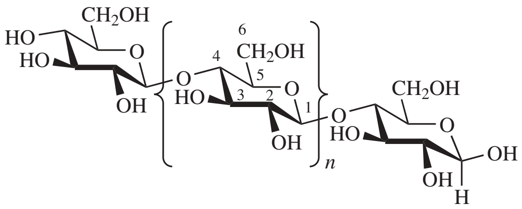
CELLULOSE ESTERS, ORGANIC ESTERS

1. Introduction

Cellulose (qv) is one of nature's most abundant structural materials, providing the primary framework of most plants. For industrial purposes cellulose is derived from two primary sources, cotton linters and wood pulp. Linters are derived from the machine by the same name used for removing the short fibers adhering to cotton seeds after ginning and consist essentially of pure cellulose (see COTTON). Wood (qv), on the other hand, contains 40–60% cellulose, which must be extracted by the chemical degradation of the wood structure.

The chemical structure of cellulose is relatively simple (Fig. 1). The simplicity lies in the repetitive utilization of the anhydroglucose unit,$C_6H_{10}O_5$, as the building block for chain structure. The term cellulose does not designate a specific chemical or homogeneous substance but serves to characterize the homologous series of compounds having specifically a $(1 \longrightarrow 4)$ β (diequatorial) linkage between each anhydroglucose unit. Many other polyglucoside structural isomers exist (Fig. 2), but few have achieved the widespread commercial applications of cellulose. Thus two samples of cellulose contain the same relative amounts of



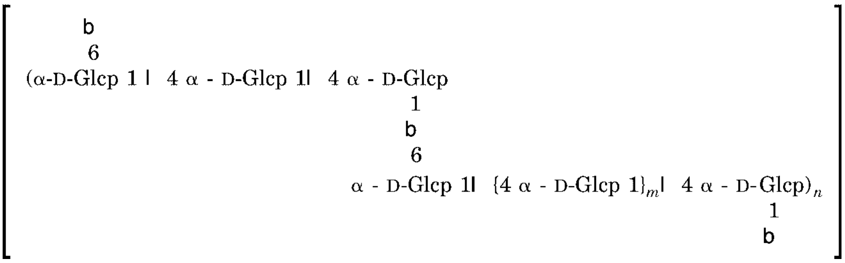
β-D-Glcp1l 4-β-D-Glcp1l {4-β-D-Glcp1l}$_n$4-β-D-Glcp1l 4-β-D-Glcp1l 4

Fig. 1. Structure of natural cellulose, $C_6H_{12}O_6$.

Starch 4α-D-Glcp 1l {4 α-D-Glcp 1l }$_n$4 α-D-Glcp 1l 4 α-D-Glcp 1l

Pustulan 6 β-D-Glcp 1l {6 β-D-Glcp 1l }$_n$6 β-D-Glcp 1l

Pullulan, $m = 1$ or 2



b
6
(α-D-Glcp 1 l 4 α - D-Glcp 1l 4 α - D-Glcp
1
b
6
α - D-Glcp 1l {4 α - D-Glcp 1}$_m$l 4 α - D-Glcp)$_n$
1
b

Fig. 2. Structural isomers of cellulose.

carbon, hydrogen, and oxygen but may vary considerably in chemical reactivity and physical properties. Molecular weight and, consequently, the number of anhydroglucose units per molecule or degree of polymerization (DP) vary as a function of the type of cellulose. Molecular weight determinations by the ultracentrifuge method have assigned a molecular weight average of 570,000 to native cellulose. In the synthesis of cellulose derivatives, however, chain cleavage determines the molecular weight of the product and hence many of the observed physical properties.

Cellulose esters are commonly derived from natural cellulose by reaction with organic acids, anhydrides, or acid chlorides. Cellulose esters of almost any organic acid can be prepared, but because of practical limitations esters of acids containing more than four carbon atoms have not achieved commercial significance.

Cellulose acetate [9004-35-7] is the most important organic ester because of its broad application in fibers and plastics; it is prepared in multi-ton quantities with degrees of substitution (DS) ranging from that of hydrolyzed, water-soluble monoacetates to those of fully substituted triacetate (Table 1). Soluble cellulose acetate was first prepared in 1865 by heating cotton andacetic anhydride at 180°C (1). Usingsulfuric acid as a catalyst permitted preparation at lower temperatures (2), and later, partial hydrolysis of the triacetate gave anacetone-soluble cellulose acetate (3). The solubility of partially hydrolyzed (secondary)

Table 1. **Relationship of Cellulose Acetate DSto Acetyl Content and Combined Acetic Acid**

DS[a]	Acetyl, wt %[b]	Combined acetic acid, wt %[c]
0.5	11.7	16.3
0.75	16.7	23.2
1.0	21.1	29.4
1.5	28.7	40.0
2.0	35.0	48.8
2.5	40.3	56.2
3.0	44.8	62.5

[a] Defined as the average number of acetyl groups in the anhydroglucose unit of cellulose.

[b] Unit molecular weight of acetyl group,CH_3CO, is 43.

[c] Degree of acetylation is often expressed as percent combined acetic acid.

cellulose acetate in less expensive and less toxic solvents such as acetone aided substantially in its subsequent commercial development.

