile.
Carolyn M. Miller

12704

Synthesis of highly crystalline poly(vinyl alcohol). Alexandru Lupu, M. Opris, and A. Ciocanei (Inst. Chem., Bucharest, Romania). *Vysokomolekul. Soedin.* 4, 613-14(1962). The use of ketones with smaller mol. wt. (acetone or MeCOEt) as solvents for the polymerization of vinyl acetate, in contradistinction to the use of aliphatic and aromatic hydrocarbons, alcs., and esters, results in the formation of polymers with a high degree of crystallinity. A highly cryst. poly(vinyl alc.) was obtained by hydrolysis of this polymer.
P. Raban

13953

Changes in the degree of polymerization [of poly(vinyl alcohol) and poly(vinyl acetate)] during polymerization. Kiyokazu Imai (Kurashiki Rayon Co., Okayama). *Kogyo Kagaku Zasshi* 62, 1127-9(1959). The degree of polymerization P_A of poly(vinyl alc.), obtained from poly(vinyl acetate) polymerized in bulk at 45°, has a max. value related to the conversion. This phenomenon is not attributed to the "gel effect" but to some impurities in the monomer. The differences between $P_{A\,\max.}$ and P_A', the value extrapolated to 0 conversion, depend on P_A or monomer purity, and the difference decreases with increasing monomer purity. The values at 60° are smaller than those at 45°. The discrepancy between the degree of polymerization of poly(vinyl acetate) and poly(vinyl alc.), which is estd. by extrapolation to 0 conversion, is caused by inaccuracy in the equation used in the estn. of the degree of polymerization from viscosity.
CA

Effects of γ-radiation on a polymer in solution. I. Poly(vinyl acetate). Ichiro Sakurada and Yoshito Ikada (Univ. Kyoto). *Bull. Inst. Chem. Res., Kyoto Univ.* 40, 1-15(1962)(in English). When 10 wt. % poly(vinyl acetate) (I) was subjected to γ radiation in various org. solvents, cross-linking occurred in MeOH and benzene, but in many other solvents, such as dioxane, toluene, acetone, AcOH, EtOAc, and $CHCl_3$, degradation occurred predominantly. As the solvent became poorer, cross-linking was promoted at low concns. but was retarded at high concns. The optimum concn. for cross-linking in MeOH was about 20%, at which concn. degradation hardly occurred. When I was irradiated in MeOH-org. solvent mixts. including EtOH, hexane, xylene, and CCl_4, the rate of cross-linking was more retarded as the soly. of the polymer in the soln. was increased. However, in MeOH-H_2O mixt., no correlation was observed between the radiation-induced change and the soly., but the rate of cross-linking increased regularly with increasing H_2O content in the mixts., which might indicate that H_2O is a very effective solvent for cross-linking. The radiation-induced change was very slight during irradiation at −50°, while rather large at 70°. The min. dose needed for gelation in 10% C_6H_6 soln. was inversely proportional to the degree of polymerization. The d. of the cross-linked units was in proportion to radiation dose, and cross-links were formed not only from the main-chain radicals (not end radicals), but also from the side-chain radicals. II. Poly(vinyl methyl ether). *Ibid.* 16-24. Poly(vinyl Me ether) was degraded more easily when irradiated in dil., air-free, org. solvent solns. including MeOH, acetone, EtOAc, and dioxane, resp., as solvent (except CS_2), the concn. of which was 0.8 and 3.0 wt. %. At higher concns. (20-50 wt. %), cross-linking proceeded more readily in the solvents of lower viscosity. In CS_2, gel was formed even at the concns. <1 wt. %, and the crit. concn. for gel formation was nearly equal to that for aq. solns. The crit. concn. in the case of polystyrene was about 0.15 wt. % in CS_2. The role of the solvent under irradiation in soln. has been discussed in some detail on the basis of the observed results. The mechanism of radiation-induced reactions could be satisfactorily explained in terms of the formation or deactivation of macroradicals by solvent radicals and the change in the rate of coupling or cage-re-

14000

Waterproof poly(vinyl alcohol) films. Walter M. Budde, Jr. (to Archer Daniels-Midland Co.). U.S. 3,043,717, July 10, 1962, Appl. Nov. 17, 1958; 5 pp. Poly(vinyl alc.) films which are chem. and intermolecularly bonded by means of an acid anhydride of pH 2-5 in water with an epoxidized fatty acid ester or fatty oil ester having an I value of at least 90, preferably those derived from unsatd. glyceryl esters obtained from animal, vegetable, and marine oils, the acyl radicals of which contain 12-26 C atoms, are resistant to moisture and therefore suitable for wrapping and packaging goods. The fatty acids used are epoxidized by any of the known epoxidn. techniques. The acid anhydride may be used preferably together with an acid as described earlier (U.S. 2,993,920, *CA* 55, 27973*h*). The fatty acid ester is mixed with the anhydride-acid soln. in a solvent in which the reactant components are mutually sol. and which do not react with the other components of the system. Additives, such as pigments, fungicides, or bactericides, may be added. This soln. is fixed on the poly(vinyl alc.) film by means of curing at 150-300°F. Thus, an epoxidized soybean oil having 6.3% oxirane O was mixed with 3,4,5,6,7,7-hexachloro-3,6-*endo*-methylene-1,2,3,6-tetrahydrophthalic anhydride and dissolved in Cellosolve acetate. This soln. can be stored indefinitely in a deep freeze. For evaluation, 1.5-mil drawdowns were prepd. on com. poly(vinyl alc.) film of 5-mil thickness and cured for 20 min. at 200°F. The fatty acid ester-anhydride soln. also adhered to glass.
Y. Hess

Poly(vinyl acetate) powder. Badische Anilin- & Soda-Fabrik A.-G. (by Walter Kunzel, Alfred Mueller, and Wilhelm Keffert). Belg. 611,799, Jan. 15, 1962, Appl. Dec. 20, 1961; 5 pp. A free-flowing product was manufd. by polymerization of vinyl acetate (I) in aq. suspension, sepn. of the aq. reaction medium, and immediate dehydration of the polymer thoroughly stirred until the H_2O content was <1%. Drying was done in a fluidized bed. The procedure was also suitable for the manuf. of powd. copolymers contg. at least 80% by wt. I. For example, 20 kg./hr. fresh polymer beads contg. 15% H_2O was introduced and 1500 cu.m. air at 25–60° was insufflated into a cylindrical drier, the lower part being conical and fitted with a perforated plate. After 42 hrs., the product was evacuated through a sieve (4 mm.) where only 1% polymer was retained. The polymer contg. 0.4% H_2O remained "fluid" after several months storage at room temp.

L. Wilputte-Steinert

High-molecular-weight poly(vinyl acetates) and poly(vinyl alcohols). James A. Snelgrove (to Shawinigan Resins Corp.). Brit. 900,571, July 11, 1962; U.S. Appl. Aug. 27, 1957; 4 pp. High-mol.-wt. poly(vinyl alc.) (I) is prepd. having an increased softening point and a high resistance to heat discoloration. Thus, 100 g. of distd. CH_2:CHOAc is sealed in an evacuated tube and exposed to 225,000 r.e.p. of α-radiation (Co^{60} source) for 47 min. at 0°. A 25% conversion to poly(vinyl acetate) (II) is obtained. II has a viscosity of 235 cp. in C_6H_6 at a concn. of 86 g./l. II is dissolved in EtOH and hydrolyzed with NaOH by conventional procedures. The av. degree of polymerization of the resulting I is approx. 4700, substantially equal to that of the II.

M. L. Kovacic

1587

Hydrolysis of poly(vinyl acetate) with dimethyl sulfate. L. Z. Kazaryan and T. O. Zaprosyan (K. Marx Polytech. Inst., Erevan). *Zhur. Priklad. Khim.* **34,** 1898–1900 (1961).—Heating (24 hrs.) 43 g. poly(vinyl acetate) resin with 150 ml. MeOH and 1.0 g. Me_2SO_4 at 63 ± 0.1° and analyzing the products every hr. showed that the rate of hydrolysis decreased as the process continued. Hydrolysis was complete in 24 hrs. I. Bencowitz

Distribution of acetyl content of partially alcoholized poly(vinyl acetate). Masakazu Matsumoto and Gozo Takayama (Kurashiki Rayon Co., Okayama). *Kobunshi Kagaku* 18, 169–74(1961).—To det. the Ac distribution of partially alcoholized poly(vinyl acetate), fractionation was carried out for the polymer contg. ~10 mole % residual acetate groups. Various fractionation methods were applied, successive pptn. method, extn.-fractionation method, and Spencer's method (*CA* 42, 9243*d*). The pptn. fractionation and Spencer's fractionation were carried out by using H_2O as the solvent, and PrOH as the precipitant. Fuchs extn. fractionation was carried out by using the mixt. of H_2O and PrOH as the extg. solvent and Al foil as the carrier of the polymer. The results obtained by these 3 methods give satisfactory agreement within the exptl. error and indicate the existance of some heterogeneity with respect to the degree of alcoholysis in the partially alcoholized poly(vinyl acetate). Eiichi Wada

1599

Poly(vinyl alcohol). Kurashiki Rayon Co., Ltd. (by Tsujiro Akadoshi, Tsugio Kominami, Seigo Fukuda, and Kikuji Urakami). Japan. 9762('60), July 25. Improved method for producing poly(vinyl alc.) by the sapon. of a MeOH-poly(vinyl acetate) soln. with an aq. NaOH is claimed. An aq. NaOH soln. and a MeOH soln. of poly(vinyl acetate) are introduced continuously into the sapon. app. The viscous MeOH soln. flows down forming a cylindrical, thin film which shrinks into a rotary disk located at the center of the sapon. app. The aq. soln. is sprayed onto the film of the MeOH soln. causing a partial sapon. The mixt. is then saponified completely on the rotary disc and scattered to the wall, along which flows a waste, saponified liquid. Agitation prevents the agglomeration of the product. Toshio Fukazawa

1609

Poly(vinyl alcohol) manufacture by saponification of poly(vinyl esters). Kurashiki Rayon Co., Ltd. Brit. 848,787. Appl. Apr. 27, 1959; Japan. Apr. 30, 1958. Improved poly(vinyl alc.) (I) was prepd. by sapon. of poly(vinyl acetate) (II). II 20.6% by wt. in MeOH was mixed with NaOH soln. in a ratio of 1:0.19 and the mixt. flowed in a continuous process at 111 l./hr. into a reactor. The I was drawn from the vessel at 18 cm./min. and passed through 2 rollers. Ronald J. Balesh

Synthesis of poly(vinyl alcohols) with improved emulsifier and foaming properties. Farbwerke Hoechst A.-G. (by Hans Dexheimer, Otto Fuchs, and Eberhard Paschke).

2586

Ger. 1,110,417 (Cl. 39*c*). Appl. July 25, 1957. Known emulsifiers are prepd. in such a manner as to improve considerably their emulsifying capability. Thus, a mixt. of 100 cc. aliphatic hydrocarbon (b.p. 190–250°), 75 cc. vinyl acetate, and 0.5 g. diacetyl peroxide is heated 4 hrs. at 60–5° and 6 hrs. at 90°. The resulting polymer is worked up, then converted to poly(vinyl alc.) (I) by treating with NaOH in a solvent composed of 1 part C_6H_6/3 parts EtOH. Shaking a 1% soln. of I in water gives an emulsion which, on standing, is stable for 4 hrs. Conventional emulsions of this type are stable for about 1 min. Maurice L. Zweigle

3656

Cleavage of oxidized poly(vinyl alcohol). Kurashiki Rayon Co., Ltd. (by Makoto Shiraishi and Shoichi Matsumoto). **Japan.** 16,039('60). Appl. July 11, 1958. In the cleavage reaction of oxidized poly(vinyl alc.) (I) with alkali, it is previously treated with acid. Thus, 1% aq. soln. of I (0.112 mole % of CO group in the main chain without terminal group) with av. mol. wt. 1590 is treated with HCl to pH 6.0, 4.4, 3.2, 1.8, and 1.5, resp., and kept 1 hr. at 30°. Then it is neutralized with alkali and 350 ml. of each soln. is treated with 10 ml. 5*N* NaOH and heated 1 hr. at 100°. The cleaved I is pptd. with acetone and washed with MeOH. The mol. wts. of the product of each pH treatment calcd. from the viscosity detn. are 990, 885, 786, 645, and 605, resp. K. Kitsuta

Modified poly(vinyl alcohol). Farbwerke Hoechst A.-G. (by Karl Heinz Kahrs and Wolfgang Zimmermann). Ger. 1,094,457. (Cl. 39*c*). Appl. June 27, 1959. Addn. to Ger.

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1,081,229 (*CA* 55, 279835.. Modified poly(vinyl alcs.) are prepd. contg. polyalkylene glycol units and org. hydrophobic radicals, such as poly(vinyl acetate) radicals, in such proportions that the no. of poly(vinyl alc.) units obtained on sapon. of the graft vinyl ester polymers or copolymers in the macromol. is <50% by wt. The sapon. was done in MeOH contg. a catalytic amt. of NaOH or KOH, possibly in an inert atm. The resulting poly(vinyl alc.) was sol. in cold H_2O and used as, e.g., surface-active agent, e.g. as a protection colloid for suspension polymerization or as raw material for the manuf. of detergents; or for the manuf. of flexible H_2O-sol. transparent sheets; or in the textile and cosmetic industry. For example, a soln. of 100 g. graft polymer prepd. from 50 g. vinyl acetate, 49 g. oxyethylated polypropylene oxide (mol. wt. 5000, OH no. 23, oxyethylene content 70%), and Bz_2O_2 1 in MeOH 180 was mixed with H_2O 2.6 and 5% aq. 12 g. soln. in MeOH, stirred for 5 hrs. at 30°, and cooled at room temp. to yield a gel into which steam was blown. After distn. of MeOH and AcOMe, evapn. of the remaining aq. soln., and drying at 40°, a product contg. 27.3% by wt. vinyl alc. groups was obtained. Polyethylene glycol derivs., 1 or both terminal OH groups of which were etherified, esterified, or substituted by mono- or polyfunctional amine or amide, and also the products of reaction with mono- or polyisocyanates, were used as raw materials. L. Wilputte-Steinert

Hydrolysis of poly(vinyl acetate). John E. Bristol (to E. I. du Pont de Nemours & Co.). U.S. 2,995,548. Appl. Oct. 8, 1957. Heating 15 g. poly(vinyl acetate) beads, 9 g. of an 8% aq. soln. of SO_2, 1.6 g. of a 10% soln. of dodecylbenzenesulfonic acid, and 26 g. H_2O for 2 hrs. at 140° gave 96% hydrolysis to poly(vinyl alc.) without discoloration. J. T. Barr

Linear poly(vinyl acetate). Air Reduction Co., Inc. Brit. 880,544. Appl. July 29, 1960; U.S. Aug. 14, 1959. Vinyl acetate (I) is polymerized with trialkyl Al or dialkyl Al hydride. Temps. down to −80° increase the amt. of

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cryst. product. The polymerization rate is increased by the use of tetrahydrofuran as solvent. The crystallinity is also increased by certain pptg. solvents, e.g. hexane. Thus, a mixt. of I 15 and hexane 10 ml. was placed in a vessel which was flushed with N and sealed. A soln. (0.5 ml.) of 50% by vol. $Al(iso\text{-}Bu)_3$ in heptane was injected and the mixt. was held at −15° for 3 days. It was then poured into 700 ml. hexane contg. 5 ml. MeOH. A polymer product (2.5 g.) was obtained, an 18.5% conversion. K. J. Durant

11816

Saponification of mixed polyvinyl esters. S. N. Ushakov, A. F. Nikolaev, and E. V. Lebedeva. U.S.S.R. 141,302, Oct. 6, 1961, Appl. Jan. 9, 1961. $NH_2CH_2CH_2OH$, $\leq$ the theoretical amt., is used as the sapong. agent. From *Byull. Izobretenii* 1961, No. 18, 42. CA

Polymerization of vinyl formate. Kurashiki Rayon Co., Ltd. Brit. 885,623, Dec. 28, 1961; Japan Appl. Sept. 3, 1959. A low percentage of vinyl acetate prevents gelation during the polymerization of vinyl formate at 30° or below.

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The sapond. copolymer gives a highly cryst. poly(vinyl alc.) (I). Thus, vinyl formate 100 contg. 2.5 wt. % vinyl acetate was mixed with Et_3B 0.275 and Bz_2O_2 0.656 part by wt. Polymerization under N for 17 hrs. at 0° gave 44.2% conversion. The degree of swelling (wt. % H_2O absorbed based on dry polymer) of the I thus prepd was 1.09, as compared with 0.94 for I from poly(vinyl formate) made in the absence of vinyl acetate. R. C. Kollman

Antistatic poly(vinyl chloride). BTR Industries Ltd. (formerly British Tire & Rubber Co., Ltd.). and Richard Tudor. Brit. 889,022, Feb. 7, 1962, Appl. Aug. 22, 1957. The plastic is made resistant to accumulation of static charges by incorporation of 2–5% of a cationic surfactant, e.g. a quarternary ammonium salt, Estax 38, AL 5, Catafor 09, Querton 1S ES 100, S.D.B.S., or a nonionic surfactant, e.g. polyethylene glycol 200. The product is useful for mine conveyor belts, footwear for hospital use, and other uses in which accumulation of static electricity may result in a fire hazard. K. J. Durant

Poly(vinyl acetate)-glue compositions. Morris Bresloff and Frederick W. Stenius (to Borden Co.). U.S. 3,011,985, Dec. 5, 1961, Appl. Jan. 22, 1957. Mixts. of poly(vinyl acetate) (I) emulsions and glue solns. for improved adhesive compns. have poor compatibility. This is overcome by emulsion polymerization in the presence of 5–20% glue. For example, vinyl acetate 546, glue 50, Triton X-100 4.8, and H_2O 200 parts by wt. were emulsified. H_2O 200.8 and $NaHCO_3$ (5% soln.) 8 were heated to 80–5° and dodecyl mercaptan 2.2 and $K_2S_2O_8$ 18 parts by wt. were added. The emulsion was run into the reactor in 3 stages, $K_2S_2O_8$ 12 and 5% $NaHCO_3$ 12 parts being added at the end of the 1st and 2nd stages. The temp. was increased to 90° and held for 0.5 hr. The pH was kept at 4–5. The emulsion is compatible with addnl. glue up to $^1/_2$ of I.

S. Guggenheimer

Prevention of depolymerization of poly(vinyl acetate) by alcohol. Electro Chemical Industry Co., Ltd. (by Shoichiro Otsuka, Yoshizo Ono, and Fumio Masuda). Japan. 16,446('61), Sept. 15, Appl. Nov. 13, 1959. To a mixt. of vinyl acetate 65, MeOH 35, and 2,2'-azodiisobutyronitrile 0.1, oxalic acid 0.05 part is added. The mixt. is polymerized at 65°, and until the extent of polymerization is 60%. Then the soln. is poured into hot H_2O. The pptd. poly(vinyl acetate) is dried, dissolved in MeOH, sapond. with NaOH, washed with MeOH, and dried to give poly(vinyl alc.) of 1540 polymerization degree; if oxalic acid is not used, the polymerization degree is 1250. AcOH may be used instead of oxalic acid. Hiroshi Kataoka

Poly(vinyl alcohol). Rudolf Novak. Czech. 95,236, May 15, 1960. From a poly(vinyl acetate) with I no. 0.96, 100 g. 40% MeOH soln. of 350 poises was prepd. (the MeOH contained ~0.02% aldehyde and 0.4% H_2O). The soln. was agitated at 5000 r.p.m. for 1 min. and treated with 1.6 g. alc. NaOH (0.155 g. NaOH in MeOH). After another 5 min., the mixt. was poured out, and the product solidified in 1 min. The title compd. formed after dissolving in H_2O to 10% soln., and, after removing the rest of the solvent, a clear soln. was produced suitable for optical materials, e.g. for the prepn. of poly(vinyl butyral).