During World War I, cellulose acetate replaced the highly flammablecellulose nitrate coating on airplane wings and the fuselage fabrics. After World War I, it found extensive use in photographic and x-ray films, spun fibers, and molding plastics.

Although cellulose acetate remains the most widely used organic ester of cellulose, its usefulness is restricted by its moisture sensitivity, limited compatibility with other synthetic resins, and relatively high processing temperature. Cellulose esters of higher aliphatic acids, C_3 and C_4, circumvent these shortcomings with varying degrees of success. They can be prepared relatively easily with procedures similar to those used for cellulose acetate. Mixed cellulose esters containing acetate and either the propionate or butyrate moieties are produced commercially in large quantities by Eastman Chemical Co. in the United States (Table 2). Bayer AG discontinued the production of mixed esters at Leverkusen in Germany in mid-1987 citing poor economics as the reason for the closing.

Cellulose esters of aromatic acids, aliphatic acids containing more than four carbon atoms and aliphatic diacids are difficult and expensive to prepare because of the poor reactivity of the corresponding anhydrides with cellulose; little commercial interest has been shown in these esters. Of notable exception, however, is the recent interest in the mixed esters of cellulose succinates, prepared by the sodium acetate catalyzed reaction of cellulose withsuccinic anhydride. The additional expense incurred in manufacturing succinate esters is compensated by the improved film properties observed in waterborne coatings (5).

Mixed cellulose esters containing the dicarboxylate moiety, eg, cellulose acetate phthalate, have commercially useful properties such as alkaline solubility and excellent film-forming characteristics. These esters can be prepared by the reaction of hydrolyzed cellulose acetate with adicarboxylic anhydride in apyridine or, preferably, an acetic acid solvent with sodium acetate catalyst. Cellulose acetate phthalate [9004-38-0] for pharmaceutical and photographic uses is produced commercially via the acetic acid–sodium acetate method.

Table 2. **Domestic and Foreign Producers of Cellulose Acetate**

Producer	Country	Annual capacity, 10^3 t
North America[a]a		
Eastman Kodak Co.[b]b	United States	197
Hoechst Celanese Corp.	United States, Canada, Mexico	241
Western Europe[c]c		
Agfa-Gevaert	Belgium	5
Tubize Plastics[d]d	Belgium	7
Rhône-Poulenc Chemie	France	25
Rhodia AG	Germany	>25
Industrias del Acetato de Celulosa	Spain	2
Courtaulds Fibres Ltd.	United Kingdom	54
Nelsons Acetate Ltd.[e]e	United Kingdom	14
Asia		
Daicel Chemical Industries, Ltd.	Japan	100
Teijin Acetate Ltd.	Japan	11.8

[a] CEH estimates as of Nov. 1, 1988(4).

[b] Also produces cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) mixed esters.

[c] CEH estimates as of Jan. 1, 1989(4); Bayer AG (Germany) discontinued CAB/CAP production at Leverkusen in mid-1987; capacity for resin-grade cellulose acetate flake had been reduced from 25,000 t in 1981 to 15,000 t prior to closing.

[d] In 1984, PMC Inc. (United States) purchased Tubize Plastics SA from government owned Fabelta Tubize SA. This facility was sold to Rhône-Poulenc in Oct. 1988.

[e] In 1988, Courtaulds took over Hercules' 50% interest in Nelsons Acetate.

2. Properties

The properties of cellulose esters are affected by the number of acyl groups per anhydroglucose unit, acyl chain length, and the degree of polymerization (DP) (molecular weight). The properties of some typical cellulose triesters are given in Table 3. In this series, with increasing acyl chain length from C_2 to C_6, the melting point, tensile strength, mechanical strength, and density generally decrease, whereas solubilities in nonpolar solvents and resistance to moisture increase. Fewer acyl groups per anhydroglucose unit, ie, increased hydroxyl content, increase the solubility in polar solvents and decrease moisture resistance. The physical and chemical properties of mixed esters vary according to the ratio of the esters used, eg, acetyl to butyl or acetyl to propionyl. General trends of the properties of mixed esters, such ascellulose acetate butyrate [9004-36-8] (CAB), as a function of composition are illustrated in Figure 3, in which increasing butyryl (decreasing acetyl) content increases flexibility, moisture resistance, and nonpolar solubility and decreases melting point and density.

The common commercial products are the primary (triacetate) and the secondary (acetone-soluble, ca 39.5% acetyl, 2.45 DS) acetates; they are odorless, tasteless, and nontoxic. Their properties depend on the combined acetic acid content (acetyl, see Table 1 and Figure 4) and molecular weight. Solubility characteristics of cellulose acetates with various acetyl contents are given in Table 4.