V. Kratochvilova

15683

Poly(vinyl alcohol) resistant to water. John O. Hawthorne and Myron H. Witt (to U.S. Steel Corp.). U.S. 3,023,199, Feb. 27, 1962, Appl. June 8, 1959. About 8 parts of 2,2'-biphenyldicarboxaldehyde or its deriv. 5-hydroxy-5*H*-dibenz[*c,e*]azepine (I) and HCl 0.5 are added to poly(vinyl alc.) (II) 100 parts. Thus, 0.375 g. I (Brit. 860,907, *CA* 55, 16581*c*) was dissolved in 0.9 cc. of 1 part concd. HCl mixed with 1 part H_2O. Then 12.5 g. H_2O and 25 g. of a 15% aq. soln. of II were added. A film of this mixt., cast on a sheet of Teflon and dried at room temp., increased only 25% in area after being kept in water at room temp. or the b.p. An untreated film increased by 122% in cold water and dissolved on boiling. Eduard Farber

4290

Structure of polyvinyl alcohol. E. I. Barg and N. N. Mel'teva. *Doklady Akad. Nauk S.S.S.R.* 92, 307–10 (1953).—Examn. of the rate of deformation at const. load at various temps. of specimens of polyvinyl alc. (I) formulated with 10% glycerol, polyvinyl acetate, polyvinyl butyral, polystyrene, and pure I indicates that the mech. behavior of I can be explained most simply on the assumption that in I, along with the fundamentally amorphous structure, there exist small areas of cryst. phase, m. 110–50°, that depend on temp. and the temporal conditions of stretching force. I obtained by acidic and alk. hydrolysis of polyvinyl acetate was also examd. After an initial straight-line relation between rate of deformation and temp., there occurs at about 60° (T_g for this polymer) a zigzag curve which indicates alternating acceleration and retardation of stretch, and only at 100–20° does the curve become again substantially straight and very steep. In relaxation of deformation I differs from amorphous polymers in that it has residual deformation of nearly 60%, whereas the amorphous polymers had zero residual deformation. This residue remained even after heating to 150–60°, i.e. near destruction temp. G. M. Kosolapoff

4882

Polyvinyl alcohol. Masataka Amagasa and Hiroyuki Masahata (to Nippon Synthetic Chemical Industries Co.). Japan. 1893('53), Apr. 30. Polyvinyl acetate in MeOH or Me_2CO ~~in an autoclave is treated with NH_3 at a low temp. and heated for 6 hrs. at 100°.~~ [redacted] alc. K. Kitsuta

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High-viscosity polyvinyl alcohol. Harold W. Bryant and Wm. R. Cornthwaite (to E. I. du Pont de Nemours & Co.). U.S. 2,668,809, Feb. 9, 1954. High-viscosity polyvinyl alcs. for paper ~~coatings and adhesives~~ are prepd. by polymerizing vinyl ac[redacted] with 0.01–10.0% of a terminally unsatd. [redacted] with NaOMe. A 4% aq. soln. of the product had a viscosity of 20,000 centipoises at 20°. R. G. Shepherd, Jr.

6202

Solutions of polyvinyl alcohol. Hector A. Dieu (Univ. Liége, Belg.). *J. Polymer Sci.* 12, 417–38(1954).—From aq. solns. of crude polyvinyl alc. 10 fractions were prepd. by acetone pptn. at 25°. The acetyl no. of the last 8 fractions was approx. 14×10^{-4} equiv./g. compared with 33.5×10^{-4} equiv./g. for the unfractionated sample. Fractions 3, 7, and 10 were studied in detail, e.g. by measurements of intrinsic viscosities [η] at 0–50 or 75° in water, 10% dioxane, and 33% dioxane, sedimentation consts. S_0 at infinite diln. and 20°, Brownian coeffs. D_0 and D_∞, osmotic-pressure measurements (from fraction 3 only) at 25°, and light scattering at a temp. of 20° and angles of 45°, 90°, and 135°. Mol.-wt. data by the various methods are tab-

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ulated and their relation to theories of Flory, of Kuhn, and of Dialer discussed. Oscar T. Quimby

Theoretical consideration of the elasticity of plasticized

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healed by heating to the second order transition temp. of 85°. J. W. Westwater

Acetalization of polyvinyl alcohol by hept- and octaldehyde. Seizo Okamura and Takuhiko Motoyama (Kyoto Univ.). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 55, 774–6 (1952).—Polyvinyl alc. was treated with aldehydes of C_1–C_8 in the presence of HCl. The degree of acetalization increased with the number of C atoms of the aldehyde; e.g., in aq. medium heptaldehyde gave 63.6 mole-% and octaldehyde 64.0 mole-%. The same trend existed when the solvent was dioxane, C_6H_6, dichloroethane, and EtCl. The solubilities of the products in various solvents were qualitatively detd. Katsuya Inouye

b Acetalization of polyvinyl alcohol by glyoxal. Seizo Okamura, Takuhiko Motoyama, and Koji Uno (Kyoto Univ.). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 55, 776–8 (1952).—The reaction of polyvinyl alc. (PVA) and glyoxal with HCl catalyst in aq. mediums is considerably slow in comparison with those of PVA and aldehydes previously reported (cf. preceding abstr.). The structural bridge-formation in the produced products is presumed from the calcns. of the degree of acetalization. The use of a mixt. of CH_2O and glyoxal in treatment with fibrous PVA makes mechanically strong acetalized products. The viscosity of aq. solns. of glyoxal-treated PVA is described. c

Katsuya Inouye

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Polyvinyl alcohol. Tsuneji Teramoto and Michitoshi Kitabatake (to Showa Synthetic Chemical Industries Co.). Japan. 3491('53), July 22. A soln. 100 parts of CH_2:CHOAc and 0.1 part Bz_2O_2 was polymerized for 1 hr. at 70° and 40 parts AcOMe contg. 0.2 part Bz_2O_2 was added dropwise in 30 min. The mixt. was heated for 25 hrs. with stirring, 200 parts MeOH was added, 2 parts NH_3 gas was passed in, and the soln. was heated for 30 min. at 40°. The soln. was sapond. at 40° with MeOH contg. 6 parts NaOH to obtain a pure white polyvinyl alc. (I). NH_3 has no effect on the degree of polymerization, sapon., and yield of I. The above reaction without NH_3 gives brown or yellow coloration of I, and the mixt. shows a tendency to foam due to heat of reaction. K. Kitsuta

Saponification of polyvinyl acetate solution. Masao Mori, *et al.* (to Nippon Synthetic Chemical Industries Co.). Japan. 3691('53), Aug. 3. A soln. of 25% polyvinyl acetate in 100 parts dry MeOH at 50° is treated with an equiv. of $Ca(OH)_2$ portionwise, and heated for 50 min. to give 12.5 parts polyvinyl alc. contg. 0.1 mole % of Ac group.

K. Kitsuta

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Saponification [redacted] *et al.* (to Nippon Synthetic Chemical Industries Co.). Japan. 5384('52), Dec. 17. [redacted] poly-vinyl acetate, 4% polyvinyl alc., and 50% water is treated with 150 g. water and 7.5 MeOH, 21.5 g. $Ca(OH)_2$ added portionwise, [redacted] to give polyvinyl alc. with 96.2% sapon. K. Kitsuta

Methyl formate from methyl alcohol and carbon monoxide. Takuya Hatano. Japan. 4569('52), Nov. 6. Through 500 ml. MeOH contg. 2 g. NaOH CO is passed 1 hr. at 100 atm. by means of circulating pump No. 1 (I) and a compressor (II) at the rate of 25 l./hr., then through a circulating pump No. 2, 2 atm. pressure at the rate of 100 l./hr., to collect HCO_2Me in a condenser at the rate of 300 g./hr. The MeOH consumed in the reaction vessel is replaced with fresh MeOH, the circuit is shifted to I and II, and the CO is circulated at 100 atm. This method prevents the decompn. of the HCO_2Me formed into MeOH and CO.

K. Kitsuta

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purity of monomer, (2) polymerization temp., (3) concn. of catalyst, and (4) concn. of monomer. The results were diagramatically given, and a brief discussion, especially on the relation between the degree of polymerization and yield of polymer, was presented. Katsuya Inouye

Viscosity properties of polyvinyl alcohol prepared by acid saponification. II. Influence of the purity of vinyl acetate. Masakazu Matsumoto (Kurashiki Rayon Co., Kurashiki). *Chem. High Polymers* (Japan) 10, 14–18(1953); cf. *C.A.* 47, 7817*a*.—The viscosity properties of two samples of polyvinyl alc., prepd. by acid (I) and alkali (II) sapon of the polymerization product of thoroughly purified vinyl acetate, were found to be the same. The intrinsic viscosity of I is greater than that of II, and the concn. increment of viscosity of I is smaller than that of II when vinyl acetate (starting material) contains more than 0.5% acetaldehyde or more than 0.05% crotonaldehyde. T. Katsurai

Emulsion polymerization of methyl acrylate. III. Emulsifiers and stability of emulsion. Shigenari Suzuki and Hiroo Ito (Toa Gosei Chem. Ind. Co. Ltd., Nagoya). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 56, 244–6(1953); cf. *C.A.* 48, 7336*g*.—The stability of polymethyl acrylate resin during the course of 4 hrs. of polymerization at 65° was detd. for various cases of addn. of emulsifiers. The mixed emulsifiers of (1) nonionic and anionic detergents, (2) nonionic detergent and alkyl naphthalenesulfonate, and (3) nonionic and cationic detergents were added at 0.5–12% of the amt. of monomer, and the appropriate admixing ratios of emulsifiers for each amt. of total emulsifier for monomer were suggested by several diagrams. Katsuya Inouye

Solution polymerization of acrylic esters. Shigenari Suzuki, Hidemaro Tatemichi, and Hiroo Ito (Toa Gosei Chem. Ind. Co. Ltd., Nagoya). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 56, 246–8(1953).—The monomer purified by repeated distns. (b. 80 ± 0.3°) was polymerized in toluene at 60–80° under the presence of benzoyl peroxide of 0.05–0.2% for the amt. of monomer. The yield and polymerization degree were examd. for various factors: (1)

11294

Vinylacetate. III. Preparation of polyvinyl alcohol by sodium or sodium hydroxide in absolute methanol. Bin Takigawa (Denki Kagaku Kogyo Co., Tokyo). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 55, 345–7(1952); cf. *C.A.* 47, 12876*h*.—[redacted] T. Katsurai

Desulfurization of heptane solutions by means of nitrogen dioxide-sulfuric acid mixtures. J. R. Meadow and R. H. Graves (Univ. of Kentucky, Louisville). *Ind. Eng. Chem.* 45, 2113–17(1953); cf. *C.A.* 44, 11074*a*.—Solns. in pure *n*-C_7H_{16} of mercaptan (I), sulfide (II), disulfide (III), or thiophene (IV), having 0.49–0.86% S by the lamp method, were shaken at 20° with various amts. (2–11 vol.-%) of treating agents prepd. by dissolving 1–20 wt.-% NO_2 (V)

12454

Dehydration of polyvinyl alcohol. S. N. Ushakov, R. K. Gavurina, and Kh. V. Tsubina (Leningrad Technol. Inst.). *Issledovaniya v Oblasti Vysokomolekul. Soedinenii, Doklady 6-oi Konf. Vysokomolekul. Soedineniyam, Akad. Nauk S.S.S.R.* 1949, 182–92.—Dehydration of polyvinyl alc. at 80–140° was examd. under the influence of various agents; the greatest loss of H_2O occurs with treatment by means of H_2SO_4 of specimens of the alc. prepd. by the acid hydrolysis method. Specimens of polyvinyl alc. which show total absence of acidity are not subject to dehydration. Treatment of the alc. with alkalies at 80–140° also leads to considerable dehydration. The dehydration produces some unsatn. and cyclic ether structures, the former accounting for some 11–13 mole %. The dehydration products are prone to uptake of O from the atm. with apparent formation of cyclic peroxides. G. M. Kosolapoff

12455

2273

Preparation of acetal resins. IV. Acetalization and butyralization of polyvinyl alcohol. Keisuke Yoshida (Osaka Municipal Inst. Ind. Research, Osaka, Japan). *Rept. Osaka Municipal Inst. Ind. Research* No. 12, 95–102(1948).—Butyralization of vinyl acetate resin in a HCl-H_2O system into a sol. (in a 5:5 mixt. of EtOH and C_6H_6) resin with PrCHO proceeded very rapidly with a dil. soln. and dil. HCl at room or lower temp., provided PrCHO added amounted to 1.2–1.4 times the theoretical value, but acetalization with MeCHO required a more concd. HCl, higher temp., and above 1.4 times the theoretical amt. of paraldehyde, and proceeded more slowly. The resin soln. was butyralized 60–70 and acetalized above 65%; addn. of MeOH to the HCl-H_2O system slightly increased these values. For the detn. of aldehyde in acetal resins Ripper's method was simplified. V. Improved butyralization of polyvinyl alcohol and mixed solvents of acetalized and butyralized resins. *Ibid.* 103–11.—Transparency of butyralized resins was slightly improved by prepg. at slightly higher temp. or adding a small amt. of dibutyl phthalate or tritolyl phosphate to the original system, but filtering the acetate resin soln. after diln. was the best way to remove the minute particles. Various mixed solvents of 2- and 3-component systems for the butyralized resins and those of the 2-component system for the acetalized resins were plotted on triangular coördinates. VI. Polyvinyl alcohol formed by various hydrolytic methods with hydrochloric acid and the properties of acetal resins. *Ibid.* 112–24.—Polyvinyl alc. [redacted] J. G. Yoshioka

Melamine-formaldehyde resins. I. The condensation and the properties of resins formed. Chojiro Kitagawa (Osaka Municipal Inst. Ind. Research, Osaka, Japan). *Report Osaka Municipal Inst. Ind. Research* No. 12, 1–3 (1949).—Purified melamine, m. 352°, was condensed with 3 and 6 mols. HCHO through the H_2O-sol.-EtOH-insol., H_2O-hot-EtOH-sol., and H_2O-insol.-EtOH-sol. stages to H_2O-EtOH-insol. resins M3F and M6F, resp. M3F jellified faster in less acid medium than M6F and after molding was harder and more resistant to chemicals but weaker in mech. strength. II. Methylolization. *Ibid.* 4–6.—The methylolization, the 1st step in the condensation, is a first-order reaction and, as detd. by the reaction velocity by titration with KCN, occurs best at 60–80° in a neutral or slightly alk. medium. III. Methylenization. *Ibid.* 7–9.—The 2nd step, methylenization, is a second-order reaction and, as detd. by the consumption of HCHO, occurs best at 60–90° in a neutral or acid medium (markedly accelerated in the latter). IV. Viscosity of the alcohol-soluble condensation product. *Ibid.* 10–12.—The viscosity of the EtOH-sol. melamine resins in dioxane was detd. and found proportional to the concn. up to 20% in M3F and 30% in M6F. Since the usual viscosity formulas applied, the mol. of the solute seems spherical. From the temp. effect M6F mols. are less firmly linked than M3F mols. V. Degree of mixing with water. *Ibid.* 13–14.—From the change of degree of mixing with H_2O during the condensation the velocity of resinification was detd. VI. Velocity of formation of water-insoluble compounds. *Ibid.* 15–17.—From 70 to 90° the velocity of formation of H_2O-insol. substances was detd., and they were analyzed for N and HCHO. In 4 hrs. at 70° N increased 1.39 in M3F and 7.13% in M6F, but HCHO decreased 1.20 in M3F and 0.89% in M6F. Hence in M3F methylenization seems to be the main reaction and in M6F other reactions seem to occur. J. G. Yoshioka

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Occurrence of head-to-head arrangements of structural units in polyvinyl alcohol. P. J. Flory and F. S. Leutner (Goodyear Tire & Rubber Co., Akron, O.). *J. Polymer Sci.* 5, 267–8(1950); cf. *C.A.* 43, 8240*f*.—Cor. values for the mol. wts. of degraded polymers are about 6.5% higher than those previously reported. The relation between the polymerization temp. and Δ, the mole fraction of 1,2-glycol units, becomes $\log \Delta = -1.00 - (283/T)$.
John R. Hill

4923

Polyvinyl alcohol. Edward Lavin (to Shawinigan Resins Corp.). U.S. 2,499,924, Mar. 7, 1950. High-viscosity polyvinyl alc. is prepd. by the partial sapon. in MeOH-C_6H_6 soln. of polyvinyl acetate, leaving 15–40% OAc groups. Raymond B. Seymour

Dichloromethyl sulfenyl chloride. Sylvan R. Wood (to Cities Service Oil Co.). U.S. 2,434,061, Oct. 11, 1949. Pure trithiane, m. 215°, with Cl forms, in a highly exothermic reaction, Cl_2CHSCl (I), yellowish red fuming liquid, d_{24} 1.6143, n_D^{24} 1.5428, sp. refractivity 0.1947. One of the Cl atoms attached to C and the Cl attached to S are active. The structure of I corresponds to the nonacidic, nonmercaptan properties. I forms addn. products with olefins. Cyclohexene forms with I a dark oil product with combined Cl and S. H. B.

Preparation of polyvinyl alcohol with ethyl alcohol as the solvent. Shigeji Michitaka and Zentaro Yokohama. *Chem. High Polymers* (Japan) 2, 196–200(1945).—EtOH [redacted] in EtOH soln. T. Matsumoto

Purification of polyvinyl alcohol for the manufacture of synthetic fiber by wet spinning. Hiroshi Kawakami and Shoki Lee. *Chem. High Polymers* (Japan) 2, 201–4 (1945).—NaOAc in polyvinyl alc. obtained from polyvinyl acetate by alk. deacetylation is a harmful constituent in the heat-treatment of polyvinyl alc. Removal by washing with MeOH is expensive, and washing with cold water causes losses of polyvinyl alc. Washing with dil. aq. Na_2SO_4 is therefore recommended. T. Matsumoto

Depolymerization of polyvinyl alcohol during butyral formation. Ichiro Sakurada and Tetsuro Osugi. *Chem. High Polymers* (Japan) 1, 113–15(1944).—There is considerable depolymerization of polyvinyl alc. during the deacetylation of polyvinyl acetate but little during butyral formation. A. Nakajima

Phase separation on mixing aqueous solutions of polyvinyl alcohol and viscose. Kasao Taka. *Chem. High Polymers* (Japan) 1, 33–40(1944).—Although aq. solns. of polyvinyl alc. and viscose are essentially incompatible, the stability of mixts. of the 2 solns. can be increased when the stability of each soln. is high. I. Sakurada

Partial saponification of polyvinyl acetate. Ichiro Sakurada and Masao Hosono. *Chem. High Polymers* (Japan) 2, 151–4(1945).—The properties of the products of partial sapon. of polyvinyl acetate by alkali were investigated. Although soly. in water is dependent on the degree of sapon., partial sapon. products are more sol. in cold than in hot water. Partial sapon. products are more easily pptd. from aq. soln. with salts than pure polyvinyl alc. Resistance to petroleum is attained at 60 and resistance to C_6H_6 at 30 mol. % sapon. Y. Sakaguchi

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The chemical analysis and nomenclature of partially hydrolyzed polyvinyl acetate polymers. P. A. J. Gate, J. E. O. Mayne, and H. Warson. *Paint Technol.* 15, No. 169, 9–10(1950).—Sapon. values will measure the residual acetate groups. Acetyl values will indicate the no. of OH groups present. Since the sapon. value is more easily detd., and to avoid further confusion in terminology, it is suggested that these polymers be designated simply by their sapon. values. Acetyl value can be calcd. from the sapon. value by use of the equation: $A = 1275 - 1.95\,S$. M. A. Glaser

Depolymerization of polyvinyl acetate during deacetylation with alkali. Ichiro Sakurada and Masaomi Fujikawa. *Chem. High Polymers* (Japan) 2, 143–50(1945).—Deacetylation in MeOH soln. with NaOH, and reacetylation in C_5H_5N with Ac_2O of polyvinyl acetate (I) samples of 6 different degrees of polymerization (D.P.) from 2000 to 20,000 were repeated 4 times, and the D.P. of I and polyvinyl alc. was estd. viscometrically. In every case, independent of the D.P. of the original I, depolymerization took place at the 1st deacetylation. Depolymerization did not occur on reacetylation and repeated deacetylation. It was concluded that the depolymerization was caused by something in the mol. structure of the original I.
A. Nakajima

.6676

Polyvinyl alcohol by alkaline alcoholysis. Leo M. Germain (to Shawinigan Chemicals Ltd.). U.S. 2,502,715, Apr. 4, 1950. [redacted] of a petroleum fraction [redacted] from 100 g. KOH in 1 l. MeOH) and [redacted] II were added. The cycle was repeated until 120 g. of II had been added; the kettle then contained a slurry of I in MeOAc, unchanged MeOH, and the petroleum fraction. The dried product was a white powder, completely sol. in water. A continuous process for the alcoholysis on a pilot-plant scale is described. Milton Orchin

1950 8161

Physicochemical studies of the reactions of high polymers. Ichiro Sakurada, Kanzo Ohashi, and Shoji Morikawa (Imperial Univ. Kioto). *J. Soc. Chem. Ind., Japan* **45**, Suppl. binding, 450-1(1942)(in German).—The *deacetylation of polyvinyl acetate* in pure or 90% aq. MeOH at various temps. and concns. of NaOH is an alcoholysis, yielding polyvinyl alc. and MeOAc. No sapon. (direct reaction with NaOH to form polyvinyl alc. and AcONa) was detected; in aq. Me_2CO, sapon. was the main reaction. In 40:60 MeOH:H_2O the ratio of rate of alcoholysis to sapon. is 5.2:1. In MeOH contg. 10% H_2O, no sapon. was detected. The rate of deacetylation is proportional to the alkali concn., but the reaction is not unimolecular, since the rate increases with the extent of deacetylation, being about 3-4 times greater at complete deacetylation. H. Burrell

Hydration of polyvinyl alcohol. Jean Neel. *Compt. rend.* **230**, 2188-9(1950); cf. *C.A.* **44**, 7023e.—Expts.

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made at 18° on purified and fractionated polyvinyl alc., using $Na_2S_2O_3$, $AcONH_4$, NaBr, KBr, and NH_4Br as reference compds., show that each $-CH_2CH(OH)-$ unit can chemically bind 0.25, 0.33, 0.50, or 0.75 mol. H_2O; the amt. of H_2O bound increases as the concn. of the salt soln. decreases. P. M. Downey

2137

[redacted] alcohol. Charles Dangelmajer (to Resistoflex Corp.), [redacted]919, Nov. 18, 1947. [redacted] alc. (I) useful for extrusion [redacted]liminated or reduced without impairing other properties by incorporating 5–25% of tetrahydrofurfuryl alc. into a mixt. contg. up to 40% glycerol and 40% H_2O all based on I. Gabriel Goldstein

1082

Drying polyvinyl alcohol. Gelu S. Stamatoff (to E. I. du Pont de Nemours & Co.). U.S. 2,430,372, Nov. 4, 1947. A[redacted], a

1083

[redacted] Cf. *C.A.* 39, 90^4. G. W. Gerhardt

Plasticizing polyvinyl alcohol with aldehyde-alcohol mixtures. Imperial Chemical Industries Ltd. Brit. 577,701, May 30, 1946. Polyvinyl alcs., including those grades which are 85 to 100% hydrolyzed, may be plasticized with aldehyde-alc. mixts. to soft, *rubberlike articles* less affected by moisture than the alcohol-polyvinyl alc.-plasticized compns. The polyvinyl alc. is mixed with a substituted alc., the mixt. is allowed to stand until swelling occurs and an aldehyde, preferably one of low-water soly. and b. above 100°, such as BzH, furfural, or crotonaldehyde, is added. The mixt. is allowed to stand overnight and is then molded. A. O. Zoss

2067

[illegible] wet polyvinyl alcohol. E. I. du Pont de Nemours & Co. Brit. 580,899, Sept. 24, 1946. Discoloration and impairment of soly. are minimized by drying above [illegible]° at 17-25 in. Hg and at a relative humidity of at least 8%. S. A. Muller

Contribution of the Wacker Corporation toward the development of acetylene chemistry. Wolfgang Gruber. *Reichsamt Wirtschaftsausbau Chem. Ber.* Prüf-Nr. 38 (PB [illegible]), 9-19(1940)(Pub. 1941).—The Wacker people were engaged in the manuf. of CaC_2 until the beginning of the first world war when their efforts were temporarily diverted toward the development of a process for the large-scale production of acetone. Consequent return to carbide production confronted them with the problem of producing the carbide in a dry, powdery form which was to be used in the building and fertilizer industries. The treating process which was developed, however, resulted in undesirable polymerization of the C_2H_2 given off. I. G Farben eliminated this C_2H_2 polymerization menace with the construction of an efficient water cooling system. Another problem, viz., ridding the C_2H_2 of impurities such as the hydrates of P and NH_3, was solved by washing with HCl. The Wacker Corporation also formulated AcH from C_2H_2. Mercurous salts were used at temps. above 50° as catalysts. Not as well known is the formation of $(CO_2H)_2$ from C_2H_2; the conditions of this reaction are similar to those necessary for the production of AcH with the exception that instead of using pure C_2H_2, a 50-50 mixt. of C_2H_2 and NO is used. At this plant AcOBu was produced by reacting BuOH, AcOH, and HNO_3. AcOMe and polyvinyl alc. were produced by reacting polyvinyl acetate with MeOH. Oxidation processes included the oxidation of AcH with O at −20° in the presence of Co to produce AcOH. Also, the Wacker chemists polymerized the C_2H_2 compds. to form a no. of high polymers. These polymers were used to replace natural rubber and wood products. David W. Young

4956

[illegible] separation in [illegible] solution. A. Dobry and F. Boyer-Kawenoki (Inst. biol. physico-chimique, Paris). *J. Polymer Sci.* 2, 90-100(1947).—The phase sepn. (incompatibility) in solns. of high polymers in the same solvents was studied for 14 high polymers (unfractionated methylcellulose, cellulose acetate, nitrocellulose, ethylcellulose, benzylcellulose, polystyrene, polyvinyl acetate, polyvinyl acetal, Me methacrylate, and rubber; fractionated polyvinyl alc., polystyrene, polyvinyl acetal, and cellulose acetate) dissolved in 13 solvents (water, acetone, AcOH, AcOEt, Me Et ketone, mesityl oxide, AcOAm, AcOPr, AcOBu, $CHCl_3$, C_6H_6, dioxane, and mesityl acetate). The influence of solvent concn. and the mol. wt. and constitution of the macromol. was studied for 78 mixts.; the results are tabulated and represented in triangular diagrams. Of the 35 pairs of high polymers tested, all show sepn. except cellulose acetate + nitrocellulose in AcOH, nitrocellulose + polyvinyl acetate (Rhodopas HH) in acetone, Me Et ketone, AcOH, AcOEt, and AcOAm, nitrocellulose + Me methacrylate in acetone and AcOEt, and benzylcellulose + polystyrene in $CHCl_3$. When 2 high polymers are incompatible in one solvent, they are generally also incompatible in other solvents. The limit of phase sepn. depends on the nature of the solvent. Thus for AcOH, mesityl oxide, and dioxane the limit of phase sepn. occurs at higher solute concns. than for esters, ketones, etc. The higher the mol. wt., the less compatible are the samples and the more is the limit of phase sepn. shifted toward smaller concns. In order to obtain sepn. of low-mol. fractions, more concd. solns. must be mixed. Branched-chain mols. do not have the same sepn. limits as linear mols. There is no obvious relation between the compatibility of 2 polymers and the chem. nature of the monomers. The similarity of the principal chain is not sufficient to insure the miscibility of 2 polymers. Thus vinyl derivs. are not miscible with each other, nor are cellulose derivs. The similarity of substituents is also insufficient. Thus polyvinyl acetate is immiscible with cellulose nitrate while benzylcellulose is miscible with polystyrene. In the few exceptional cases of high miscibility, e.g. nitrocellulose and Me methacrylate, there is no structural analogy. Phase sepn. is discussed in its relation to osmotic pressure, soly., and the isomorphism of the mols. Phase sepn. furnishes new means of measuring the mol. wt. of macromols. L. S.

Polymerization of vinyl compounds in the gas and in the liquid phase. H. W. Melville. *J. Chem. Soc.* 1947, 274-80.—Methods are described for detg. initiation rate (K_I), propagation rate (K_P), and termination rate (K_T) for the liquid-phase polymerization of vinyl acetate. J. D. Matlack

6436

Products from polyvinyl compounds. Lonza-Werke elektrochemische Fabriken G.m.b.H. Belg. 448,685, Feb., 1943. Polyvinyl alcs. (or partially sapond. polyvinyl esters) are partially [illegible] temp. by AcH in presence of catalysts (mineral acids) in such a way that the product remains sol. in water, below a relatively high coagulation temp. (28-30° for 25% acetalization). After aging 1-2 days at 15° the soln. can be made into fibers, ribbons, or sheets by discharging through nozzles into water at a temp. slightly above the coagulation point (e.g. 35°), or by spreading over similarly heated surfaces. The resultant products can be insolubilized in water by subsequent heating at about 100° A. P.-C.

2453

Stabilization of polyvinyl alcohol. E. I. du Pont de Nemours & Co. [illegible], Aug. 3, 1944. See U.S. 2,[illegible] (C.A. 39, [illegible]). J. Davidson

Photochemical preparation of thio ethers. Frederick F. Rust and William E. Vaughan (to Shell Development Co.). U.S. 2,392,294, Jan. 1, 1946. *Thio ethers* are prepd. by abnormal addn. of an aliphatic mercaptan to unsatd. org. compds., such as olefins, at or below room temp. under the influence of ultraviolet light (below 3000 A.). Thus a 1:1 mixt. of liquid CH_2:CHMe and PrSH was placed in an evacuated quartz tube which was then sealed and maintained at 0°. The reactants in the tube were subjected for 6 min. to the full radiation of a 400-w. quartz Hg-arc lamp placed 20 cm. from the reactor. The tube was chilled, opened, the excess CH_2:CHMe was evapd., and the residue was washed with 10% NaOH, which left 96% *dipropyl sulfide*, b. 141.5°, n_D^{20} 1.4480. A similar expt. in which the same reactants were kept in the dark for 24 hrs. at 15–25° yielded less than 10% of the thio ether. The possible variations of the process are discussed at length. Irwin A. Pearl

3000

Polyvinyl compounds. Robert P. Roberts, Edgar B. Johnson, and Harry H. Taylor. Brit. 563,991, Sept. 7, 1944. Polyvinyl esters are sapond. in soln. in a medium contg. an alkali, a lower aliphatic alc. and a small proportion of water. The amount of alkali should be less than the equiv. of the ester groups to be displaced.—Cf. Brit. 563,960 (preceding abstr.). J. Davidson

7697

Fundamentals and techniques. Dry extrusion of thermoplastics. William L. Hess. *Ind. Plastics* 2, No. 5, 22–4, 29(1946).—Descriptive. Leopold Scheflan

The rheometry of organic glasses. III. Rheometry as a method for studying the mode of action of plasticizers. Walter Scheele, Margret Alfeis, and Ilse Friedrich (Reichsforschungsanstalt, Celle). *Kolloid-Z.* 108, 44–58(1944); cf. *C.A.* 38, 7324.—In the system polystyrene–Palatinol F, the work of deformation (W) decreases on addn. of plasticizer. The temp. coeff. (K) also decreases up to a crit. concn. of plasticizer, above which K does not change with further addn. of plasticizer. The relationship between W and K is: log $(1/W)$ = const. $-(K/T)$, where T = abs. temp. The existence of a crit. concn. is attributed to a change in the type of intermol. cohesion. The plasticizer content at the crit. concn. is not stoichiometric. The binding of the plasticizer to the polymer seems to be of the type described by Würstlin (*C.A.* 37, 4826) for polyvinyl chloride. W. suggested that solvation occurs between plasticizer mols. and polar groups of the polymer, but at the crit. concn. the polymer becomes satd. with plasticizer and has no further binding capacity. The plasticization of polyvinyl acetate by homologous phthalic acid diesters shows a greater decrease in W with increasing mol. wt. of the esters, when the mixts. are compared at equimol. concns. of the plasticizers. The η at temps. from 20 to 95° is given for 40 plasticizers, including 8 different Palatinols, glycerol, isopropyl adipate, butyl stearate, hexyl phosphate, tritolyl phosphate, the mixed esters isohexyl isoheptyl phthalate and butyl benzyl phthalate, and the sym. diesters of phthalic acid and MeOH, EtOH, BuOH, $MeOCH_2CH_2OH$, $BuOCH_2CH_2OH$, and AmOH. The data are in accord with the equation: log $(1/\eta)$ = const. $-(K'/T)$. K' is a function of T given by: $K' = -aT + b$, where a and b are consts. Particular importance is given to the const. b, which has a characteristic value for each plasticizer. For plasticized polyvinyl acetate, the η and the K' values of the plasticizer are not the only factors influencing the rheological relationships. H. K. Livingston

7698

Polyvinyl alcohol in Germany. G. M. Kline (Nat. Bur. Standards, Washington, D.C.). *Modern Plastics* 23, 165–7(1946).—[redacted] I is a partial-[redacted]h; aging is hastened by drying and by treatment with acids (60% conc. H_3PO_4) or chromates and dichromates. I which has been rendered insol. can be vulcanized with SCl_2 or S. I prepd. by the foregoing processes contains acetylated and unacetylated mols. which can be sepd. by extn. II dissolved in concd. HCl and allowed to stand 4 weeks gives a form of *I* in

1413

Synthetic resins. Kodak-Pathé. Fr. 830,746, Aug. 8, 1938. Resins are prepd. by causing a polyvinyl ester, e. g., polyvinyl acetate, to react with a lower aliphatic aldehyde contg. at least 2 C atoms, in the presence of a saponifying agent chosen from the group comprising primary and secondary alcs., and in the presence of a strong acid as catalyst in amt. of 1–5% by wt. of the total reaction mixt. The amt. of catalyst does not exceed 20% by wt. of the polyvinyl ester, at not above 50°, and the reaction mixt. is homogeneous throughout the reaction. The polyvinyl ester may be replaced by polyvinyl alc. The catalyst may be H_2SO_4, HCl, a sulfonic acid or CCl_3-COOH. Films and sheets may be made from the resins.

7652

I. Alkaline saponification of the polyvinyl acetates. S. Lee and I. Sakurada. *Z. physik. Chem.* A184, 268–72 (1939).—T [redacted]. The polymers had a mol. wt. of 24,000 and 79,000, i. e., a polymerization factor of 280 and 920, resp. All the substances had the same velocity const., 0.006 at 20° and 0.033 at 40°; the same heat of activation (15.5 kg.-cal.); the same collision no. and the same probability factors.

Victor R. Deitz

2541

Polyvinyl alcohol. Chemische Forschungsges. Fr. 832,-065, Sept. 20, 1938. Compds. of polyvinyl alc. are converted into polyvinyl alc. by mixing them with abs. alc. and small quantities of acids or alkalies in a mixer such as is used for mixing pastes or plastics. Mixing is preferably effected at low temp. Polyvinyl acetate is mixed with abs. MeOH and dry AcOMe together with sodium methylate in a cooled malaxator. AcOMe is distd. from the product and polyvinyl alc. is obtained as a white powder.

2248

Synthetic resins. Kodak-Pathé. Fr. 817,330, Sept. 1, 1937. The properties of resins, obtained by condensing a hydrolyzed polyvinyl ester with a substance contg. a reactive carbonyl group, e. g., AcH, are improved by subjecting the resin to a deësterification so that the ester group content of the resin is reduced to 3% or to a value in wt. below the polyvinyl ester. The deësterification increases the content in OH groups to 10–20% calcd. on the wt. of polyvinyl alc. in the final product. The deesterification is effected by means of a lower fatty alc. The condensation may be carried out in the presence of at least 3 mols. of a lower fatty alc. for 1 mol. of aldehyde so that the content in ester groups of the resulting resin is not above 3%.

Vinyl resins. Maurice Belloc (to Société Nobel française). U. S. 2,105,208, Jan. 11. A resin prepd. from a polyvinyl alc. and an aliphatic aldehyde has incorporated with it about 1% of an antioxidant of the polyhydroxybenzene type such as hydroquinone to suppress yellowing at a temp. of 100°.

1356

Plasticizers for nitrocellulose, cellulose acetate, styrene, vinyl resins, etc. Lucas P. Kyrides (to Monsanto Chemical Co.). U. S. 2,098,190, Nov. 2. Dibutyl butoxysuccinate or other compds. of the general formula R'OOC-CH(OR)CH_2COOR", in which R is a hydrocarbon radical and R' and R" are alkyl groups, are used as plasticizers in film compds., etc. Several examples with details are given.

3425

Polymerized vinyl alcohol. Willy O. Herrmann, Wolfram Haehnel and Herbert Berg (to Chemische Forschungsges. m. b. H.). U. S. 2,109,883, Mar. 1. See Ger. 642,531 (*C. A.* 31. 5905^{9}).

c) Polimerización

4419–7176

Stabilization of vinyl polymers. Stanley Tocker (to E. I. du Pont de Nemours & Co.). U.S. 3,17[illegible],024(Cl. 260-837), March 23, 1965, Appl. Sept. 9, 1960; 7 pp. Polyolefins and other vinyl polymers were stabilized against uv irradiation damage by copolymerizing with 0.1–10 mole % o-CH$_2$:C(R)CO$_2$C$_6$H$_4$COCH$_2$COR′ (I), where R is H or C_{1-4} alkyl and R′ is C_{1-18} alkyl or substituted Ph. Protection was also afforded by brushing or spraying a soln. of a homopolymer of I on the surface of the vinyl polymer. Copolymers were prepd. in soln. by using initiators of either the peroxide, redox, azo, or coordination type. Thus, I (R = Me, R′ = Ph) was prepd. by reaction of 0.021 mole salicyloylbenzoylmethane with 0.027 mole CH$_2$:C(Me)COCl in 10 ml. anhyd. pyridine. After 1 hr., the reaction mixt. was poured into a mixt. of 150 ml. 3% HCl and 50 g. ice, the mixt. extd. with Et$_2$O, the ext. dried over anhyd. Na$_2$SO$_4$, and the solvent evapd. to give a light-yellow oil. In a 0.3-l. shaker tube, was placed 112 ml. C$_6$H$_6$, 0.2 g. *α,α′*-azodicyclohexanecarbonitrile, and 0.5 g. of this oil. C$_2$H$_4$ was pressured in at room temp. and the mixt. was heated at 115° and 13,000 psig. for 1.5 hrs. The product, 20.2 g., after washing with MeOH had an inherent viscosity of 0.81 (0.1% in *α*-chloronaphthalene at 125°). A 3–4 mil film melt-pressed at 100° and contg. 0.2 mole % I was flexible after 600 hrs. exposure to uv lamps. A polyethylene control film cracked after 150 hrs. Other polymers similarly protected were polypropylene, poly(Bu acrylate), poly(vinyl acetate), polystyrene, polyacrylonitrile, and poly(vinyl fluoride). The stabilizers include (*o*-methacryloxybenzoyl)benzoylmethane, (*o*-methacryloxybenzoyl)acetylmethane, (*o*-acryloxybenzoyl)benzoylmethane, (*o*-acryloxybenzoyl)stearylmethane, (*o*-methacryloxybenzoyl)toluoylmethane, and (*o*-methacryloxybenzoyl)(chlorobenzoyl)methane. F. Edward Bentley

Poly(vinyl acetate) dispersions. Was de Wit N.V. and N.V. Electro Zuur- en Waterstoffabriek. Neth. Appl. 294,294 (Cl. A 23l), April 12, 1965, Appl. June 20, 1963; 8 pp. Vinyl acetate is polymerized with a catalyst in the presence of a protective colloid (Me, Et, hydroxymethyl, hydroxyethyl, or carboxymethyl cellulose), and of nonylphenyl ethylene glycol ether or alkylphenol condensate. Then, poly(NH$_4$ acrylate) or hexylene glycol, and an alk. Mg–Al silicate, are added to disperse the pigment. F. J. Vanreusel

7207

Resistivity of some vinyl polymers and copolymers to the action of ultraviolet and γ-irradiation. Zdzisław Hippe and Alicja [illegible] (Inst. Farb Lakierow, Gliwice, Poland). *Przemysl Chem.* 44(6), 336–7(1965)(Pol). Of the no. of polymers studied, most resistant to uv irradiation were: poly(vinyl alc.), poly(vinyl butyral), poly(vinyl acetate), and the copolymer of styrene with acrylic acid. The above polymers behaved similarly towards γ irradiation, except for poly(vinyl butyral) whose resistivity to γ irradiation was lower than that of the styrene/acrylic acid copolymer. Generally, substances that contain Cl in their mol. display lower resistivity to both uv and γ irradiation. In preliminary testing of lacquer coatings intended for use in the nuclear industry, the samples can conveniently be exposed to more accessible uv radiation. Edward A. Ackermann

10070

Continuous control of vinyl acetate polymerization. A. V. Yanishevskii, A. A. [illegible], and G. N. Luss. *Plasticheskie Massy* 1965(6), 1–2(Russ). The degree of conversion in the soln. polymerization of vinyl acetate (I) in MeOH could be detd. by the refractometric method, the automatic refractometers being the most suitable. The relations between the *n* and the compn. of the ternary system MeOH–I–poly(vinyl acetate) were detd. The refractometer used had 2 cells, one of which contained the soln. to be measured, the other a standard I–poly(vinyl acetate)–MeOH soln. Only differences in the n_D^{20} values obtained by passage of the light through the 1st and the 2nd cell needed to be recorded. Frantisek Lesek

15606

The flocculation of kaolin suspensions. [illegible] Co. Ltd., Tokyo). *Kogyo Kagaku Zasshi* [illegible] (Japan). Polymers that do not dissolve in [illegible] are dispersed in a concd. detergent soln. This is because [illegible] detergent to form a complex. With the complex [illegible] kind of polymer electrolyte, the flocculation of kaolin suspensions was discussed. The effect of polymer was in the order: poly(vinyl formal) > poly(vinyl acetate) > poly(vinyl butyral). Effect of detergent was in the order: Na oleate > Na dodecyl[illegible]ate > Na propylnaphthalenesulfonate > Na butylnaphthalenesulfonate. The effect of mol. wt. of polymer was relatively small. The effect was almost none in pH 3–6. The effect of adding an inorg. electrolyte was great. K. A.