Table 3. **Properties of Cellulose Triesters**[a]

Cellulose ester	Shrinking point, °C	Mp[b], °C	Water tolerance[c] value	Moisture regain[d], %			Density, g/mL	Tensile strength, MPa[e]
				50% rh	75% rh	95% rh		
cellulose[f]				10.8	15.5	30.5	1.52	
acetate		306	54.4	2.0	3.8	7.8	1.28	71.6
propionate	229	234	26.9	0.5	1.5	2.4	1.23	48.0
butyrate	178	183	16.1	0.2	0.7	1.0	1.17	30.4
valerate	119	112	10.2	0.2	0.3	0.6	1.13	18.6
caproate	84	94	5.88	0.1	0.2	0.4	1.10	13.7
heptylate[g]	82	88	3.39	0.1	0.2	0.4	1.07	10.8
caprate	82	86	1.14	0.1	0.1	0.2	1.05	8.8
caprate[h]	87	88		0.1	0.2	0.5	1.02	6.9
laurate	89	91		0.1	0.1	0.3	1.00	5.9
myristate	87	106		0.1	0.1	0.2	0.99	5.9
palmitate	90	106		0.1	0.1	0.2	0.99	4.9

[a] Ref. 6. Courtesy of the American Chemical Society.

[b] Char point is 315°C or higher unless otherwise noted.

[c] Milliliters of water required to start precipitation of the ester from 125 mL of an acetone solution of 0.1% concentration.

[d] At 25% rh moisture regain for cellulose is 5.4%; for the acetate, 0.6%; for the propionate and butyrate, 0.1%; all others are zero.

[e] To convert MPa to psi, multiply by 145.

[f] Starting cellulose, prepared by deacetylation of commercial, medium viscosity cellulose acetate (40.4% acetyl content).

[g] Char point = 290°C.

[h] Char point = 301°C.

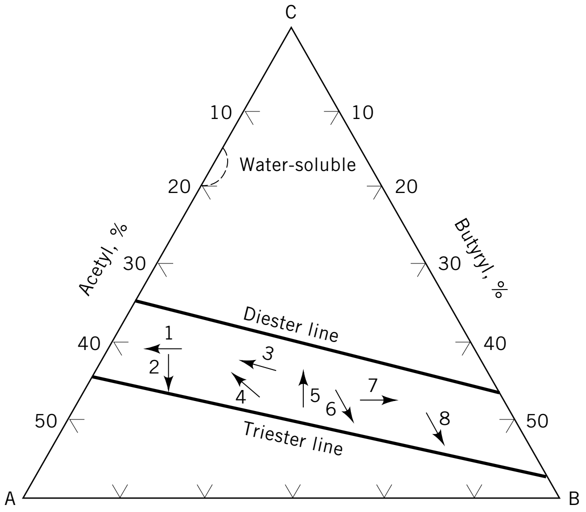


Fig. 3. Effects of composition on physical properties. A, acetyl; B, butyryl; C, cellulose. 1, increased tensile strength, stiffness; 2, decreased moisture sorption; 3, increased melting point; 4, increased plasticizer compatibility; 5, increased solubilities in polar solvents; 6, increased solubilities in nonpolar solvents; 7, increased flexibility; 8, decreased density (7).

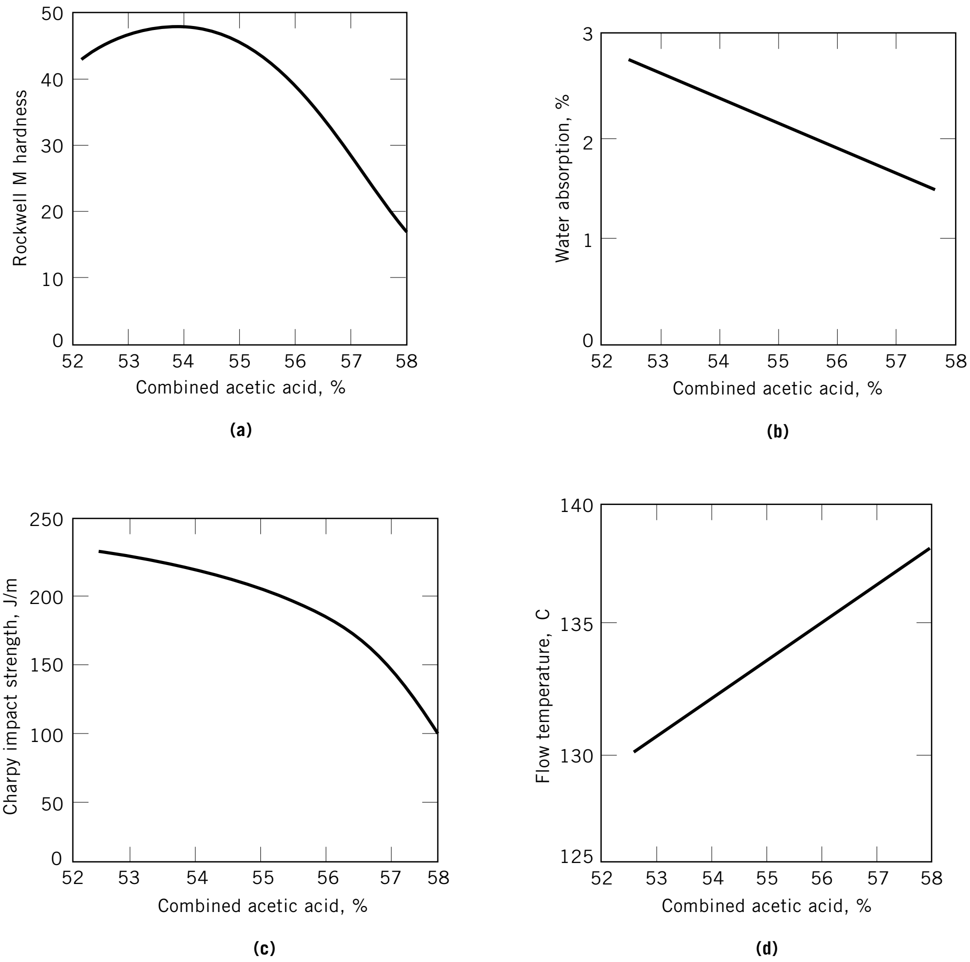


Fig. 4. Effect of combined acetic acid content on (**a**) hardness, (**b**) absorption, (**c**) impact strength, and (**d**) temperature of cellulose acetate (8). To convert J/m to ft·lbs/in., divide by 53.38.