16500

Poly(vinyl acetate). Mitsubishi Chemical Industries Co., Ltd. and Kurashiki Rayon Co., Ltd. (by Seizo Okamura and Toshinobu Higashimura). Japan. 11,626('65), June 9, Appl. Mar. 27, 1961; 1 p. Reaction of amorphous poly(vinyl *tert*-Bu ether) with Ac$_2$O in haloalkanes or arenes in the presence of ZnCl$_2$ gave amorphous poly(vinyl acetate) in excellent yields. Cf. Japan. 9972('65). [illegible] Matsumoto

16563

Continuous preparation of aqueous polymer dispersions. Consortium für Elektrochemische Industrie G.m.b.H. Belg. 649,023, Sept. 30, 1964; Ger. Appl. June 11, 1963; 16 pp. Addn. to Belg. 618,678; See Ger. 1,157,216, (*CA* 58, 3559*c*). The process of Belg. 618,678 is improved to give a bubble-free polymer dispersion by allowing the product leaving the reactor to expand adiabatically in an insulated tube of specific dimensions. The b.p. of the dispersion decreases 2-20° during the expansion as unreacted monomer and part of the H_2O are removed by evapn. In an example, 9 l./hr. of an emulsion of vinyl acetate 48.8, H_2O 48.1, poly(vinyl alc.) 2.85, and a 75:25 mixt. of 0.25% *tert*-BuOOH and (*tert*-BuO)$_2$ in 0.6 l. of a 0.5% aq. soln. of Rongalite C is polymerized at ~1.6 atm. and 70-80° in a tubular reactor. The dispersion then passes through a valve into a tube where it expands at ~0.4 atm. while the temp. decreases to ~70°. It is then led into a steam-jacketed separator where a geared pump draws off the bubble-free product as a vacuum pump removes the volatile materials for recycling. Details of the app. used for the improved process are given. F. L. Decker

Polymer pulverization. Asahi Chemical Industry Co., Ltd. Fr. 1,398,342 (Cl. C 08f,g), May 7, 1965; Japan. Appl. June 11, 1963; 5 pp. Water-insol. polymers which are insol. at between room temp. and the b.p. of H_2O, soly. parameter >10, such as polyamides, polyesters, and polyacrylonitrile, are added to H_2O, the mixts. are heated under pressure, and the mixts. are cooled, or atomized, to give powd. materials with uniform granulometry. Thus, a mixt. of 15 g. nylon 6 (diam. 2 mm., height 2 mm.) in 300 g. H_2O is heated 1 hr. at 160° and 6.1 kg./cm.^{2}; the product is dried to give a powd. material, particle size 1-2 μ. BDPF

18304

Poly(vinyl acetate). Kurashiki Rayon Co., Ltd. ([illegible] Okamura and Toshinobu Higashimura). Japan. 997[illegible] May 21, Appl. May 27, 1961; 2 pp. Reaction of poly(vinyl *tert*-Bu ether) (I) with Ac_2O in haloalkanes or arenes in the presence of $BF_3.Et_2O$ (II) gave poly(vinyl acetate) (III) in excellent yields. Thus, to a soln. of 0.4 g. amorphous I in [illegible] CH_2Cl_2, 0.1 g. II in 1 ml. Ac_2O was added. The mixt. was stirred at 30° for 7 hrs., poured into petroleum ether, filtered, and washed with hot H_2O to give III, [illegible] Me_2CO and contg. >98% of the theoretical amt. of Ac [illegible]. Treatment of cryst. I gave stereoregular III in a quant. [illegible] [illegible]

18374

Poly(vinyl acetate) plasticizer. Wallace & Tiernan Inc. Brit. 1,005,092 (Cl. C 08f), Sept. 22, 1965; U.S. Appl. April 20, 1961; 4 pp. Polyester plasticizers prepd. from diglycolic acid (I), a glycol, and a monohydric alc. contg. an ether group have excellent compatibility with and contribute to the adhesive properties of poly(vinyl acetate). For example, I 603, propylene glycol 274, and ethylene glycol mono-Bu ether 425 g. were heated under CO_2 in C_6H_6 soln. The H_2O formed during esterification was continuously removed by azeotropic distn. During the 1st 20 hrs. of reaction, the temp. was gradually raised to 185° by removing some C_6H_6. At the end of this time, the acid value was 25. During a final 11-12 hrs., the reaction mixt. was heated to 215° while gradually reducing the pressure to 3-5 mm. The resultant polyester had a acid value of 1.2, a sapon. value of 525.3, and a mol. wt. of 855. P. D. Schuman

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10835

Terminal carbonyl group of poly(vinyl acetate) polymerized in the presence of aldehydes and of the derived poly(vinyl alcohol). Makoto Shiraishi (Kurasiki Rayon Co., Okayama, Japan). *Kobunshi Kagaku* 19(211), 676–81(1962). Vinyl acetate was polymerized in the presence of an aldehyde to give low-mol.-wt. poly(vinyl acetate) (I) having a carbonyl end group. The polymer was sapond. by an alk. soln. in MeOH and the reaction mixt. was acidified and distd. In the distillate, only a ketone was found. On the other hand, if the acidified reaction mixt. was again made alk., both ketones and AcH were found in the distillate of the mixt. The amt. of AcH produced increased with increasing time of distn. The ketones liberated were Me_2CO or MeCOPr, depending on whether the polymer was prepd. in the presence of AcH or PrCHO. The polymer prepd. by sensitized photopolymerization at low temp. gives less ketone. These results show that the carbonyl end groups of I prepd. in the presence of an aldehyde are mostly ketonic [$\sim CH_2CH(OAc)CH_2COR$], and are easily converted to aldehyde end groups by the elimination of a ketone [$\sim CH_2CH(OH)CH_2CHO + MeCOR$]. Thus, the depolymerization of poly(vinyl alc.) in an aq. alkali soln. occurs at the aldehyde group by the reverse aldol reaction.

Eiichi Wada

8475

Water vapor diffusion through polymer films. cellulose acetate and poly(vinyl acetates). Yuji Tadokoro, Yohei Uchitomi, Yasunori Nagahara, and Hitoshi Yamamura (Univ. Hiroshima, Japan). *J. Sci. Hiroshima Univ.*, Ser. A-II 27(2–3), 133–40 (1964). The non-Fickian diffusion of H_2O through cellulose acetate and poly(vinyl acetates) was investigated indirectly by evaluation of a rheological parameter *k* (*CA* 54, 6184*b*) for creep which is assumed to be equiv. to a parameter *α* (Crank and Park, *CA* 46, 3832*a*) characteristic of the diffusion process. The value of *k* increased as the temp. became higher at const. humidity and as the relative humidity increased from 30 to 60% at const. temp. and passed through a very low min. between 60 and 80% relative humidity. The parameters *k* and *α* were compared, and passable agreement was obtained which supported the application of such a parameter as *k* although the 2 values did not show sufficient numerical agreement.

Joanne Burger

13498

Poly(vinyl acetate) dispersions. Farbwerke Hoechst A.-G. (by Carolyn E. Breed). Ger. 1,173,252 (Cl. C 08*f*), July 2, 1964, Appl. Oct. 10, 1961; 4 pp. Poly(vinyl acetate) dispersions are prepd. by mixing vinyl acetate 77, di-Bu maleate (plasticizer) 23, acrylamide (stabilizing monomer) 0.7, H_2O 0.15, condensation product [of 88 moles ethylene oxide and 1 mole nonylphenol (nonionic surfactant)] 1.25, Na octylbenzenesulfonate (anionic surfactant) 0.8, Na citrate (buffer, electrolyte) 0.16, NaOA (buffer, electrolyte) 0.45, $K_2S_2O_8$ (initiator) 0.30, fumaric acid (stabilizing monomer) 0.161 part, enough H_2O for 57 wt.% solids in the final soln., and enough AcOH to establish a pH of 4.6–4.7. The reaction temp. is 75–85°. The dispersions are useful as binders for aq. coating compns., as paper coatings, as adhesives, as textile impregnants, etc. Cf. *CA* 52, 16758*e*; 55, 20513*c*; Ger. 893,956, *CA* 46, 10684*d*.

L. F. W. Buurlage

3203

Plasticizing poly(vinyl acetate) dispersions with dibutyl phthalate. H. Cunesch, R. Draghici, and E. Florea. *Rev. Chim.* (Bucharest) 15(6), 342–4(1964). In an attempt to develop a convenient method for detn. of the vitrification temp. of poly(vinyl acetate) (I) dispersions plasticized with di-Bu phthalate (II), a series of difficulties were encountered when the variation of the sp. vol. as a function of the temp. was chosen. The detn. of the *n* of a film dried directly on the prism as a function of the temp. gave much better results and was much more suitable for exptl. adaptation. The temp. of the thermostat was slowly raised by heating the precooled EtOH. The EtOH was precooled to −15° followed by advanced cooling with solid CO_2. The graphical method used by Jenckel and Heusch (*CA* 47, 6221*b*) according to which 2 straight lines intersected at the desired point was adopted for this detn. This method gave the following vitrification temps. for dispersions of I plasticized with II (the % plasticizer and the resp. vitrification temp.): are given 0, 17.5°; 5, 15°; 10, 10.5°; 20, 1.5°; 25, −7.5°; and 50, −32°. Agitation had very little effect on the vitrification temp., and hence the min. agitation necessary for effective plasticizing was that required for homogenizing the contents of the autoclave (2 m.^{3}). This result was confirmed by a series of other detns. in which diverse characteristics of the specimens (viscosity, plasticizer extn., resistance to tearing, resistance of the fibers to elongation, and wt. loss were found to reach nearly const. values after agitation for 1 hr. Plasticizing could be performed during cooling of the dispersion, thus practically eliminating the plasticizing time. 12 references.

M. Lapidot

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Polymerization of vinyl acetate at a low temperature. Japan Synthetic Chemical Industry Co., Ltd. (by Ken Noro, Goro Morimoto, and Eiichi Uemura). Japan. 18,542('63), Sept. 17, Appl. Sept. 4, 1961; 2 pp. Vinyl acetate (99.7 parts) is mixed with 0.2 part diisopropyl dicarbonate peroxide and 0.11 part *N,N*-dimethylaniline with ice cooling, cooled at −50°, and kept at 20 ± 1° for 100 min. to give colorless poly(vinyl acetate), which is sapond. with alkali to give colorless poly(vinyl alc.) of degree of polymerization 2080 and degree of crystn. 53%.
Hiroshi Kataoka

1846

The emulsion polymerization of vinyl acetate. G. Mueller. *Oesterr. Chemiker-Ztg.* 64(2), 33–5(1963). A preparative method is presented and some properties and applications of poly(vinyl acetate) dispersions are discussed.
M. Ternbah

1856

Effect of polymerization conditions on the hydrolytic degradation of poly(vinyl acetate). Maria Tokarzewska and Halina Pietkiewicz. *Polimery* 8(2), 52–5(1963). The kinetics of polymerization of vinyl acetate (I) in MeOH and the effect of various parameters on the hydrolysis to poly(vinyl alc.) were studied. At 60°, virtually no induction period was observed; on lowering the temp., the induction period became apparent (80 sec. at 50°). The rate of polymerization decreased with decreasing temp. of reaction. The mol. wt., as detd. by viscosity, decreased with increasing temp. of polymerization. Change of initiator ($[Me_2C(CN)N:]_2$) concn. in the range of 0.05 to 0.50% (based on I) caused an increase in the rate of polymerization; the rate was proportional to the square root of initiator concn. The mol. wt. increased slightly with an increase of initiator concn. up to about 0.2%, then fell off fairly rapidly (I:MeOH ratio = 1, temp. 60°, conversion 60%). The rate of polymerization decreased slightly with increasing amount of MeOH, while the degree of polymerization at the same conversion depended on the initial I:MeOH ratio.
E. Wieckowski

New system in emulsion polymerization of vinyl acetate. A. E. Akopyan, L. S. Grigoryan, and N. A. Markosyan. *Zh. Prikl. Khim.* **37**(2), 408–13(1964). To obtain a high-quality fiber-forming polymer, the emulsion polymerization of vinyl acetate (I) was investigated using $(NH_4)_2S_2O_8$ (II) as a catalyst, poly(vinyl alc.) (III) as an emulsifying agent, and AcOH for regulating the pH. Optimum catalyst concn. is 0.15–0.20%, giving conversions of 97.5–98.5% after 7–8 hrs. at 60° in an emulsion of 474.32 g. I. in a soln. of 28.52 g. III and 3.12 g. AcOH in 455.02 g. H_2O. In the presence of 22.5 ml. of a 4% soln. of II (i.e., 0.09% II) under the same conditions, the optimum concn. of III with a degree of polymerization (D.P.) of 1200 is 3.0–3.8%, yielding during 6–8 hrs. a stable latex which has a viscosity of 10–20 poises, while 0.3–0.4% is the optimum concn. of AcOH. The viscosity of the latexes prepd. can be easily controlled by adding III with 2 different mol. wts. In the above formulation, a standard amt. of III (30.7 g.) was used, this amt. consisting of 2 species with D.P. 900 and 2,000, resp. The viscosity increase is almost directly proportional to the ratio of the latter to the former. Thus, the viscosity 15 or 95 poises, resp., corresponds approx. to the ratio 0.25 or 1.0, resp., the conversion remaining practically const. These results make it possible to carry out the polymerization in a continuous procedure. The exptl. cascade app. consisted of 2 flasks for supplying the aq. soln. and I, resp., and of 4 round-bottomed 1-l. flasks, one serving for mixing and 3 for polymerizing at 60–62°. The optimum ratios of the components (in parts by wt.): I 100, II 0.1–0.2, III 5–6, AcOH 0.7–0.8, H_2O 100. If the total inlet rate of the individual streams reaches 0.1 or 0.3 l./hr., the conversion drops from 98.96 to 87.76%; 0.13–0.16 l./hr. is the optimum rate, yielding a conversion of 97.6–98.7% and an output of 64.8–77.8 g./hr. of a latex contg. 49–50% solids and 1–2% I. The product has a viscosity of 12–18 poises, and does not freeze above −30°. The D.P. of poly(vinyl acetate) is 1700–2500.
V. Zvonar

13326

3101

The theory of heterophase polymerization. II. Comparison of molecular-weight distributions of polymers prepared under conditions of homo- and heterophase polymerization. L. G. Shaltyko, V. G. Baranov, T. I. Volkov, V. V. Lutsenko, and S. Ya. Frenkel (Inst. High Mol. Wt. Compds., Acad. Sci. U.S.S.R., Leningrad). *Vysokomolekul. Soedin.* 5(10), 1527–33(1963); cf. *CA* 57, 15333*f*. The classification of polymer processes based on the kinetics and mechanism of polymerization and the resulting mol.-wt. distributions (MWD) was made, and the influence of mechanism and topology of reaction on the shape and modality of the MWD curves was discussed. The MWD of several fiber-forming polymers were investigated, and the dependence of rheological properties of fibers on their MWD was briefly discussed. MWD were obtained by using the Svedberg ultracentrifuge and a simple pptn. technique. Both methods give essentially the same MWD. MWD curves of polyacrylonitrile (I) and poly(vinyl acetate) (II) obtained in various conditions are given. I polymerized in an aq. suspension, in homogeneous soln. ($HCONMe_2$) initiated by azodiisobutyronitrile in the extensive range of temps. and concns., emulsion-polymerized II, II obtained in *n*-heptane (polymer precipitant) with the catalytic system $Et_3Al–O_2$, II photopolymerized in block at −35°, and several lab. and pilot-plant samples of poly(vinyl alc.) (III) were investigated, and corresponding MWD curves are given. The 1st type of MWD was obtained for I polymerized in an aq. dispersion. This is a "classic" heterophase system in which the growth of macromols. take place simultaneously in soln. and on the surface of pptd. polymer particles. In this case, a MWD curve with 3 max. should be obtained. In practice, only bimodal curves were observed; an explanation of the "absence" of the 3rd max. is given. A process of polymerization corresponding to the 2nd type of distribution is characterized by the presence of the main part of the monomer in the emulsion oil phase, the polymer being completely sol. in its own monomer (e.g. emulsion polymerization of vinyl acetate). In the ideal emulsion, the polymerization (monomer insol. in the H_2O phase) process is homophase in nature in spite of the heterogeneous character of the system. In some cases, initiation is possible in the H_2O and in the oil phases; it depends on the soly. of the initiator used. In the 3rd system, the polymer is sol. in the monomer and insol. in the solvent used and the monomer is sol. in the solvent (e.g. polymerization of vinyl acetate in *n*-heptane). The 3-modal MWD curve is characteristic for this type of system. The 4th group is represented by the systems of homogeneous polymerization. In all cases, ordinary Flory-Schulz distributions with a single peak take place. Sepn. of the homogeneous process into 2 stages with time leads to the same result as the spatial sepns. of phases.
St. Penczek

13453

Polymerization of vinyl acetate and hydrolysis to poly(vinyl alcohol) for use as a sizing, coating, and thickener. Arthur L. Lowell and Orville L. Mageli (to Wallace & Tiernan Inc.). U.S. 3,121,705 (Cl. 260–91.3), Feb. 18, 1964, Appl. Sept. 20, 1961; 2 pp. Aq. vinyl acetate I, polymerized in the presence of a protective colloid with *tert*-butyl peroxypivalate (II) at 40°, gives a poly(vinyl acetate) (III) with fewer branched chains which remain as long chains after hydrolysis and permit prepn. of a fully hydrolyzed poly(vinyl alc.) (IV) of a higher viscosity at a given concn. than previously possible. I 100, hydrolyzed III 0.5, H_2O 100 parts, and II 0.16 % were stirred at 40° for 8 hrs. The III beads were sepd., washed, and dried. The dried beads were hydrolyzed by treatment with alc. NaOH. The resulting IV, which gradually pptd. from the soln., produced, in 4% aq. soln. at 20°, a product having a viscosity of 540 cp. (Brookfield).
Harlan E. Tiefenthal

7609

Branching of poly(vinyl acetate). IV. Temperature dependence of certain transfer constants of the radically initiated polymerization of vinyl acetate. G. V. Schulz and Lesley Roberts-Nowakowska (Univ. Mainz, Ger.). *Makromol. Chem.* 80, 86-13(1964)(Ger); cf. CA 61, 10787f. The activation energies of the transfer reactions of growing poly(vinyl acetate) (I) chains with vinyl acetate and EtOAc, calcd. from the corresponding transfer-rate consts. between 20 and 60° were 3.15 and 3.45 kcal./mole, resp. The equation log $C_p = -1.54 - 723/T$, where C_p is the transfer const. of growing I chains to polymer and T is the abs. temp., for the relative transfer reaction between radical-initiated growing I chains and terminated I chains was derived. The rate const. of end-group branching (incorporation of vinyl end groups into growing chains) was recently detd. by Stein (CA 61, 9581c) and is approx. equal to the rate const. of propagation; the ratio of these 2 rate consts. is approx. independent of temp. The overall degree of branching I can be calcd. as a function of temp. and conversion from the various rate consts. and their temp. dependence. H. P. Frank

10536

Mechanical degradation of poly(vinyl acetate) in solution induced by vigorous stirring. Kunio Goto and Hideki Fujiwara (Tech. Inst., Osaka, Japan). *Kobunshi Kagaku* 21(235), 716-20(1964). The mol. wt. of poly(vinyl acetate) and its hydrolyzed polymers is detd. before and after degradation. Chain scission does not occur at the C–C linkage, but at ester linkages at the branched point. The mol. wt. decreases with decreasing soln. concn. and solvent power and increasing rate of shear. Eiichi Wada

13909

The kinetics of the streaming potential for the system poly(vinyl acetate)–water. Walery Misniakiewicz (Politech. Slaska, Gliwice, Poland). *Zeszyty Nauk. Politech. Slask., Chem.* No. 13, 33-42(1963)(Pol). Kinetics of the streaming potential (v_t) obtained from capillaries of poly(vinyl acetate) were investigated by the Sokalski-Misniakiewicz method (*Przemysl Chem.* 40, 456-60(1961)). The v_t increased with time of flow up to 2.5 hrs. and then remained at a const. level. The slightly rising shape of the curve showed that the main process was diffusion of monomers from the plastic. The process was partially obscured by 2 opposite processes: swelling and penetration of H_2O into the plastic. After drying of the capillary at 105° the curve v_t vs. time (starting at a much higher value of v_t) had a neg. slope, which indicated that monomers were removed and the main processes were now swelling and penetration of H_2O into the plastic. Increase in v_t value showed that annealing at 105° and subsequent rinsing with H_2O changed the structure of the capillary surface. As a consequence of this, adsorption of ions increased. Penetration of H_2O into the plastic is represented by the equation $\log v_t = A - b \log t$ and the diffusion of monomers by the equation $\log v_t = A + b \log t$, where A and b are consts. and t = time. A. Janowski

14850

[illegible] Oberreigner, and D. Lim (Inst. Macro-[illegible], Prague). *Chem. Ind.* (London) 1965(12), 508-9 (Eng). The course of chain scission was followed for a liquid model compd. with 1 double bond, e.g. 4-chloro-2-dodecene, and 2 double bonds, e.g. 6-chloro-2,4-octadiene. The reaction was investigated simultaneously by chem. detn. of HCl and by spectrometric detn. of the increasing amt. of the corresponding diene, or of the wt. decrease in the case of chlorooctadiene. Dehydrochlorination results suggest an accelerated course for 4-chloro-2-dodecene. The decompn. of 6-chloro-2,4-octadiene is 1st order in the regions of low conversion. The decompn. of 4-acetoxy-2-octene in the range 200-40° is autocatalytic, and the dehydrochlorination is accelerated by HOAc. The splitting of unbranched models, 2,4-diacetoxypentane and 2,4,6-triacetoxyhept[illegible] ~300°, is not accelerated by HOAc.

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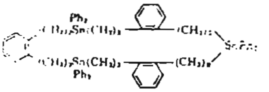
Synthesis of linear Group IV organometallic polymers by polyaddition. J. G. Noltes and G. J. M. van der Kerk (Inst. Org. Chem. T.N.O., Utrecht, Neth.). *Chimia* (Aarau) 16, 122-7 (1962)(in English). Reaction of dialkyl- or diaryltin dihydrides with diolefins gives linear heteropolymers (R is alkyl or aryl, R' is an aromatic diradical): $[Sn(R)_2CH_2CH_2R'CH_2CH_2]_x$, and with polyacetylenes: $[Sn(R)_2CH:CHR'CH:CH]_x$. Properties of these polymers, reaction conditions, synthesis of starting materials, and side reactions are described. The basic polymer-forming reaction is an example of H-transfer polymerization. Ring formation occurs to various extents during reaction of an organotin dihydride with dienic or diynic compds. having the unsatd. groups in sterically favorable positions. Ph_2SnH_2 reacts with PhC:CH to form *cis* and *trans*-1,1,2,4,4,[illegible]-hexaphenyl-1,4-distannacyclohexane, m. 72° and 144°, resp. Ph_2SnH_2 and $(CH_2:CH)_2SiPh_2$ give 1,1,4,4-tetraphenyl-1-stanna-4-silacyclohexane, m. 131°; $(CH_2:CH)_2GePh_2$ gives the 4-germa analog, m. [illegible]1°. Ph_2SnH_2 and *o*-divinylbenzene give polymer, 3,3-diphenyltetrahydro-3-benzostannepin, m. 99°, and I, m. 277-8[illegible]°.



I

Roberta H. Brandenberger

Solution polymerization of vinyl acetate in aqueous solutions of partially acetylated poly(vinyl alcohol). IV. The interfacial properties of the graft copolymer. Chen-Cheng Lin (Prov. Ind. Res. Inst., Formosa). *J. Chinese Chem. Soc.* (Taiwan), Ser. II 8, 276-83(1961)(Pub. 1962)(in English); cf. *CA* 57, 13978g. No significant difference between the inward and outward form of the graft copolymer in interfacial tension was observed, but remarkable differences in the ability to form fine droplets and in the stability of the emulsion were found. This was attributed to the existence of 2 configurational forms of the graft copolymer the affinities of which with the oil phase are different from each other. It is conceivable that neither form of the graft copolymers has a solubilization power for water-insol. substances. The effect of substances slightly sol. in water on the viscosity of the polymer soln. is dependent on the different configurational conditions of the polymer mol. in soln. This depends on the interaction of the polymer mols., the interaction between the polymer mols., and the medium into which the substances dissolve.

P. Y. Yeh

9233

Detection of poly(vinyl acetate) in vinyl acetate monomer. [illegible] and Y[illegible] Okumura. *Bunseki Kagaku* 11, [illegible](1962). Set up a filter paper strip on vinyl acetate monomer for a few min., dry the strip, spray with a soln. of 0.26 g. KI and 0.13 g. I in [illegible] ml. H_2O, and detect the polymer by development of a red band just above the immersed part.

Akimasa Masuda

10309

Preparation of pearl poly(vinyl acetate). Antonin Rysanek and Dagmar Parizkova (*Chem. Prumysl* 12, 271-3(1962). Vinyl acetate (I) dispersions contg. 20 g./l. poly(vinyl alc.) contg. 12% AcO groups, 44.8 g./l. NaCl, and 1.15 g./l. AcOH were polymerized at 50° in the presence of 0.5% lauroyl peroxide. The ratios of I to dispersion medium were 0.46-1.13:1. The max. particle diam. was inversely proportional to the sq. of the no. of rotations of the stirrer. Addn. of 1-3% poly(vinyl acetate) to I increased the max. particle diam.

J. Sebenda

1963

585

Isotactic poly(vinyl alcohol). I. Acetylation of poly(vinyl benzyl ether) with acetic anhydride and stannic chloride. [illegible] Fujii (Kurashiki Rayon Co.). *Kobunshi Kagaku* 19, [illegible] (1962). In order to obtain isotactic poly(vinyl esters), acetylation of a poly(vinyl ether) (presumably isotactic) by use of an org. acid anhydride and a Lewis acid was tried. Vinyl benzyl ether, which has a cleavable ether bond, was chosen as a monomer and synthesized by the Reppe process. A white [illegible] crystallizable polyether was obtained in low-temp. [illegible]phase polymerization with $BF_3.Et_2O$ as the catalyst. The acetylation product of the polymer with Ac_2O and $SnCl_4$ was sol. in MeOH and Me_2CO, unlike the original poly(vinyl ether). The infrared spectrum and anal. results show that substitution of the benzyl ether group by the acetate group took place almost completely. The x-ray pattern and infrared spectrum of the

1548

poly(vinyl acetate) (I) obtained have characteristics of amorphous polymers like those of ordinary I obtained by free-radical polymerization. The acetylated polymer was hydrolyzed in methanolic NaOH. The hydrolyzed polymer was sol. in H_2O. Its degree of polymerization was estd. to be about 500 from viscosity measurement of the aq. soln. II. Synthesis of isotactic poly(vinyl formate). Kiyoshi Fujii and Takani Mochizuki. *Ibid.* 124–30. Crystallizable and noncrystallizable polymers were prepd. from vinyl *tert*-Bu ether in the presence of a Ziegler catalyst or $SnCl_4$ as the initiator. Two types of poly(vinyl *tert*-Bu ethers) (I) were acetylated with Ac_2O and $SnCl_4$ or $ZnCl_2$ and then sapond. to give poly(vinyl alc.) (II). The two types of II thus obtained were formylated by HCO_2H. The anal. results and infrared studies show that the formylation takes place almost completely to give poly(vinyl formates) (III). III derived from crystallizable I is crystallizable, while III derived from noncrystallizable I is noncrystallizable. The crystallizable III gives a sharp fiber diagram and the fiber period is 6.55 A., which corresponds to the isotactic configuration. Syndiotactic propagation in the free-radical polymerization of vinyl esters is enhanced over isotactic propagation by decreasing the polymerization temp. Stretched films of isotactic and syndiotactic III were subjected to heterogeneous hydrolysis. The II films obtained have similar fiber diagrams; they both give the same fiber period of 2.5 A.

Eiichi Wada

Poly(vinyl alcohol). VII. Influence of the polymerization solvent for vinyl acetate. Luper Alexandru and M. Opris. *Rev. Chim.* (Bucharest) **13**, No. 5, 279–81(1962); cf. *CA* 57, 16857*b*. Vinyl acetate was polymerized in various solvents. While in EtOH the degree of polymerization is 200, in glycerol it can reach 5000. The depolymerization of the poly(vinyl acetate) during hydrolysis to poly(vinyl alc.) is highly dependent on the reaction medium. The solvent used for polymerization affects the degree of crysty. of the poly(vinyl alc.). Thus, in MeCOEt, a poly(vinyl alc.) with 65% relative crystallinity was obtained.

Erwin Glotter

4662

Hydrolysis of poly(vinyl esters). Eugene C. Martin and Joseph F. Jennings (to Standard Oil Co. (Indiana)). U.S. 3,066,121 (Cl. 260–91.3), Nov. 27, 1962, Appl. July 3, 1959; 2 pp. Homogeneous poly(vinyl alc.) solns. are prepd. by the hydrolysis of poly(vinyl esters). Anhyd. poly(vinyl acetate) (1 part) is dissolved in 8.5 parts abs. MeOH and guanidine carbonate catalyst, 0.01–0.05 g./g. ester, is added. Hydrolysis is carried out at 25°, first under anhyd. conditions and later in the presence of H_2O. The reaction is terminated by AcOH. The

11478

Syndiotactic poly(vinyl formate) and derived poly(vinyl alcohol). Irvin Rosen, G. H. McCain, A. L. Endrey, and C. L. Sturm (Diamond Alkali Co., Painesville, Ohio). *J. Polymer Sci.* Pt. A. 1, 951–64(1963). Low temp. polymerization of vinyl formate, initiated by ultraviolet light-activated 0.1 mole % $[Me_2C(CN)N:]_2$ yielded a polymer having considerable syndiotacticity. After the polymerization proceeded to 10–20% conversion, the poly(vinyl formate) (I) was isolated, purified, and hydrolyzed to the corresponding poly(vinyl alc.) (II). The intrinsic viscosities $[\eta]$ of I in $CHCl_3$ were proportional to those of the corresponding II in H_2O. Thus, for I, the relation $[\eta] = 4.42 \times 10^{-4}\,DP^{0.64}$ was used to det. the av. degree of polymerization (DP). DP increased with polymerization temp., from which the difference between the energy of activation for propagation and termination was calcd. as 4.5 kcal./mole. Detn. of the Huggins const. indicated essentially no branching of the polymer. Detn. of the 1,2-glycol content showed that a lowering of the temp. reduced head-to-head addn. X-ray diffraction patterns of oriented samples of I, and the color of iodine complexes of the corresponding II, indicated a higher stereoregularity for lower polymerization temps. A higher stereoregularity did not result in a higher crystallinity or higher d., but lowered the swelling and soly. in solvents. Infrared spectra of I polymerized at different temps. were identical.

A. G. Tsuk

11486

Low-swelling poly(vinyl alcohol). Kurashiki Rayon Co., Ltd. (by Kiyokazu Imai). Japan. 3140('62), May 31, Appl. May 25, 1960; 2 pp. Poly(vinyl alc.) (I), obtained from poly(vinyl acetate) prepd. by soln. polymerization of vinyl acetate (II) in the presence of H_3BO_3, had a low degree of swelling, which was confirmed by the value of $t_{eq}P_a^{0.5}$ (t_{eq} is [illegible] of the time required to reach equil. turbidity, and P_a is mean degree of polymerization of I). Thus, 10 g. II in 8 g. MeOH was polymerized in the presence of 2 g. H_3BO_3 by using 0.01% azobisisobutyronitrile as an initiator at 60° for 21 hrs. to give a polymer in 73% yield. I from the above polymer had a $t_{eq}P^{0.5}$ value of 1.43 × 10[illegible] hrs. On the contrary, I prepd. by an ordinary method without H_3BO_3 had a value of 2–5 × 10^3 hrs.

H. Kawazura

11487

(by Masakazu Matsumoto and Kiyokazu Imai). Japan. 3293('62), June 1, Appl. June 4, 1959; 1 p. By an irradiation polymerization of vinyl acetate in alc. contg. > 3% H_2O, highly crystallizable poly(vinyl alc.) was obtained. Vinyl acetate (50 parts) in 50 parts MeOH contg. 30% H_2O was γ-irradiated at 4.45 × 10^4 r./hr. at 30–5° for 2.2 hrs. to give a polymer in 69.3% yield. Poly(vinyl alc.) prepd. from the polymer had a low degree of swelling, suggesting high crystallinity.

H. Kawazura

1962

Poly(vinyl acetate) emulsions. British Celanese Ltd. (by Dennis Grady, Philip R. Hawtin, and Kenneth Jones). Brit. 854,191, Nov. 16, 1960. Poly(vinyl acetate) (I) emulsions of fine particle size are prepd. by the catalytic polymerization of vinyl acetate (II) in emulsion form by starting the polymerization of II in an emulsion contg. (*a*) at least 2.2% of a protective colloid, and (*b*) 0.5–2.5% by wt. of a plasticizer for the I, and thereafter adding II slowly, keeping the concn. of II during the polymerization not greater than 12%, based on the wt. of the emulsion. Wetting agents are not necessary. The H_2O-sol. cellulose ethers are the preferred protective colloids, and di-Bu phthalate (II) is the preferred plasticizer. Thus, hydroxyethyl cellulose 160, II 72, Na_2CO_3 4.8, and H_2O up to 3075 parts were heated to 50°, 88 parts by wt. of a freshly prepd. 10% aq. sol. of $(NH_4)_2S_2O_8$ was added, and then 348 parts of II was added. The temp. was raised to 68° and then slowly to 75° until reflux ceased. II (3456 parts) was added at a uniform rate to keep the temp. at 82–4°. After 165 min., 24 parts more of II was added slowly, the temp. was raised to 90°, and 12 parts more of II was added. After 35 min. more heating, the emulsion was cooled to 30°. The particle size of the emulsion was 0.5–1.5 μ.
John H. Dittmar

8935

Polymerization of vinyl esters. Harry Wechsler and Stanley S. Levy (to Borden Co.). U.S. 2,965,623, Dec. 20, 1960. Vinyl esters are suspended as the dispersed phase in H_2O. The process is esp. useful for producing poly(vinyl acetate) of low mol. wt., and making possible the prepn. of polymerized beads having surfaces that resist agglomeration. Vinyl esters of C_2–C_{18} monocarboxylic aliphatic acids may be used. Poly(vinyl alc.) is used as the dispersing or suspending agent and a lipophilic org. peroxide as a polymerization initiator for the surfaces of the particles. Results are given which show the effect of variations in proportions on the properties of the polymerized suspension, esp. the need for an org. peroxide, H_2O_2, and an alkali as well as poly(vinyl alc.) in preventing instability of the suspension. AcH, EtCHO, or PrCHO are used to decrease the av. mol. wt. of the polyester. The mixt. is warmed with a H_2O-sol. alkali, addnl. portions of alkali being added to maintain the pH at 4.5–10. The approx. proportions by wt. are: vinyl ester 100, H_2O 25–1000, org. peroxide 0.02–2, H_2O_2 0.0003–0.3 part (anhyd. basis), poly(vinyl alc.) 0.04–5% of the wt. of H_2O, and alkali in an amt. sufficient to establish the pH of the aq. phase initially at >7.
Arthur Lyem

8938

Poly(vinyl acetate) of low molecular weight. Romania, Ministry of Petroleum and Chemical Industry (by Costescu Dan, Oprescu Niculae, and Mateescu Mihaela). Ger. 1,060,142, June 25, 1959 (Cl. 39*c*). Thirty l. of a 1% aq. soln. of poly(vinyl alc.) was heated to 68–9°. Vinyl acetate (30 l.), in which 450 g. Bz_2O_2 and 133.7 g. butyraldehyde were dissolved, was added at a rate of 6 l./hr. The temp. was then raised to 95°. The filtered and dried polymer beads had a *K*-value of 35 ± 3%.
Richard Seekircher

9960

Adiabatic compressibility of polymer solution. I. Poly(vinyl acetate) solutions. Yutaka Miyahara and Yuzo Masuda (Univ. Nagoya). *Nippon Kagaku Zasshi* 81, 602–4 (1960).—Poly (vinyl acetate) was dissolved in various solvents (CH_2ClCH_2Cl, cyclohexanone, C_6H_6, toluene, acetone, Me Et ketone, and MeOH), and the propagation velocities of ultrasonic waves in these solns. were measured. The values of partial specific compressibility (p.s.c.) of the solute in these media were detd., and the possible relation of p.s.c. to the shape and size of macromols. in soln. is discussed.
K. Sone

11047

Effect of stabilizers on the production economy of poly(vinyl acetate) polymerized in suspension. František Gregor and Eduard Pavlačka (Vyzk. ust. pre petrochémiu, Nováky, Czech.). *Chem. průmysl.* 10, 669–71(1960).—The suspension polymerization of vinyl acetate (I) was studied in the presence of gelatin (II), poly(vinyl alcohol) (III), or the ammonium salt of a copolymer of styrene with maleic anhydride (IV) as stabilizers at 72°. The most efficient was IV; the suspension of 50% I is stable in the presence of 0.1% IV or 0.4% III (calcd. on the aq. phase), whereas with 0.6% II only 45% I could be suspended. With 0.5% IV, suspensions contg. 90% I could be polymerized, but at concns. higher than 50% I, the particles of the polymer formed are imperfect.
J. Šebenda

20490

Polymerization of vinyl esters. Kurashiki Rayon Co., Ltd. Brit. 866,881, May 3, 1961. A nitrile which does not polymerize with the vinyl esters is used as a polymerization medium. The resulting polyvinyl ester may be sapond. to yield an aq. soln. of poly(vinyl alc.) which is highly resistant to gelation. Thus, a mixt. of vinyl acetate 70, acetonitrile 30, and azodiisobutyronitrile 0.01 part was polymerized in a sealed tube at 60° for 48 hrs. The poly(vinyl acetate) obtained was sapond. to produce poly(vinyl alc.) having a degree of polymerization of 1630. A 15% aq. soln. of the poly(vinyl alc.) showed no gelation after 10 days at 30°. Brit. 866,882. Ethylene carbonate is used as the polymerization medium.
John T. Byrne

20506

Poly(vinyl acetate) dispersions. United States Rubber Co. (by Robert S. Holdsworth). Ger. 1,093,558, Nov. 24, 1960 (Cl. 39*c*). Poly(vinyl acetate) dispersions are described which resist freezing, vigorous stirring, and pptn. by salts. The dispersions are polymerized in the presence of 3–6 parts/100 parts monomer of an emulsifier (I), which is made by the reaction of polypropylene glycol (800–2100 mol. wt.) with enough ethylene oxide to give 40–90% poly(oxyethylene) in the emulsifier. Vinyl acetate may be copolymerized with 40% dialkyl maleate or fumarate, vinyl esters of fatty acids, or alkyl acrylates or methacrylates. The discoloration of films of these dispersions is avoided by adding 0.1–0.4 part NaOH, LiOH, or MgO, but not KOH or NH_4OH. For example, H_2O 836.5, I 5.2, K_2SO_3 4.2, and a mixt. 109 kg. from vinyl acetate 7.7, Bu maleate 2.3, and I 0.45 part were mixed and heated for 0.5 hr. to 65.5–71.0°. During 10 hrs., a mixt. of vinyl acetate 721.6, di-Bu maleate 216.0, and I 42.2 kg. was introduced, and the whole was heated for 4 more hrs. The I was made from polypropylene glycol (mol. wt. 1500–1800) and ethylene oxide to obtain 80% by wt. in the emulsifier. This dispersion had 55.2% solids. After stirring 100 g. of the dispersion with 15,000 r.p.m., for 30 min., 0.06 g. coagulum did not pass a 100-mesh screen. The addn. of 50 cc. soln. contg. 5% alum or $CaCl_2$ caused no pptn.
H. J. Schünemann

26536

Poly(vinyl acetate). Kurashiki Rayon Co. Ltd. Brit. 872,773, July 12, 1961. The starting material for catalytic polymerization of vinyl acetate (I) is deoxygenated before polymerization by countercurrent contact with gases generated by decompn. of the polymerization catalyst, thus shortening the reaction time. If 2,2′-azobisisobutyronitrile (II) is used as a catalyst, N is liberated, while Bz_2O_2 generates CO_2 by decompn. during the polymerization. Thus, 0.03% II in 136 kg. I and 34 kg. MeOH at 20° was charged hourly into a deoxygenation preheater. After preheating to 60°, the material was charged to a polymerization kettle and the reaction proceeded continuously at 15% conversion. The temp. at the top of the preheater was 60° and in the cooler tower 25°. The amt. of O dissolved in the soln. charge was $1.0 \times 10^{-\text{[illegible]}}$ mole/l. and that in the mixed soln. charged into the polymerization kettle had been reduced to $5 \times 10^{-\text{[illegible]}}$ mole/l. The amt. of waste gas was 27 l./hr. contg. 9% O and 86% N.
John H. Dittmar

14295

acceleration effect for sapon. of I was mainly due to the catalyst adsorption by the OH groups in the same mol. and partly due to the decrease of the steric hindrance. Eiichi Wada

14990

Poly(vinyl alcohol) of high purity. Farbwerke Hoechst Akt.-Ges. (by Werner Starck, Karl H. Kahrs, Alfred Kühlkamp, and Werner Ehmann). Ger. 1,084,477, June 30, 1960 (Cl. 39c). Polyvinyl esters, esp. poly(vinyl acetate), are sapond. in the presence of 5–15% H_2O and 1 of the following solvents: Acetone, *tert*-BuOH, MeOAc, or tetrahydrofurfuran, or their mixts. at 10–95° by the use of H_2SO_4 as sapon. catalyst. The process yields powd. poly(vinyl alc.)