Cellulose triacetate [9012-09-3] has the highest melting point (ca 300°C) of the triesters; melting points generally decrease to a minimum of ca 230°C as the acetyl content decreases to 38–39% (secondary acetate).

Moisture sensitivity and vapor-permeability rate of cellulose acetate increase with decreasing acetyl (increasing hydroxyl) content. Thermoplastic

Table 4. **Solubility Characteristics of Cellulose Acetates**

Acetyl, %	Soluble in	Insoluble in
43.0–44.8	dichloromethane	acetone
37–42	acetone	dichloromethane
24–32	2-methoxymethanol	acetone
15–20	water	2-methoxymethanol
$\leq$13	none of the above	all of the above

characteristics are greatly improved as the acetyl content is increased from ca 20% (DS(acetyl) = 1) to ca 39% (DS(acetyl) = 2.4) (9).

The bulk density of cellulose acetate varies with physical form from 160 kg/m^3 (10 lb/ft^3) for soft flakes to 481 kg/m^3 (30 lb/ft^3) for hammer-milled powder, whereas the specific gravity (1.29–1.30), refractive index (1.48), and dielectric constant of most commercial cellulose acetates are similar.

In fibers, plastics, and films prepared from cellulose esters, mechanical properties such as tensile strength, impact strength, elongation, and flexural strength are greatly affected by the degree of polymerization and the degree of substitution. Mechanical properties significantly improve as the DP is increased from ca 100 to 250 repeat units.

2.1. Liquid Crystalline Solutions. Cellulose esters, when dissolved in the appropriate solvents at the proper concentration, show liquid crystalline characteristics similar to those of other rigid chain polymers (10) because of an ordered arrangement of the polymer molecules in solution. Cellulose triacetate dissolved at 30–40 wt% in trifluoroacetic acid, dichloroacetic acid, and mixtures of trifluoroacetic acid and dichloromethane exhibits brilliant iridescence, high optical rotation, and viscosity–temperature profiles characteristic of typical aniostropic phase-containing liquid crystalline solutions (11). Similar observations have been made for cellulose acetate butyrate (12), cellulose diacetate (13), and other cellulose derivatives (14,15). Wet spinning of these liquid crystalline solutions yields fibers with much higher strength properties than fibers normally obtained from cellulose esters (16,17).

3. Manufacture and Processing

Simple triesters such as cellulose formate [9036-95-7] (7), cellulose propionate [9004-48-2] (9,18), and cellulose butyrate [9015-12-7] (19) have been prepared and their properties studied; none of these triesters is produced in large quantities. Cellulose formate esters, prepared by reaction of cellulose with formic acid, are thermally (20) and hydrolytically (7) unstable. Cellulose propionate and cellulose butyrate triesters are synthesized by methods similar to those used in the preparation of cellulose acetate with propionic or butyric anhydride in the presence of an acid catalyst (21). These anhydrides, especially butyric, react more slowly with cellulose than acetic anhydride. Therefore, the cellulose must be activated and the temperature must be controlled to avoid degradation. Esterification rates decrease with increasing acyl chain length, and degradation becomes more severe in the order acetic < propionic < butyric < isobutyric anhydride. Esterification with isobutyric anhydride is normally so slow that highly activated cellulose must be used and thesulfuric acid catalyst must be distributed uniformly. Swelling agents, eg, water, containing dissolved acid catalyst are used to ensure uniform catalyst distribution for the preparation of isobutyrate esters. The swelling agent is removed by solvent exchange, leaving sorbed acid uniformly distributed in the activated cellulose (22).

Cellulose activated with ethylenediamine [107-15-3] is used to prepare high molecular-weight cellulose butyrate (23). Cellulose so activated has a larger measured surface area (120 m^3/g) than cellulose activated with acetic acid (4.8 m^3/g).

The diamine is removed with water, followed by solvent exchange with acetic acid and butyric acid before esterification.

More recently, however, a process for the manufacture of ultrahigh molecular-weight cellulose esters has been developed by reaction of nonactivated, secondary cellulose with trifluoroacetic acid, trifluoroacetic anhydride, and either an organic acid or acid chloride (24). This process is amenable to a larger variety of organic esters not normally available through conventional means. The technique requires less reaction time, less excess solvent, and it is easier to control the extent of the reaction than conventional sulfuric acid activation. Unfortunately, the handling and toxic nature of trifluoroacetic acid and the anhydride currently prevent its use on a large scale.

Cellulose valerates have been synthesized by conventional methods using valeric anhydride and sulfuric acid catalyst (25,26). Alternatively, the cellulose is activated by soaking in water, which is then displaced bymethylene chloride or valeric acid; the temperature is maintained at $<38^\circ$C to minimize degradation.

Production of cellulose esters from aromatic acids has not been commercialized because of unfavorable economics. These esters are usually prepared from highly reactive regenerated cellulose, and their physical properties do not differ markedly from cellulose esters prepared from the more readily available aliphatic acids. Benzoate esters have been prepared from regenerated cellulose withbenzoyl chloride in pyridine–nitrobenzene (27) or benzene (28). These benzoate esters are soluble in common organic solvents such as acetone or chloroform. Benzoate esters, as well as the nitrochloro-, and methoxy-substituted benzoates, have been prepared from cellulose with the appropriate aromatic acid and chloroacetic anhydride as the impelling agent and magnesium perchlorate as the catalyst (29).

Cellulose chloroacetates (30) and aminoacetates (30,31), acetate sorbates (32), and acetate maleates (33) have been prepared but are not commercially important. These esters are made from hydrolyzed cellulose acetate with the appropriate anhydride or acid chloride in pyridine.

Cellulose esters of unsaturated acids, such as the acetate methacrylate, acetate maleate (34), and propionate crotonate (35), have been prepared. They are made by treating the hydrolyzed acetate or propionate with the corresponding acyl chloride in a pyridine solvent. Cellulose esters of unsaturated acids are cross-linkable by heat or uv light; solvent-resistant films and coatings can be prepared from such esters.

Amine-containing cellulose esters, eg, the acetate *N,N*-diethylaminoacetate (36) and propionate morpholinobutyrate (35), are of interest because of their unique solubility in dilute acid. Such esters are prepared by the addition of the appropriate amine to the cellulose acrylate crotonate esters or by replacement of the chlorine on cellulose acrylate chloroacetate esters with amines. This type of ester has been suggested for use in controlled release, rumen-protected feed supplements for ruminants (36,37).

Mixed esters, such as cellulose acetate propionate and cellulose acetate butyrate, have desirable properties not exhibited by the acetate or the high acyl triesters. These mixed esters are produced commercially in multiton quantities by methods similar to those for cellulose acetate; they are prepared over a wide range of acyl substitutions and viscosities. The ratio of acetyl to higher acyl

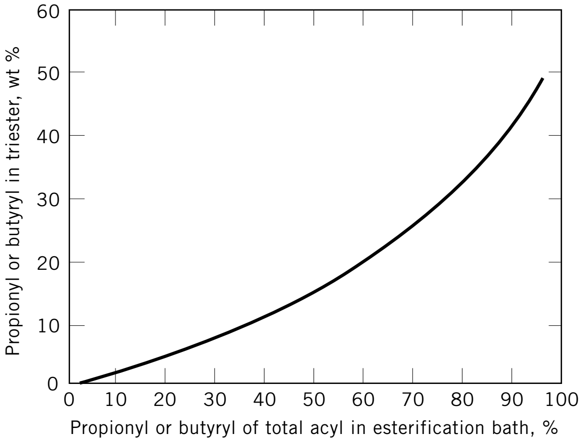


Fig. 5. Composition of cellulose acetate butyrate (propionate) as a function of butyryl (propionyl) content of esterification bath.

in the product is proportional to the concentration of components in the esterification solution (Figs. 5 and 6). Thus it is possible to esterify cellulose with propionic or butyric anhydride in the presence of acetic acid to produce the mixed esters. In a similar manner, acetic anhydride can be used in the esterification with either propionic or butyric acid to produce a cellulose ester containing both acyl moieties. The commercial production of cellulose acetate butyrate

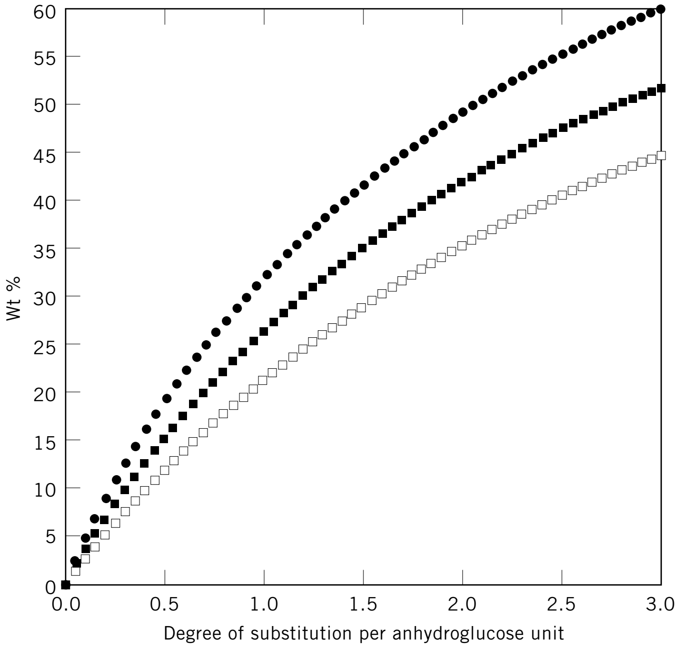


Fig. 6. Conversion of weight percent to degree of substitution per anhydroglucose unit (max = 3.0), where • is butyryl, ◆ is propionyl, and ♢ is acetyl.

has been described (38), and the different reactivities of lower anhydrides toward cellulose have been investigated in detail. Cellulose butyrate has been prepared in homogenous solution by the reaction of cellulose in dimethyl sulfoxide (DMSO)-paraformaldehyde with butyric anhydride and pyridine catalyst (39). The maximum degree of substitution is ca 1.8, and the products are soluble in common organic solvents. Dichloromethane has been used in the preparation of cellulose acetate butyrate to prevent excessive degradation and provide an ester with higher molecular weight (40).