14991

which is removed from the reaction mixt. by filtration or centrifugation and which is washed free from acid residues to give poly(vinyl alc.) of high purity. The acid, esp. AcOH, which is released during the sapon. process is recovered almost free of impurities. Heinz Sontag

Heat-hardenable poly(vinyl acetate) films. Leo M. German (to Shawinigan Chemicals Ltd.). Can. 612,922, Jan. 17, 1961. The process of dissolving poly(vinyl acetate) and a metal halide in a suitable solvent, casting the soln. on a smooth surface in a thin layer and evapg. the solvent gives a heat-hardenable film. Thus, Gelva V-10 [poly(vinyl acetate), 10 cp. viscosity] 33, di-Bu phthalate 2, and $FeCl_3.6H_2O$ 1.65 parts were dissolved in 65 parts MeOH. The soln. was cast on a smooth polished belt and subjected to 105–40°F. for about 8 min. to evap. the solvent and leave a film about 2 mils thick. This film was used to join the ends of 2 webs of paper by overlapping the ends, placing the dried film between the overlapped ends, and applying a hot iron. John T. Byrne

Poly(vinyl alcohol) graft Copolymers. Tsukumo Tomonari, Kenichi Shinohara, and Ayao Amemiya. Japan. 3388('61), Apr. 18. Wet-spun poly(vinyl alc.) fiber is soaked in a 10% aq. soln. of 2-methyl-5-vinylpyridine, irradiated with Co^{60}, and neutralized with 1% NH_4OH. Then MeOH is completely removed by using a Soxhlet extractor, and the fiber is dyed with an acid dye.
Hiroshi Kataoka

21671

Low-molecular-weight poly(vinyl alcohols) having terminal carbonyl groups. Masakazu Matsumoto and Makoto Shiraishi (to Kurashiki Rayon Co., Ltd.). U.S. 2,983,759, May 9, 1961. The prepn. of the title products having terminal CO groups is accomplished by partially oxidizing 0.1–10 mole % of the OH groups of high-mol.-wt. poly(vinyl alc.) (I) followed by cleaving the oxidized I with NaOH at the CO groups in a reverse aldol-condensation reaction. Thus, treating I with an av. degree of polymerization (*DP*) of 1080 with 200% by wt. *N*-bromosuccinimide at 60° for 40 min. gave an oxidized product, in which 0.255% of the OH groups was oxidized. Treating 350 g. of a 1% oxidized I soln. with 10 cc. 5*N* NaOH at 95° for 10 min. gave a I with an av. *DP* of 320 and contg. 0.453 mole % CO groups. These compds. are used as cross-linking agents for I through acetal formation. P. E. Templin

27983

Modified poly(vinyl alcohols). Farbwerke Hoechst Akt.-Ges. (by Karl Heinz Kahrs, Wolfgang Zimmermann, and Alfred Kühlkampf). Ger. 1,081,229, May 5, 1960 (Cl. 39c). H_2O-sol. modified poly(vinyl alcs.) with improved surface and interface activities contg. at least 50 wt. % poly(vinyl alc.) units are prepd. by acid or alk., complete or partial sapon. or reesterification of special graft copolymers (*CA* 55, 12935*e*). Films made of these products are softer in air on account of absorbed water. Addnl. softeners, e.g. glycerol, are desirable. Dieter Greiber

Vol 54 1960

11566

Crystalline poly(vinyl acetate). Hercules Powder Co. Brit. 819,291, Sept. 2, 1959. A cryst. poly(vinyl acetate) (I) is made by bringing vinyl acetate (II) into contact with a catalyst prepd. by mixing a V compd. with an organometallic compd. of an alkali metal, alk. earth metal, Zn, or Al. The new I has a cryst.-type x-ray diffraction powder pattern and on hydrolysis yields a poly(vinyl alc.) (III) of a high degree of crystallinity. The I is used in the prepn. of films, fibers, plastics, or as a film-forming coating compn., or in the prepn. of a new type of III. Thus, Et_2O 29.3, II 10, and iso-Bu_3Al 0.4 in heptane 1.3 were warmed to 30°, and a suspension of VCl_3 0.16 in *n*-heptane 5 parts was added. After 19 hrs. agitation, 4 parts anhyd. EtOH was added to stop the polymerization. The sepd. insol. polymer of I was extd. with boiling cyclohexane, dried at 80° for 16 hrs. *in vacuo*, and then dissolved in boiling xylene. The hot xylene soln. was filtered, and the xylene was removed. The polymer was dried for 4 hrs. at 80° *in vacuo*. The I had a cryst.-type x-ray diffraction powder pattern.

John H. Dittmar

13741

Vinyl emulsion polymers. Badische Anilin- & Soda-Fabrik Akt.-Ges. (by Hellmut Scholz and Fritz Kieferle). Ger. 1,026,962, Mar. 27, 1958 (Cl. 39*c*). Polymeric metaphosphates (I) are used as protective colloids in the polymerization of vinyl emulsions. The I do not incorporate into the polymer mols. and therefore do not detrimentally affect their stability and soly. properties. They are obtained by melting hydrated cryst. K mono-orthophosphate and are dissolved in a soln. of a Na salt. Thus, I 0.75, Na tripolyphosphate 0.5, and primary Na phosphate 0.125 were dissolved in H_2O 300 parts in a stainless-steel autoclave. The aq. soln. of pH 7.5 had a relative viscosity of 5.1. Lauroyl peroxide (0.25 part) and 100 parts vinyl chloride (II) were added, and the reaction mixt. was stirred and heated. After 12 hrs., the pressure dropped and the mixt. was cooled down. A bead polymer of *K*-value 71 was obtained which was sol. in cyclohexanone and possessed good stability to light and heat. When the polymer was pressed at 250 atm. and 150°, no discoloration was observed after 3 min. and only a slight reddish tint was observed after 9 min. A similar polymer, prepd. with 0.25 part poly(vinyl alc.) as the protective colloid, showed a red tinge after 3 min. and was colored deeply violet after 9 min. Similarly prepd. were poly(vinyl propionate) (III) of *K*-value 73.5 and a copolymer of II and III of *K*-value 62.

F. Franks

Polymerization of vinyl compounds. Wolfgang Jurgeleit (to Vereinigte Glanzstoff-Fabriken Akt.-Ges.). U.S. 2,924,589, Feb. 9, 1960. See Fr. 1,134,751 (*CA* 51, 9213*b*).

P. M. B.

Plasticized vinyl resin composition containing vinylcyclohexanol esters. Allied Chemical Corp. (by Robert C. Kuder). Brit. 827,388, Feb. 3, 1960. See U.S. 2,754,281 (*CA* 50, 16184*a*).

P. M. B.

Deodorization of poly(vinyl acetate) dispersions. Farbwerke Hoechst Akt.-Ges. vorm. Meister Lucius & Brüning (by Erich Feld and Hajo Eilers). Ger. 1,029,155, Apr. 30, 1958 (Cl. 39*c*). Poly(vinyl acetate) dispersions are deodorized by treating them with steam or hot air. The steam or air is mixed for a short time with the dispersion and the phases are sepd. The app. is described. The dispersion keeps its good fiber-forming properties. From *C.Z.* 1959, 16490.

R. W. Rosner

16024

Alkylated poly(vinyl alcohols) as dispersing agents in vinyl emulsion polymerizations. Wacker-Chemie G. m. b. H. (by Klaus Bauer, Eduard Bergmeister, Eduard Enk, and Joseph Heckmaier). Ger. 1,026,074, Mar. 13, 1958 (Cl. 39*c*). Partially (5–20%) alkylated poly(vinyl alcs.) (I), derived from the copolymerization of vinyl acetate (II) and isopropenyl acetate and subsequent hydrolysis, provide good dispersing agents for the free radical-initiated polymerization of vinyl monomers. The amt. of I to be added varies from 0.05% to 0.2% for suspension- to 2–10% for emulsion-polymerization. Thus, II 300 contg. Bz_2O_2 0.3 and H_2O 40 parts was heated with reflux to 63°. After 1 hr., the upper layer consisted of monomeric II dissolved in a low-mol. polymer. Then 0.2 part I (11% isopropenyl alc., 89% vinyl alc.) in 15 parts H_2O was stirred in so that the II was dispersed in the aq. phase. The polymerization was complete during an addnl. 4 hrs. After cooling, the bead polymer was filtered off, washed, and dried. A molar soln. in EtOAc was completely transparent and free flowing. When a partly acetylated vinyl alc. was used as dispersing agent, the polymeric II yielded an opaque, jellylike soln. and, when vinyl alc. was used, a block polymer was obtained. The uses of I in emulsion-polymerizations are also described.

F. Franks

Vol. 52 1958

9646

Branching and cross-linking during vinyl acetate polymerization. John T. Clarke (Dewey and Almy Chem. Co., Cambridge, Mass.). *Kunststoffe-Plastics* 3, 151–4 (1956)(in English).—The intrinsic-viscosity data of Wheeler, *et al.* (*C.A.* 46, 11760*d*) obtained from polymerization, saponification, and reacetylation of $CH_2{:}CHOAc$ was recalcd. The no. av. of polymerization, $\bar{P}_n$, for poly(vinyl acetate) (I) was as high as 7700, but $\bar{P}_n$ for the poly(vinyl alc.) reached a limiting value of 910. Consideration of all possible branching and cross-linking reactions led to the conclusion that the very high mol. wts. were produced by a transfer reaction that gives saponifiable branches. The α H is the principal point of attack in this reaction since this rate is 3 times as fast as any other. On saponification of I much lower mol. wt. alcs. were obtained, and reacetylation did not produce the original mol. wt. of the polymer. Transfer consts. were evaluated for a series of agents, the values for I and iso-PrOAc being 0.0007 and 0.00072, resp. From the consts. of the different rates involved and the concn. of monomer were calcd. the mol. chain lengths and kinetic chain lengths. From the kinetic chain-length calcn., $\bar{P}_n$ for the basic chain of I was found to be 830, which agrees with $\bar{P}_n$, above, for poly(vinyl alc.). Claire Bluestein

1696

Branching of poly(vinyl acetate) at initial polymerization (polymerization yield=0). Masakazu Matsumoto, Kiyo-kazu Imai, Masayasu Maeda, Yasuji Oyanagi, and Takao Saito (Kurashiki Rayon Co., Kurashiki). *Chem. High Polymers* (Japan) 12, 398–401(1955).—The relation between the intrinsic viscosity $[\eta]_A$ of poly(vinyl alc.) (I) and that $[\eta]_{Ac}$ of poly(vinyl acetate) (II) prepd. by the acetylation of the poly(vinyl alc.) was detd. from data in the literature as $[\eta]_A = 0.897\ [\eta]_{Ac}$[illegible]. The same relation was also obtained between II and I prepd. by the sapon. of II. From the fact that the polymerization degree (*PD*) remains const. during the acetylation of polyvinyl alc., it is concluded that *PD* is not affected by the sapon. Eiichi Wada

8473

Poly(vinyl alcohol) as an emulsifying agent in vinyl polymerizations. J. N. Coker (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.). *Ind. Eng. Chem.* 49, 382–5 (1957).—Poly(vinyl alc.) acts as a nonionic emulsifying agent and as such can be used to prep. fluid polystyrene latexes contg. 30 to 40% solids. Leon Sternberg

9218

Poly(vinyl acetate)emulsions. Société Nobel Française, Fr. 1,000,338, Apr. 22, 1952. Oil-in-water emulsions of poly(vinyl acetate) (I) are made from monomeric vinyl acetate by use of protective colloids which also act as emulsifiers, e.g. poly(vinyl alc.) contg. some Ac groups, together with gelation agents for poly(vinyl alc.) solns., especially H_3BO_3 and its derivs. A small amt. of a solvent for I which is somewhat sol. in water is also added. The product is neutralized by addn. of an ethanolamine. Thus, a mixt. of 100 kg. 5% aq. poly(vinyl alc.) soln., 4 kg. of a 0.5% aq. Na_3BO_3, 8 kg. EtOH. 3 kg. 33% aq. $(NH_4)_2S_2O_8$, and 1 kg. Na sulforicinoleate was heated to 55° under reflux, 100 kg. vinyl acetate being added then with cooling and the temp. being kept for 3 min. at 80°. On cooling, the product was neutralized. Friedrich Epstein

15175

Polymerization of vinyl acetate. David H. Coffey and John M. Phillipson (to Imperial Chemical Industries Ltd.). Brit. 776,181, June 5, 1957. To an agitated soln. of poly(glyceryl methacrylate) (I) 3.1, Na_2CO_3 0.63, and water 59 parts at 65–7° were added concurrently vinyl acetate (II) 137 and a soln. of I 3.1, $(NH_4)_2S_2O_8$ 0.63, and water 64 parts over a period of 2–3 hrs. The temp. was allowed to rise gradually to 85°. Steam-stripping removed unreacted II and left a dispersion of poly(vinyl acetate) with particles of 30 μ, which remained stable on prolonged storage.

E. D. Witman

Aqueous dispersions of poly(vinyl acetate) at high viscosity. Lonza Elektrizitätswerke und Chemische Fabriken A.-G. Swiss 316 762, Dec. 15, 1956 (Cl. 41). The viscosity of poly(vinyl acetate) dispersions may be controlled during polymerization by varying the ratio of poly(vinyl alc.) (or other protective colloid) to the amt. of vinyl acetate monomer in each portion. Thus 360 g. of 10% aq. poly(vinyl alc.) soln. (3[illegible] g. solids of 38% vinyl acetate) having a viscosity of 25 centipoises in 5% aq. soln. at 20° and 290 g. water, in a closed vessel, are purged with H and heated at 65–70° with stirring. From a separate vessel there are introduced 0.2 g. glucose dissolved in 50 cc. water and 60 cc. (56 g.) vinyl acetate monomer (having dissolved in it 2.0 cc. 30% H_2O_2 in 650 g.) and an addnl. 0.5 cc. 30% H_2O_2 for this first portion. On further heating at 68–70°, the internal pressure reaches 1.8–2.0 kg./sq. cm. When the pressure is stabilized at 1.5 kg./sq. cm., an addnl. 60-cc. portion of monomer is added. In this way, a total of 650 g. monomer and 0.5 g. glucose is allowed to react over a period of 2 hrs. to give on cooling a dispersion contg. 55% solids, 1.5% residual monomer and having 1.5 μ av. particle diam., pH 4.15, and 180 poise viscosity. With the use of 120-cc. portions of monomer in the above example, the dispersion contained 55% solids, 1.6% residual monomer, and had a 2 μ av. particle diam., pH 4.2, and 100 poise viscosity. With 180-cc. portions of monomer, the dispersion contained 54.9% solids, 1.7% residual monomer and had a 2–2.5 μ av. particle diam., pH 4.3, and 30 poise viscosity. With the addn. of the whole 650-g. monomer in one portion, the dispersion contained 55% solids and had a 3 μ av. particle diam., pH 4.1, and 10 poise viscosity. Mark Plunguian

Emulsion polymerization of vinyl acetate. Dorothy J. Guest and John M. Phillipson (to Imperial Chemical Industries Ltd.). Brit. 777,484, June 26, 1957. An aq. dispersion of poly(vinyl acetate) was prepd. by emulsifying vinyl acetate in water in the presence of partially hydrolyzed poly(vinyl acetate), an alkali salt of poly(methacrylic acid), and a polymerization catalyst. Thus, a mixt. of 2.5 parts of 87% hydrolyzed poly(vinyl acetate), 0.63 part of NH_4 polymethacrylate (viscosity of a 15% aq. soln. at 20°, 700 poises), and 0.63 part of Na_2CO_3 was dissolved in 58 parts of water and charged into a polymerization flask fitted with a thermometer and 2 dropping funnels. Vinyl acetate (138 parts) was charged to one dropping funnel; a soln. of 2.5 parts of 87% hydrolyzed poly(vinyl acetate), 0.63 part of NH_4 polymethacrylate, and 0.63 part of $(NH_4)_2S_2O_8$ (catalyst) in 58 parts of water was charged to the other. The temp. of the content of the flask was raised to 65–7°, and addns. of monomer and catalyst soln. were started and continued for 2.5 hrs., during which the monomer refluxed and the temp. was allowed to rise to 80°. The ratio of monomer to catalyst was kept const. during the addn. period. After the addns. were complete, heating was continued until the temp. reached 85° and refluxing ceased. Polymerization was then substantially complete. Traces of residual monomer could be removed by steam distn. The product was a smooth,

14324

creamy dispersion. The av. particle size was 15 μ. Na polymethacrylate can be substituted for NH_4 polymethacrylate and $K_2S_2O_8$ substituted for the $(NH_4)_2S_2O_8$.