Mixed esters containing the dicarboxylate moiety, eg, cellulose acetate phthalate, are usually prepared from the partially hydrolyzed lower aliphatic acid ester of cellulose in acetic acid solvent by using the corresponding dicarboxylic acid anhydride and a basic catalyst such as sodium acetate (41,42). Cellulose acetate succinate and cellulose acetate butyrate succinate are manufactured by similar methods as described in reference 43.

Other mixed esters, eg, cellulose acetate valerate [55962-79-3], cellulose propionate valerate [67351-41-1], and cellulose butyrate valerate [53568-56-2], have been prepared by the conventional anhydride sulfuric acid methods (25). Cellulose acetate isobutyrate [67351-38-6] (44) and cellulose propionate isobutyrate [67351-40-0] (45) have been prepared with a zinc chloride catalyst. Large amounts of catalyst and anhydride are required to provide a soluble product, and special methods of delayed anhydride addition are necessary to produce mixed esters containing the acetate moiety. Mixtures of sulfuric acid and perchloric acid are claimed to be effective catalysts for the preparation of cellulose acetate propionate in dichloromethane solution at relatively low temperatures (46); however, such acid mixtures are considered too corrosive for large-scale productions.

Mixed esters are hydrolyzed by methods similar to those used for hydrolyzing cellulose triacetate. The hydrolysis eliminates small amounts of the combined sulfate ester, which, if not removed, affects thermal stability. Sulfuric acid is the preferred catalyst for hydrolysis since it is already present in the esterification mixture. On a large scale, partial neutralization of the catalyst may be necessary before hydrolysis. Increasing the amount of water during hydrolysis reduces the rates of viscosity reduction and acyl hydrolysis of cellulose acetate propionate and acetate butyrate esters (47). Several methods of hydrolyzing cellulose esters of higher aliphatic acids are described (48,49). Acetate phthalate mixed esters preferentially lose acetyl groups when hydrolyzed in aqueous acetic acid media with sulfuric acid catalyst. On the other hand, hydrolysis with a basic catalyst such as sodium or potassium acetate in aqueous acetic acid results in preferential loss of the phthaloyl moiety (50). Ester properties can be modified by changing the DS, ie, removing acyl groups.

3.1. Stabilization. After hydrolysis, precipitation, and thorough washing of the cellulose esters to remove residual acids, the esters must be stabilized against thermal degradation and color development, which may occur during processing, such as extrusion or injection molding. Thermal instability is caused by the presence of oxidizable substances and small amounts of free and combined sulfuric acid (51). The sulfuric acid combines with the cellulose almost quantitatively and most of it is removed during the latter stages of hydrolysis. The remaining sulfuric acid can be neutralized with alkali metal salts, such as sodium, calcium, or magnesium acetate, to improve ester stability. The combined sulfate ester may also be removed by treatment in boiling water or at steam temperatures in an autoclave. Treatment with aqueous potassium or calcium iodide reportedly stabilizes the cellulose acetate against thermal degradation (52).

Dialkyl esters of 3,3′-thiodipropionic acid (53), cyclic phosphonites such as neopentylphenyl phosphite, derivatives of phosphaphenathrene-10-oxide (54), secondary aromatic amines, eg, diphenylamine (55), and epoxidized soybean oils (56) are effective stabilizers for preventing discoloration of cellulose esters during thermal processing.

Exposure to uv radiation may cause chain scission and loss of physical properties in cellulose esters exposed to outdoor environments; esters formulated for such use must be stabilized accordingly. Some resorcinol and benzophenone derivatives, such as resorcinol monobenzoate and 2-hydroxy-4-methoxybenzophenone, are reportedly excellent uv-light stabilizers for cellulose esters (57,58). Other stabilizers include piperidine derivatives (59) and substituted triazole compounds alone (60) and in combination with resorcinol monobenzoate (61).

3.2. Cellulose Acetate. Almost all cellulose acetate, with the exception of fibrous triacetate, is prepared by a solution process employing sulfuric acid as the catalyst with acetic anhydride in an acetic acid solvent. The acetylation reaction is heterogeneous and topochemical wherein successive layers of the cellulose fibers react and are solubilized in the medium, thus exposing new surfaces for reaction. The reaction course is controlled by the rates of diffusion of the reagents into the cellulose fibers, and therefore the cellulose must be swollen or activated before acetylation to achieve uniform reaction and avoid unreacted fibers in the solution (62).