J. K. Sullivan

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Vol 5o 1956 ✓ Metodo Empleado

603

Studies on the branching of vinyl polymers. I. Synthesis of branched polyvinyl acetate. Junji Ukida, Saburo Imoto, and Tsugio Kominami (Kurashiki Rayon Co., Toyama). *Chem. High Polymers* (Japan) 11, 332–6 (1954).—For the purpose of synthesizing branched polyvinyl acetate, the condensation reaction between polyvinyl acetate-acetylacetate coester and polyvinyl acetate having carbonyl group at the end of the mol. was carried out in benzene in the presence of triethylamine. Formation of branched polymer was postulated by measuring the viscosities of the products. Eiichi Wada

Studies on the effect of aldehyde on the polymerization of vinyl acetate with heavy hydrogen as a tracer. Toshizo Chitani, Gisuke Meshitsuka, and Arika Matsumoto (Osaka Univ.). *Chem. High Polymers* (Japan) 11, 337–43(1954).—In a study of the effect of aldehyde and O on the polymerization reaction of vinyl acetate with dilatometer, it was confirmed that these 2 substances markedly accelerate the reaction velocity. To elucidate the reaction mechanism, aldehyde having heavy H in its component was used. Polyvinyl acetate mols. thus obtained combined about 3 atoms of heavy hydrogen/mol. Eiichi Wada

Relaxation processes in polyvinyl acetate. P. F. Veselovskiĭ and A. I. Slutsker. *Zhur. Tekh. Fiz.* 25, 1204–8(1955).—Both for hard and for highly elastic polyvinyl acetate (I) the results of measurements are presented for the dielec. loss (tan δ) and for the dielec. permeability (ε) as a function of temp. Thus, for hard I at 1.6 kilocycles at about 62° tan δ reaches its max. of 0.20. Another max. (not so high) is reached at about −58°. These measurements were conducted, as far as the elastic I is concerned, with I which was plasticized with 40% naphthalene. Werner Jacobson

Swelling of polyvinyl formal films in binary mixtures of methylal, ethylal, methanol, acetone, and water. Osamu Yoshizaki (Univ. Kyoto). *Chem. High Polymers* (Japan) 11, 306–11(1954).—Swelling of polyvinyl formal films having various degrees of formalization was studied in binary mixts. of water and other solvents, i.e. methylal, ethylal, methanol, and acetone. Max. swelling was observed on a sample having proper degree of formalization in a certain binary mixt., e.g. for the film having 30 mole % of formalization degree, the max. swelling was observed at 30° in satd. aq. soln. of methylal. Eiichi Wada

6833

Poly(vinyl acetate) emulsion polymerization and utilization. John C. Luckman and Donald D. Howell. *Paint, Oil & Chem. Rev.* 118, No. 25, 12, 14, 16(1955).—Polymerization of vinyl acetate is characterized as a free-radical addn. reaction initiated by radicals resulting from the decompn. of initiators such as $K_2S_2O_8$, $(NH_4)_2S_2O_8$, H_2O_2, or other peroxides. Emulsions of poly(vinyl acetate) contain water, surface-active or emulsifying agents, colloids, catalysts, and a buffer to maintain the pH at about 5. Processes are classified as batch, delayed action, and continuous. Most widely used is the delayed-action system in which 5 to 10% initial monomer is added to start and the remainder is added during polymerization 10 to 15° above the azeotrope temp. Addn. periods vary from 2 to 4 hrs., finer particles being obtained in the 3–4-hr. period. With low colloid content, these give improved water resistance, and better coalescence and pigment wetting. The films have greater tensile strength and better adhesion. G. K. H.

Aqueous dispersions of poly(vinyl acetate). Farbwerke Hoechst A.-G. vorm. Meister Lucius & Brüning (Werner Starck, inventor). Ger. 915,744, July 29, 1954 (Cl. 39*c*, 25_{01}). Polymerizing $AcOCH:CH_2$ (I) in an aq. soln. of a surface-active agent and (or) protective colloid, e.g. poly(vinyl alc.) (II) or its water-sol. deriv., and in the presence of a polymerization catalyst and a small amt. of CCl_4 gives aq. poly(vinyl acetate) dispersions yielding clear, lustrous coatings of good water resistance. Thus, 1 part by wt. 40% H_2O_2 was added to 500 parts of a 5% aq. II soln. The pH was adjusted to 3.5 by addn. of HCOOH, the mixt. heated at 75°, and a soln. of 1.5 parts CCl_4 in 500 parts I introduced in 45 min. The mixt. was then heated 0.5 hr. at 80° to give a dispersion (III) of a creamy consistency. The coating compn. obtained by triturating III with a mixt. of 62.5 parts di-Bu phthalate and 5 parts

12504

MeOH gave clear, lustrous films fast to wiping even in the moist state. G. Stargard

Dispersions of poly(vinyl esters). Farbwerke Hoechst Akt.-Ges. vorm. Meister Lucius & Brüning (Werner Langbein, inventor). Ger. 901,936, Jan. 18, 1954 (Cl. 22*g*, 2_{01}). Dispersions of poly(vinyl esters) of high mol. wt. which can easily be applied by brushing are prepd. by polymerization of vinyl esters in a bath contg. poly(vinyl alc.) (I) in the presence of a nonionic emulsifier, e.g. a hydroxyalkylation product of a higher-mol. alc. or alkyl-phenol. Thus, 0.165 part 40°Bé. sulfite liquor and 0.1 part of an alkylphenyl polyglycol ether were added to 25 parts of a 5% I soln. having a viscosity of about 100 centipoises and a pH of 6.3 and from which the O had been removed. The Fe content of the mixt. was adjusted to 0.004% by addn. of Mohr's salt and 25 parts vinyl acetate was added. The mixt. was heated to the b.p., 1.5 parts 1% H_2O_2 soln. was slowly dropped in with agitation, and heating was continued for 0.5 hr. A poly(vinyl acetate) emulsion of a high *k* value was recovered. G. Stargard

4.2. The acid or the acid salt can be formed during the polymerization, e.g. by use as polymerizing catalysts of salts of strong peracids, e.g. $K_2S_2O_8$ or $(NH_4)_2S_2O_8$. The resulting polymer emulsions are compatible with the usual softeners and filling agents and give films of high resistance to water. Thus, EtCHO 0.33, $KHSO_4$ 0.05, and 20% H_2O_2 1.3 were added to a soln. of a partially acetylated I 6 in water 100 parts. The mixt. was heated to 64° and 100 parts AcOCH:-CH_2 (II) was added dropwise. A stable, creamy emulsion, pH 3.6, contg. 50% solids, was recovered. II similarly copolymerized with vinyl butyrate gave a viscous, stable emulsion yielding clear, transparent, water-resistant *coatings*. G. Stargard

Poly(vinyl ethers). I. G. Farbenindustrie Akt.-Ges. (Adolf Burgard, Hans Fikentscher, Friedrich Hölscher, and Hans Krzikalla, inventors). Ger. 751,603, May 11, 1953 (Cl. 39*c*, 25_{01}). Polymerization of decahydronaphthyl vinyl ethers (I), possibly in mixts. with similar vinyl compds., gives polymerization products sol. in aliphatic and aromatic hydrocarbons, chlorohydrocarbons, esters, ketones, etc., and suitable as *lacquer* resins. I are obtained by treating decahydro-1- or 2-naphthol with C_2H_2 at an elevated temp. in the presence of strong alkalies. Thus, a soln. of 1.2 parts of a BF_3-Et_2O addn. compd. in 98.75 parts dioxane was gradually added to decahydro-2-naphthyl vinyl ether (II). The mixt. was gradually heated at 140° and addnl. II and catalyst soln. (III) were added to give 25 parts III per 1000 parts II. A pale-yellow resinous product (IV), m. 80°, was recovered. A 23% IV soln. in ligroine is useful for impregnating bark-tanned *leather*. II or decahydro-1-naphthyl vinyl ether copolymerized with cresyloxyethyl vinyl ether in the ratio 66:34 in the presence of III at 140° gives a product suitable for impregnating *wood*. The copolymer obtained from 30 parts II and 70 parts vinyl chloride in a 2% aq. Na α-hydroxyoctadecanesulfonate soln. contg. a small amt. of $Na_2S_2O_8$ is useful for impregnating unsized *paper*. II (40 parts) similarly copolymerized with 60 parts Me acrylate gives a product which, dissolved in org. solvents or dispersed in an aq. medium, is useful as a *coating compn*. A brittle, yellowish resinous product, softening point about 70°, is obtained by copolymerization of 360 parts II and 240 parts vinyl isobutyl ether. G. Stargard

Polymerization products from vinyl ethers. Badische Anilin- & Soda-Fabrik Akt.-Ges. (Eugen Müller, inventor). Ger. 846,794, Aug. 18, 1952 (Cl. 39*c*, 25_{01}). The copolymerization of vinyl isobutyl ether (I) with diisobutylene (II) and (or) triisobutylene (III) at low temps. with the use of catalysts of the Friedel-Crafts type or addn. compds. thereof gives copolymerizates having nonadhesive properties. A weak flow of BF_3 is introduced into a mixt. of 80 parts by vol. highly purified I, 20 parts II, b. 101-3°, and 3050 parts liquefied propane cooled at −60°. The introduction of BF_3 is interrupted when the polymerization is initiated and the mixt. begins to boil. The polymerization is finished after about 30-45 sec. and BF_3 is then once more bubbled through for 5 sec. The viscous, gluey, colorless mass is treated with water to evap. the solvent. Thus, the polymerizate is converted to a white, nonadhesive, readily friable, swollen mass, which is disintegrated by cutting or plucking, suspended in water, and treated with water in order to remove the catalyst particles still present. Washing with water and drying in streaming air at about 55° gives a product, m. 74-8°, *k* value 83. A polymerizate, m. 85-90°, *k* value 90, is similarly obtained from I and III, b. 176-8°, in the ratio 75:25. Ger. 868,353, Feb. 23, 1953. I along with olefins contg. more than 4 C atoms and an isopropylidene radical (except II and III) are used as copolymerization components in the process described in Ger. 846,794 (cf. above). Thus, the BF_3-catalyzed copolymerization of 85 parts I and 15 parts of an olefin mixt. contg. about 61% 2,3-dimethyl-2-butene and 7.5% 4-methyl-3-pentene in liquid propane gives a product, m. 70-5°, *k* value 82. A product m. 73-8°, *k* value 85, is similarly obtained from 85 parts I and 15 parts of an olefin mixt. contg. about 70% 2,4-dimethyl-3-pentene. G. Stargard

Poly(vinyl acetals). Morris Kaufman (to British Oxygen Co. Ltd.). Brit. 745,686, Feb. 29, 1956. Vinyl esters are polymerized in aq. media in the presence of poly(vinyl alc.) contg. 8-50 mole % residual acetate groups and a catalyst for producing suspensions of discrete particles of the polymer. If desired, the water may be removed and the residual wet polymer dissolved in an org. solvent other than an aldehyde or ketone, but completely miscible with water. The soln. formed is treated with an acid catalyst and an aldehyde or ketone. Thus, 100 parts by wt. vinyl acetate contg. 0.8 part Bz_2O_2 was added to 300 parts 0.04% aq. poly(vinyl alc.) contg. 12 mole % residual acetate groups. The mixt. was stirred at 300 r.p.m. and boiled under reflux for 5 hrs. The temp. was about 60° until the greater part of the monomer had polymerized, after which it rose to about 100° and was maintained at this temp. for 2 hrs. The poly(vinyl acetate) was present in the form of beads of 0.5-1 mm. diam. Water (212 parts) was removed and 176.5 parts glacial AcOH was added to the suspension and stirring resumed. After 20 min., the polymer dissolved to give a homogeneous soln. and 1.9 parts concd. H_2SO_4 and 19.3 parts paraformaldehyde were added. The temp. was raised to 75° and maintained for 24 hrs. The soln. was then cooled to 45° and 7 parts 0.880 d. NH_3 was added. Stabilization was complete after stirring for 0.5 hr. at 45°. The poly(vinyl formal) was pptd. by addn. of about 500 parts water to the soln. Analysis of the polymer showed that it contained 9 mole % hydroxy groups, 9 mole % acetate groups, and 82 mole % formal groups. Cf. *C.A.* 32, 6767^6. R. E. Pemrick

Styrene-modified poly(vinyl acetate) resins. John C. Lukman and Ora L. Wheeler (to Shawinigan Resins Corp.). U.S. 2,741,650, Apr. 10, 1956. Styrene (I) is combined with poly(vinyl acetate) (II) by bead polymerization to form a polymer with better heat resistance and stiffness at 40-60° than II or mixts. of II and polystyrene. Thus, a mixt. of vinyl acetate 100, H_2O 143, $NaHCO_3$ 0.3, H_2O_2 0.03, and poly(vinyl alc.) 0.2 g. contg. 11% residual II groups was refluxed until polymerization was complete. The temp. was raised to 80° and 42.8 g. I and 1.0 g. Bz_2O_2 were added slowly. When the reaction was complete, the slurry was cooled and the beads were sepd. from the aq. layer. The products are useful in *adhesives* and *coatings*. R. P. A.

Polymerization of vinyl acetate. Tsugio Kominami and Junji Ukida (¼ to Omni Products Corp.). U.S. 2,746,947, May 22, 1956. The polymerization of vinyl acetate (I) at 40° takes place rapidly in a homogeneous liquid phase by use of a catalyst mixt. of 0.14-0.3% aromatic sulfinic acid, 0.13-0.3% amine, 0.2% Bz_2O_2, and sometimes 0.003-0.001% $FeCl_2.4H_2O$. Compared to other catalysts, the induction period is shortened and the rate of polymerization increased. Thus, a mixt. of I 70, MeOH 30, and Bz_2O_2 0.2% polymerized at 60° and 40° showed induction periods of 3 and 13 hrs., polymerization periods of 5 and 15 hrs., and yields of 80 and 50%, resp. The same mixt. with 0.15% *p*-chlorobenzenesulfinic acid was polymerized at 40° with an induction period of 4 hrs., a polymerization period of 10 hrs., and a yield of 70%. P. Dreyfuss

Heat-stable poly(vinyl alcohols). Wacker-Chemie G. m. b. H. (Josef Heckmaier and Eduard Bergmeister, inventors). Ger. 928,558, June 2, 1955 (Cl. 39*c*, 25_{01}). Heat-stable poly(vinyl alcs.) are prepd. from products obtained by alkali ester interchange or sapon. by neutralization in alc. suspensions or solns. with strong acids. Thus, a MeOH-contg. poly(vinyl alc.) prepd. by an alkali ester interchange in MeOH was suspended in MeOH and exactly neutralized with 4% methanolic HCl with potentiometric control. The product was sepd. from the mother liquor by filtration. It contained 0.65% Na_2SO_4 and remained pure white even after heating for 10 min. at 220°. G. Stargard

Emulsion polymerization of vinyl esters. Wacker-Chemie G. m. b. H. (Eduard Bergmeister and Josef Heckmaier, inventors). Ger. 936,063, Dec. 1, 1955 (Cl. 39*c*, 25_{01}). The polymerization of vinyl esters in aq. media contg. poly(vinyl alc.) (I) or partially esterified I derivs. acting as emulsifiers is improved by partially acetalizing the emulsifier during the polymerization by addn. of a small amt. of an aliphatic aldehyde having 2 or more C atoms, e.g. 5-15% AcH or EtCHO, and a small amt. of an acid or an acid salt in order to obtain a pH of 2.5-4.2, preferably 3.5-

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6735

Measurement of the flow behavior of polyvinyl acetate dispersions. Karl Mehnert (Farbwerke Hoechst, Frankfurt, Ger.). *F.A.T.I.P.E.C.* (Féd. assoc. tech. inds. peintures, vernis, émaux et encres imprimerie Europe Continental). 2° *Congr.* 1953, 154-8(in German).—Polyvinyl acetate aq. dispersions were manufd. with 25% and 50% dibutyl phthalate or protective colloids such as polyvinyl alc., and their flow properties were detd. in a falling-ball viscometer. The particles were 2 μ and 0.3 μ, resp. The flow behavior of the dispersion contg. protective colloids was thixotropic; the return of the liquid phase to the gel state after stirring proceeded slowly and depended upon the amt. of agitation. Examn. of thixotropy by means of flow curves was facilitated by a rotational viscometer equipped with a recorder for the continuous measurement of variations in stress with time. Raymond R. Myers

11106

Vinyl acetate. VII. Average degree of polymerization of the partial saponified polyvinyl acetate. Bin Takigawa and Ken Goto (Elec. Chem. Ind. Co., Research Inst., Tokyo). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 56, 458-9

11107

(1953); cf. *C.A.* 48, 10374g.—Polyvinyl acetates (I), having a degree of polymerization (D.P.) of 2800, 1700, and 800, were sapond. up to various degrees of sapon. (A). A and apparent viscosity were measured to calc. the intrinsic viscosity (η). The relation between A, η, and the av. D.P. of fully saponified I (P) was: $\log P = 1.613 \log (\eta \times 10^4/8.67) - \log (0.011 A/(0.021 A - 1))$. Katsuya Inouye

Emulsions of vinyl polymers and their application. M. Turner. *Chim. peintures* 17, 209-14(1954). J. H. E. H.

Vinyl plastics. Their dermatological and chemical aspects. George E. Morris (Tufts Coll. Med. School, Boston). *Arch. Ind. Hyg. Occupational Med.* 8, 535-9(1953); cf. *C.A.* 46, 10679i.—Plastomers of the vinyl or polymerization type include polyvinyl, polyacrylate, polyvinylidine, polyethylene, polystyrene, and coumarone and indene resins. Workers incurring exposures to partially polymerized resins of this class may develop sensitization dermatitis. Only rarely does dermatitis occur from contact with the finished form of these resins. C. L. Campbell

14290

polymerization of vinyl acetate with cation-type emulsifier. Takuhiko Motoyama and Seizo Okamura (Kyoto Univ.). *Chem. High Polymers* (Japan) 10, 103-8(1953); cf. *C.A.* 48, 9102i.—With a cation surface-active agent as emulsifier, the emulsion polymerization of vinyl acetate was studied. When the surface-active agents such as dodecylpyridinium chloride and dodecylpicolinium chloride were used, stable emulsion of polyvinyl acetate was not obtained. When quaternary ammonium salts, e.g. trimethylammonium bromide is used, a stable emulsion was obtained. The particle size, coagulation value, and the mixing behavior toward pigment of the emulsion were studied. **VII. Emulsion polymerization of vinyl acetate with water-soluble high polymers as protective colloid.** Takuhiko Motoyama, Shoji Yamamoto, and Seizo Okamura. *Ibid.* 108-16.—With water-sol. high-mol. compds. as protective colloid, the emulsion polymerization of vinyl acetate was studied. The rate of polymerization and the stability of the resulting emulsions were studied. The protective colloids used were: (1) polyvinyl alcs. and their derivs. polyacrylic acids, polyvinyl amine, copolymers of anhyd. maleic acid, (2) Na salts of alginic acids, casein, gum arabic, etc. T. Katsura

Color reactions and simple chemical reactions for vinyl polymers. Horst Winterscheidt. *Seifen-Öle-Fette-Wachse* 80, 239-40(1954).—Most vinyl polymers give a color reaction when a small amt. (finely ground) is added to a melt (approx. 5 cc.) of $ClCH_2CO_2H$ (I) or Cl_2CHCO_2H (II) in a test tube. Polyvinyl ethers are tested in the form of a concd. soln. in CH_2Cl_2 (3-5 drops). The colors obtained with homopolymers by using I and II, resp., are: polyvinyl chloride, blue, reddish purple; polyvinyl chloride, post-chlorinated, none, none; polyvinyl chloroacetate, bluish purple, reddish purple; polyvinyl acetate, reddish purple, bluish purple; methyl polyvinyl ether, green, bluish green; ethyl and isopropyl polyvinyl ether, bluish green, greenish blue; dodecyl, hexadecyl, and octadecyl polyvinyl ether, green, greenish blue; polyvinylcarbazole, light green, blue; and polyvinylpyrrolidone (careful heating with I), rapid transition from pink-purple to blue-green. Copolymers of vinyl chloride (III) and vinyl acetate (IV)(13-40%); a copolymer of III 90, IV 4, and vinyl alc. 6%; a copolymer of III 86, IV 13, and maleic acid 1%; and a copolymer of III 80 and isopropyl vinyl ether 20% give a maroon to purple color with I, a blue to purple color with II; a copolymer of III 33.3, IV 33.3, and butyl acrylate 33.3% becomes weakly red, then bluish purple when added to I. The presence of polyvinyl alc. (V) is detd. by adding 2 drops 0.1N I-KI soln. to 5 cc. of neutral aq. soln., dilg. with H_2O until the blue, green, or yellowish green color formed is barely visible, adding a pinch of borax to 5 cc. of this soln. and then 5 drops of concd. HCl; V gives a strong green color. The reaction can be used to det. V colorimetrically in amts. to below 5%, to detect as little as 20 γ V in 5 cc., or to detect 5 mg. borax. Aromatic polyvinyl ethers give nonspecific colors from yellow to red. Decahydronaphthyl polyvinyl ether can be detected by the Molisch reaction for cellulose; cellulose and 5 cc H_2SO_4 are added, and the mixt. is slightly heated, giving a purple color. Maria E. W. Torok

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1979

Emulsion polymerization of vinyl acetate. John E. Bristol and Norris Turnbull (to E. I. du Pont de Nemours & Co.). U.S. 2,614,088, Oct. 14, 1952. Stable polyvinyl acetate emulsions are prepd. for use in casting nonredispersible films. To an aq. soln. contg. 2–10% by wt. of a hydrophilic dispersing agent, such as a completely hydrolyzed polyvinyl alc. or sol. starch, is added 1.5–3.0% vinyl acetate (I) and an activated peroxide catalyst, such as H_2O_2, combined with Zn formaldehydesulfoxylate. The mixt. is heated, and further small amts. of I are added so as to maintain a monomer concn. below 5% when the polymer concn. is less than 20% and below 3% when the polymer concn. exceeds 20% by wt. The pH is held between 4 and 6. The resulting compns. have polymer concns. of about 40% and are useful for water-base paints and adhesives. R. G. Shepherd, Jr.