Cellulose dissolved in suitable solvents, however, can be acetylated in a totally homogeneous manner, and several such methods have been suggested. Treatment in dimethyl sulfoxide (DMSO) with paraformaldehyde gives a soluble methylol derivative that reacts with glacial acetic acid, acetic anhydride, or acetyl chloride to form the acetate (63). The maximum degree of substitution obtained by this method is 2.0; some oxidation also occurs. Similarly, cellulose can be acetylated in solution with dimethylacetamide–paraformaldehyde and dimethylformamide-paraformaldehyde with a potassium acetate catalyst (64) to provide an almost quantitative yield of hydroxymethylcellulose acetate.

Several derivatives of cellulose, including cellulose acetate, can be prepared in solution in dimethylacetamide–lithium chloride (65). Reportedly, this combination does not react with the hydroxy groups, thus leaving them free for esterification or etherification reactions. In another homogeneous-solution method, cellulose is treated with dinitrogen tetroxide in DMF to form the soluble cellulose nitrite ester; this is then ester-interchanged with acetic anhydride (66). With pyridine as the catalyst, this method yields cellulose acetate with DS < 2.0.

In the fibrous acetylation process, part or all of the acetic acid solvent is replaced with an inert dilutent, such astoluene,benzene, orhexane, to maintain the fibrous structure of cellulose throughout the reaction. Perchloric acid is often the catalyst of choice because of its high activity and because it does not react with cellulose to form acid esters. Fibrous acetylation also occurs upon treatment with acetic anhydride vapors after impregnation with a suitable catalyst such as zinc chloride (67).

Table 5. **Typical Specifications for Acetylation-Grade Pulp**[a]

Property	Value
α-cellulose, min %	95.6
moisture, %	5.8[b]
pentosans, max %	2.1
cuprammonium viscosity[c], mPa · s(=cP)	1100–4000
intrinsic viscosity, dL/g	5.5–7.5
ether extractable, max %	0.15
ash, max %	0.08
iron, max ppm	10
trial acetylation	
haze, max ppm	100
color, max ppm	600

[a] Ref. 62.

[b] Off supplier's dryer.

[c] 2.5% solution.

An apparatus for the continuous fibrous acetylation of cellulose in benzene has been described (68, 69). The process involves continuous activation, acetylation, partial saponification of the resulting triacetate, and drying of the product.

Activation of Cellulose. The activation required depends on the source of cellulose (cotton linter or wood pulp), purity, and drying history. Typical specifications for an acetylation-grade cellulose are given in Table 5. Cellulose that has never been dried or has been mildly dried to ca 5% moisture requires little, if any, further activation.

Normally, water or aqueous acetic acid is the activating agent; glacial acetic acid may also be used. Water is more effective because it swells the fibers more than other agents and alters the hydrogen bonding between the polymer chains to provide a greater surface area for reaction. When water or aqueous acids are used, the cellulose must be dehydrated by displacing the water with acetic acid before the start of acetylation. Commercially, it is not unusual to activate cellulose with glacial acetic acid containing a small part of the total required sulfuric acid catalyst; this reduces the molecular weight of the cellulose as needed to obtain a satisfactory product. The efficiency of activation is increased by increased temperature, time, amount of catalyst, and lower acetic acid–cellulose ratio. Several other swelling agents and methods for cellulose activation have been reported but have little commercial value because of cost and performance considerations.

Ethylenediamine (70,71), benzyl alcohol and acetone (72), ethylene glycol (73) and C_2–C_{18} carboxylic acids (74) are claimed to increase the reactivity of cellulose toward acetylation. Sodium hydroxide and liquid ammonia (71) are excellent swelling agents and have been used to activate cellulose before esterification. Ultrasonic treatment of cellulose slurries (75) reportedly swells the fibers and improves reactivity.

In one process to produce highly activated cellulose for acetylation, cellulose is treated with NaOH (mercerization) followed by a hydroxyalkylating agent, eg, ethylene oxide or propylene oxide, to give a cellulose hydroxyalkyl ether with a DS of 0.05–0.3 (76). The resulting water-insoluble material is highly reactive to conventional acetic anhydride–sulfuric acid acetylation.

Catalysts for Acetylation. Sulfuric acid is the preferred catalyst for esterifying cellulose and is the only known catalyst used commercially for this function. The role of sulfuric acid during acetylation has been discussed (77,78). In the presence of acetic anhydride, sulfuric acid rapidly and almost quantitatively forms the cellulose sulfate acid ester (77). Even in the absence of anhydride, the sulfuric acid is physically or mechanically retained (sorbed) on the cellulose. The degree of absorption is a measure of the reactivity or accessibility of different celluloses.

Sulfuric acid reacts with acetic anhydride to form acetylsulfuric acid (79). This reaction is favored by low temperature and high anhydride concentration. In cellulose acetylation, probably both sulfuric acid and acetylsulfuric acid exist and react with cellulose to form cellulose sulfate acid ester.

Perchloric acid is a well-known acetylation catalyst, especially in the fibrous method of preparing cellulose triacetate. Unlike sulfuric acid, perchloric acid does not combine with cellulose (78), ie, it does not form esters, and therefore virtually complete acetylation (DS 3.0, 44.8% acetyl) occurs. However, the extremely corrosive nature of perchloric acid and explosive nature of its salts have precluded its use industrially as an acetylation catalyst.