2542

Polyvinyl acetate emulsions. Norris Turnbull (to E. I. du Pont de Nemours & Co.). U.S. 2,614,087, Oct. 14, 1952. Polyvinyl acetate emulsions having high diln. stability are prepd. by stepwise polymerization of vinyl acetate in the presence of an aq. soln. contg. 2–10% by wt. of a completely hydrolyzed polyvinyl alc. (as dispersing agent), an activated peroxide catalyst such as H_2O_2 and Zn formaldehysulfoxylate, and a high-mol. alc. such as lauryl alc. pH is held between 4 and 6. R. G. Shepherd, Jr.

3615

Polymerization of vinyl acetate emulsions. Tsuguo Komami (to Kurashiki Rayon Co.). Japan. 5346('51), Sept. 15. A polyvinyl acetate emulsion prepd. by polymerization of vinyl acetate is mixed with vinyl acetate contg. H_2O or an aq. suspension of catalyst. The latter is adsorbed by the polyvinyl acetate and the mixt. is polymerized. The catalyst increases the rate of polymerization and makes it possible to obtain a more uniform product. K. Kitsuta

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1290

Insoluble vinyl acetate polymer. Seizo Okamura and Takao Yamashita. *Chem. High Polymers* 6, 444–7(1949).—It was found that the degree of polymerization of polyvinyl acetate (I) increased by heat treatment with Bz_2O_2 in vinyl acetate, EtOAc, or C_6H_6 soln. When the amt. of catalyst increased above a certain limiting value, the I became insol. in acetone or MeOH. The degree of polymerization of polyvinyl alc. obtained by sapon. of I was almost const. These changes are assumed to be caused by cross-linkage at the active H atom attached to C in the α-position to the Ac group in the side chain of I. The insol. polymer can be changed to a sol. polymer by heating in glacial AcOH contg. Ac_2O and H_2SO_4. The polyvinyl alc. obtained by sapon. of the solubilized I was often insol. in hot water. I. Sakurada

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3195

Polymerizing vinyl acetate in granular form. Gwyn Benson and Robert L. Perks (to Shawinigan Chemicals Ltd.). U.S. 2,535,139, Dec. 26, 1950. Coarse-grained polymer particles that can be dried quickly without fusing together are obtained by the polymerization of vinyl acetate in suspension in aq. medium in the presence of 0.12–0.14%, on the total suspension, of emulsifing agent, such as polyvinyl alc., and preferably 0.2–0.5% of an anion-active dispersing agent. The latter is the condensation product of 2 mols. of sulfonic acids of aromatic hydrocarbons with 1 mol. HCHO (*C.A.* 30, 5740^{h,i}, 8691^{g}) e.g. the polymerized Na salts of alkyl naphthalenesulfonic acids ("Darvan #1", "Daxad" or "Triton R-100"). Its 1% aq. soln. should have a surface tension of not less than 50 dynes/cm. at 25°. Cf. *C.A.* 34, 4834^{3}; 40, 1063^{4}. K. Fox

Polymerizing organosiloxanes. James F. Hyde and Oscar K. Johannson (to Dow Corning Corp.). Brit. 647,167, Dec. 6, 1950. See U.S. 2,453,092 (*C.A.* 43, 386). H. L. D.

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7103

Emulsion polymerization of vinyl acetate. Distillers Co., Ltd., Desmond Cleverdon, and Johann J. P. Staudinger. Brit. 601,191, April 29, 1948. An aq. emulsion contg. between 30 and 60% by wt. of vinyl acetate is polymerized at atm. pressure under nonturbulent conditions at temps. between 40 and 60°. The reaction is run at an overall rate of 8–10% by wt. per hr. in a tubular vessel having a high ratio of cooling area to vol.

R. G. Shepherd, Jr.

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1751

Emulsion polymerization of vinyl acetate. Wm. R. Cornthwaite and Harold W. Bryant (to E. I. du Pont de Nemours & Co.). U.S. 2,485,141, Oct. 18, 1949. Approx. 1% Me_2CO or other ketone of less than 10 C atoms is added to $CH_2:CHOAc$ before emulsion polymerizing which limits the mol. wt. The polymers are easily sol. and hydrolyzed to polyvinyl alcs. which maintain their viscosity. Cf. *C.A.* 43, 5230*h*. H. B.

3300

Polymerization of vinyl esters in an aqueous emulsion. Edward Lavin and Charles L. Boyce (to Shawinigan Resins Corp.). U.S. 2,486,855, Nov. 1, 1949. Vinyl esters of satd. aliphatic acids are polymerized in aq. dispersion with a heteropolymer of vinyl acetate and maleic anhydride as the dispersing agent. J. D. Matlack

Polymerization and chemical resistance. Massimo Rolla. *Materie plastiche* 15, 119–25(1949).—The av. chem. resistance of org. compds. is expressed as the sum of the internal bond energies of the compd. divided by the product of the total no. of its terminal atoms and their valencies; e.g. in compds. C_nX_{2n+2}, in which X is H or halogen, the av. chem. resistance is $[(2n + 2)E_{C-X} + (n - 1)E_{C-C}]/(2n + 2)$. By using bond energies given by Remick (*Electronic Interpretation of Org. Chemistry*, 1947, p. 148), it is calcd. that the I rises toward a limiting value with increasing chain length in homologous series, and a formula is given for the calcn. of the limiting value. The av. chem. resistance of the series C_nF_{2n+2} is greater, and that of the series C_nCl_{2n+2} smaller, than the I of C_nH_{2n+2}. By dividing the av. chem. resistance of a compd. by the av. chem. resistance of the corresponding hydrocarbon, the *relative medium chem. resistance* is obtained. In the case of alcs., the relative medium chem. resistance falls to a min. for BuOH; it rises slowly with increasing chain length in fatty acids. NH_2 groups raise I, CO groups lower it. The chem. stability of *high polymers* is expressed by the av. chem. resistance and the relative medium chem. resistance of its unit cells: polyethylene, 116.6, 1.00; polyisobutylene, 116.6, 1.00; polytetrachloroethylene, 105.8, 0.91; polytetrafluoroethylene, 147.3, 1.26; poly(vinylidene chloride), 131.9, 1.13; poly(vinyl chloride), 113.9, 0.98; poly(vinyl alc.), 112.9, 0.97; poly(acrylic acid), 108.6, 0.92; poly(methacrylic acid), 110.3, 0.93; poly(vinyl Me ether), 112.8, 0.97; poly(vinyl acetate), 110.4, 0.95; poly(Me acrylate), 109.1, 0.94; poly(Me methacrylate), 115.6, 0.99; polystyrene, 192.6, 1.65. Several hypothetical unit cells are also given. The concept of the av. chem. resistance is also applied to explain the comparative chem. stability of certain compds., the effect of cross linking, and the polymerization mechanism. H. A. G.

3872

B. BOORD, R. W. BOST, EDGAR C. BRITTON, AND G. B. COHEEN

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1499

Granular polyvinyl acetate. E. I. du Pont de Nemours & Co. Brit. 566,920, Jan. 23, 1945. A process is described for preventing the agglomeration of finely divided polyvinyl acetate. The finely divided material is prepd. and suspended in an aq. vehicle. It is then sepd. and stirred with added sebacic acid until all the particles are coated with it. The granules are then dried at an elevated temp. J. Davidson

1883

Aqueous dispersions of vinyl acetate polymers. Joseph E. Smith and Wm. A. Drummond (to E. I. du Pont de Nemours & Co.). U.S. 2,413,197, Dec. 24, 1946. Stable aq. dispersions of vinyl acetate polymers which can be stored for 3-6 months are prepd. by an emulsion-polymerization technique. Vinyl acetate monomer contg. a polymerization catalyst, is mixed with 3-10% of its own wt. of a refined petroleum hydrocarbon or an oxidized castor oil. This mixt. is dispersed in an aq. soln. contg. 1.8-7.2% of a long-chain alc. sulfate, so that a particle size of 2 γ or less is obtained. An aq. soln. contg. 0.37-2.25% of a long-chain alkyl betaine or another cationic surface-active agent is added to the emulsion (figures based on oil phase). The emulsion is now heated to above 50° to effect polymerization. The product is suitable for use in the *leather*, *textile*, or *paper trade*. Cf. *C.A.* 39, 2008^7. K. R. Hesse

2072

Stabilization of vinyl esters. E. I. du Pont de Nemours & Co. (to Imperial Chemical Industries Ltd.). Brit. 567,464, Feb. 15, 1945. Vinyl esters, particularly vinyl acetate, are stabilized against polymerization by incorporating in them a small proportion of an anhydrous NH_4 salt of an org. carboxylic acid. J. Davidson

Improved catalysts for vinyl esters. The Distillers Co. Ltd., Johann J. P. Staudinger, Phillip D. Coppock, and David J. Hadley. Brit. 578,405, June 27, 1946. Zn or Zn compds. or Cd or Cd compds. supported on activated alumina serve as catalysts for the synthesis of vinyl esters from C_2H_2 (I) and org. acids. The exit gases, after the removal of the product, are enriched and recirculated. Due to an accumulation of by-product gases, chiefly CO_2, the exit gases are occasionally vented. Thus 800 g. activated alumina, 4-8 mesh, is heated 12 hrs. at 200° and

2745

Stabilization of vinyl esters. E. I. du Pont de Nemours & Co. and Allan Berne-Allen, Jr. Brit. 567,879, March 7, 1945. Polymerization of vinyl esters, such as monomeric vinyl acetate, is inhibited by incorporating in them a small proportion of quaternary onium compds. contg. a quinquevalent atom of Group V of the periodic table, e.g., N, P, As, or Sb. Particularly satisfactory compds. are the tetraalkylammonium salts. This treatment stabilizes monomeric vinyl acetate and other vinyl esters of carboxylic acids against polymerization during storage, especially where they are liable to be exposed to heat, or during rectification. Cf. *C.A.* 41, 2072h. J. D.

4005

Aqueous dispersions of vinylacetate polymors. Imperial Chemical Industries Ltd. Brit. 585,423, Feb. 6, 1947. Aq. dispersions of vinyl acetate polymers, which are stable in storage for 3-6 months, can be prepd. by emulsion-polymerization. A mixt. of vinylacetate monomer, 0.5-1% by wt. of a polymerization catalyst, e.g., Bz_2O_2, and 3-10% of a stabilizing agent, e.g., a refined petroleum hydrocarbon or an oxidized castor oil, is added with high-speed agitation to an aq. soln. contg. 1.8-7.2% (based on nonaq. phase) of a long-chain (12-18 C atoms) alc. sulfate ester (I), e.g., Na salt of sulfated oleyl acetate. Agitation is continued until a particle size of 2 μ or less is obtained. The dispersion can contain 10-40% of resulting resin. An aq. soln. contg. 0.37-2.25% (based on nonaq. phase) of a long-chain (12-18 C atoms) alkyl betaine or alkyl ammonium or pyridinium cationic surface-active agent (II), e.g., cetyl betaine (*C.A.* 32, 8631^5) is added to the emulsion, which is then heated to 50-80° to induce polymerization. I and II comprise a composite dispersing agent. The process is applicable also to the prepn. of dispersions contg. plasticizers for the vinyl acetate. The products are useful as *finishes* for *leather*, *textiles*, and *paper*. The patent contains 5 examples. Ned E. Jaffa

4334

Emulsion polymerization. Henry M. Collins (to Shawinigan Chemicals Ltd.). Brit. 568,684, April 25, 1945. A stable aq. emulsion of a polymer is made by polymerizing, with heating under reflux, an aq. emulsion of a H_2O-insol. vinyl or acrylic ester in presence of a peroxide catalyst, a surface-tension depressant, such as the Na salt of the sulfonic acid of dioctyl succinic ester, and at least 2 hydrophilic org. colloids, such as methyl- and benzylcellulose, a partially hydrolyzed polyvinyl acetate having an acetate group content of 37 ± 2% — 43%, starch, gum arabic, etc. The total amt. of colloid should be at least 0.1% by wt. of total charge and should not exceed 1.2%. Brit. 568,885. Stable aq. coarse-grained dispersions of polyvinyl esters are produced. Brit. 568,886. Dispersions and stable emulsions of polyvinyl esters of predetd. viscosities of 1-150 are produced. Cf. *C.A.* 40, 1083^1. J. Davidson

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1063

Polymerization in emulsion. Henry M. Collins (to Shawinigan Chemicals Ltd.). U.S. 2,388,600, Nov. 6, 1945. Thicky, creamy, stable, emulsions of vinyl polymers in water are described. A surface-tension depressant (0.1% of the total charge), e.g., Aerosol O.T., and the emulsifying agent (I) (approx. 1%) are first dispersed in the water (approx. 50%), and the vinyl monomer (approx. 50%) slowly run in with stirring. After a suitable peroxide catalyst is added (0.05%), heat is applied, and temps. held to gentle reflux, i.e., 60–90° for 2 hrs. At the end of the reaction only about 1–5% of unreacted monomer remains. I must be a protective colloid which will stabilize the emulsion at all temps. encountered, say from 0° to 90°, and contains several colloids having complementary stabilizing properties. Emulsions contg. 50% solids are readily obtained. Examples of suitable combinations of colloids for I are: methyl cellulose (II)-gum tragacanth (III) (3:1), II-potato starch (1:1), hydrolyzed polyvinyl acetate (IV) with 40% acetate content-IV with 10% acetate (1:1), IV (40% acetate)-III (2:1), II-IV (33% acetate) (1:1), II-III-IV (33% acetate) (2:1:1), and III-IV (31% acetate) (1:3). Harold L. Kandiner

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Gel formation in addition polymerization. Cheves Walling. *J. Am. Chem. Soc.* 65, 441–7(1945).—Based on Flory's method (cf. *C.A.* 36, 312^{7}) an equation was developed predicting the gel point in the addn. polymerization of a mixt. of mono- and bifunctional monomers. This equation is equiv. to that developed by Stockmayer (cf. *C.A.* 36, 2546^{2}). Gel points for the systems methyl methacrylate–ethylene dimethacrylate and vinyl acetate–divinyl adipate were detd. under a variety of exptl. conditions. Results are in reasonable agreement with the above equation only in the presence of 0.2 mol. % or less of bifunctional monomer. Exptl. results in the presence of more bifunctional monomer are explained qualitatively on the basis that the reaction mixt. consists of discrete swollen polymer mols., the rate of diffusion of which is slow compared with the fate of polymer chain growth. By use of a model based on this concept, it is calcd. that gelation can occur only after these swollen mols. have filled 13–23% of the reaction mixt. Exptl. results indicate 25–46% in fair agreement with calcn. A. B. G.

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Polymerization of vinyl acetate. A. C. Cuthbertson, G. Gee and E. K. Rideal. *Proc. Roy. Soc.* (London) A170, 300–22(1939).—AcH (I) and Bz_2O_2 (II) are effective catalysts for the polymerization of vinyl acetate (III). The course of the polymerization has been followed by dilatometric measurements, both for II as a catalyst and in toluene soln. The temp. rise in the dilatometer is appreciable for strongly catalyzed reactions. Viscosity data allow the computation of chain lengths of various polymers. Chain branching occurs at high temps. Catalytic decompn. takes place also during the reaction. The reaction is characterized by an induction period and the reaction kinetics are shown to be consistent with the view that a complex formed from catalyst and monomer breaks down to give a reaction center. Termination involves the interaction of 2 growing reaction chains. A growing polymer may terminate its life by initiation of a new reaction center on collision with a monomer, in addn. to propagation on collision with a monomeric mol. Toluene is shown to be a participant in the transfer mechanism. The energy of activation for the decompn. of the catalyst is found to be about 29 kg. cal./g. mol. and for the process of polymerization about 17.2 kg. cal./g. mol. S. Z.

5093

Polyvinyl resin compositions. The British Thomson-Houston Co. Ltd. Brit. 499,931, Jan. 31, 1939. Polyvinyl halides are plasticized with esters of polymerized, acetylated or acetylated polymerized ricinoleic acid. The products may be made into sheets or films. In examples, a mixt. of polyvinyl chloride (I) and acetylated castor oil is swollen in MeAmCO and rolled into sheets, and films are prepd. by dipping a glass sheet into a hot soln. of I and acetylated castor oil in MeAmCO or fenchone.

Stabilizing polyvinyl resins. Kodak-Pathé. Fr. 836,151, Jan. 12, 1939. The resin is treated in soln., before or after sepn. from its reaction mixt. and before drying at a raised temp., to the action of a reducing agent in such a manner that no reducing agent is left in the resin. The treatment may be a catalytic or an electrolytic hydrogenation, or it may be a reduction with a nonmetallic reducing agent, e. g., one contg. NOH, such as phenylhydroxylamine, acetoxime, dimethylglyoxime or salicyloxime. The process is particularly applicable to the stabilizing of polyvinyl acetal resins.

5414

Stabilizing vinyl compounds. Sylvia M. Stoesser (to Dow Chemical Co.). U. S. 2,154,389, Apr. 11. Vinyl esters such as vinyl acetate and aromatic vinyl compds. such as styrene are stabilized against polymerization by addn. of about 0.5% or more of a salicylate of Cu or Fe.

5949

Vinyl polymerization products. The Dow Chemical Co. Brit. 501,169, Feb. 22, 1939. Monomeric vinylidene chloride of b. p. 31.5–32° is polymerized by being subjected to a temp. of 25–125° in the presence of a polymerization catalyst, e. g., O_2, Bz peroxide, and with or without exposure to the action of light. The polymerization may be effected under pressure. The product is a powder, a soft porous solid or a hard bone-like material, which is only slightly sol. in boiling *sym*-tetrachloroethane and is insol. in $CHCl_3$, CS_2, ethylene dibromide and C_6H_6. The powder and porous forms may be used as a filter aid.

7440

Vinyl polymerization products. The Distillers Co. Ltd., Hanns P. Staudinger and Henry M. Hutchinson. Brit. 504,301, Apr. 24, 1939. Polyvinyl aromatic hydrocarbons are plasticized by substantially homogeneously incorporating therein an ester or mixt. of esters resulting from the reaction of an aliphatic alc. contg. 1, 2 or 3 C atoms with a satd. or unsatd. org. acid contg. more than 10 C atoms, e. g., Me Et oleate, stearate, palmitate or laurate.

Polymerization of olefins. Donald R. Stevens and Wm. A. Gruse (to Gulf Research & Development Co.). U. S. 2,161,392, June 6. Normally gaseous olefins are subjected to contact with a mixt. of concd. H_2SO_4 1–10 and strong H_3PO_4 99–90% at a temp. of 100–250°

X.- Conclusiones

Con el fin de sumarme a los esfuerzos, realizados en el pasado y el presente, para fabricar en nuestro país, el alcohol polivinílico, resina sintética que aun no se elabora en México y que representa una fuga considerable de divisas, debido a que la demanda es cubierta mediante importaciones, decidí efecturar el presente trabajo, lo más completo posible- obteniendo los siguientes resultados.

a) Se llevó a cabo un estudio de la información reportada en la - literatura en los años de 1938 a 1965, la cual fué clasificada en tres - áreas que comprenden la reacción de polimerización de acetato de vinilo, para la producción del polímero requerido, la reacción de alcohólisis de la cual se obtiene el alcohol polivinílico y el análisis de ambos productos lo cual confío será de utilidad no solo para el desarrollo de esta - tesis, sino para cualquier otra investigación que se lleve a cabo.

b) En base a esta información, se probaron las diversas técnicas - ahí expuestas, resultando finalmente un procedimiento para la polimerización de acetato de vinilo, que posee la particularidad de que utilizando materias primas que se fabriquen en México, tiene las características - adecuadas para producir el alcohol polivinílico de baja viscocidad y que la emulsión puede romperse fácilmente obteniéndose así en forma sencilla el acetato de polivinilo como sólido. En cuanto al alcohol polivinílico se refiere, se desarrolló una reacción que dio como resultado un alcohol polivinílico de baja viscocidad cuyas propiedades fueron comparadas con- un producto comercial, el cual se obtuvo también en la forma sólida.

c) Teniendo como fundamento lo anterior, fué seleccionado el equipo necesario para llevar a cabo industrialmente la técnica desarrollada y - así mismo una estimación de las características requeridas y el costo - del mismo, excepto el correspondiente a recuperación de solventes.

d) Contando con todos estos datos, se procedió a realizar un estudio preliminar del proyecto el cual arroja como resultado que es factible fabricar el alcohol polivinílico de baja viscocidad mediante la técnica desarrollada.

XI.- Bibliografía

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