Zinc chloride is a Lewis acid catalyst that promotes cellulose esterification. However, because of the large quantities required, this type of catalyst would be uneconomical for commercial use. Other compounds such as titanium alkoxides, eg, tetrabutoxytitanium (80), sulfate salts containing cadmium, aluminum, and ammonium ions (81), sulfamic acid, and ammonium sulfate (82) have been reported as catalysts for cellulose acetate production. In general, they require reaction temperatures above 50°C for complete esterification. Relatively small amounts ($\leq$0.5%) of sulfuric acid combined with phosphoric acid (83), sulfonic acids, eg, methanesulfonic, or alkyl phosphites (84) have been reported as good acetylation catalysts, especially at reaction temperatures above 90°C.

Hydrolysis. The primary functions of hydrolysis are to remove some of the acetyl groups from the cellulose triester and to reduce or remove the combined acid sulfate ester to improve the thermal stability of the acetate.

The acetylation reaction is stopped by the addition of water to destroy the excess anhydride, causing rapid hydrolysis of the combined sulfate acid ester (Fig. 7). This is followed by a much slower rate of hydrolysis of the acetyl ester groups. The rate of hydrolysis is controlled by temperature, catalyst concentration, and, to a lesser extent, by the amount of water. Higher temperatures and catalyst concentrations increase the rate of hydrolysis. Higher water content slightly increases the hydrolysis rate and helps minimize degradation (85). The amount of water also influences the ratio of primary to secondary hydroxy groups in the hydrolyzed cellulose acetate; high water content favors primary hydroxyl formation (86).

In commercial processes, the water content during hydrolysis ranges from 5 to 20 wt % based on total liquids and depends on the temperature and the final product desired. Hydrolysis reactions can be performed at temperatures ranging from ca 38°C to pressurized reactions at 229°C (87). In a continuous process at 129°C, a triacetate solution is passed vertically upward through three consecutive chambers containing rotating disks to maximize plug flow of the solution (88). Kinetics of cellulose triacetate hydrolysis have been investigated (89) and,

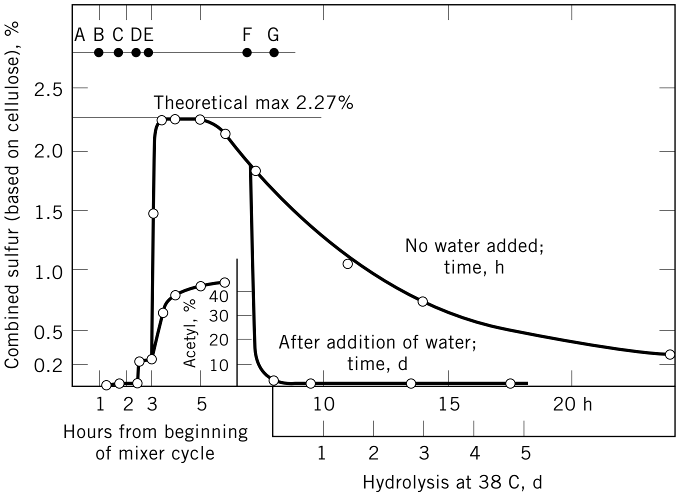


Fig. 7. Combined sulfur during preparation of cellulose acetate; hydrolysis of sulfate and esters (6). Acetylation schedule: A, mixer charged with linters and acetic acid; B, minor portion of catalyst added; C, began cooling to 18°C; D, acetic anhydride added and continued cooling to 16°C; E, significant portion of catalyst added; F–G, water added during 1 h.

with sulfuric acid as the catalyst, the rate constant was found to be linear for both catalyst concentration and water content.

The rate of hydrolysis of cellulose acetate can be monitored by removing samples at intervals during hydrolysis and determining the solubility of the hydrolyzed acetate. When the desired DS is reached, the hydrolysis is stopped by neutralizing the catalyst with magnesium, calcium, or sodium salts dissolved in aqueous acetic acid.

Precipitation and Purification. During the hydrolysis, control tests are made by turbidimetric titration of samples taken intermittently. When the desired degree of hydrolysis is reached, the ester is precipitated from the reaction solution into water. It is important for the precipitate to have the proper texture for subsequent washing to remove acid and salts for thermal stabilization. Before precipitation, the reaction solution is usually diluted with additional aqueous acetic acid to reduce the viscosity. If a flake texture is desired, the solution is poured into a vigorously stirred, 10–15% aqueous acetic acid. To precipitate the acetate in powder form, dilute acetic acid is added to the stirred reaction solution. In both cases, the precipitated ester is suspended in 25–30% aqueous acid solutions and finally washed with deionized water. The dilution, precipitation temperature, agitation, and strength of the acid media must be controlled to ensure uniform texture.

Another method for direct precipitation of cellulose acetate powder suitable for extrusion into plastics is described (90). The reaction solution is precipitated with dilute aqueous acetic acid at 80–85°C in the presence of a coagulant such as isopropyl acetate. The resulting powder particles have a higher bulk density and absorb plasticizers more readily than powders obtained by the usual methods.

Granules can be precipitated and formed by extruding the viscous reaction mixture through a circular die containing several holes over which a knife blade

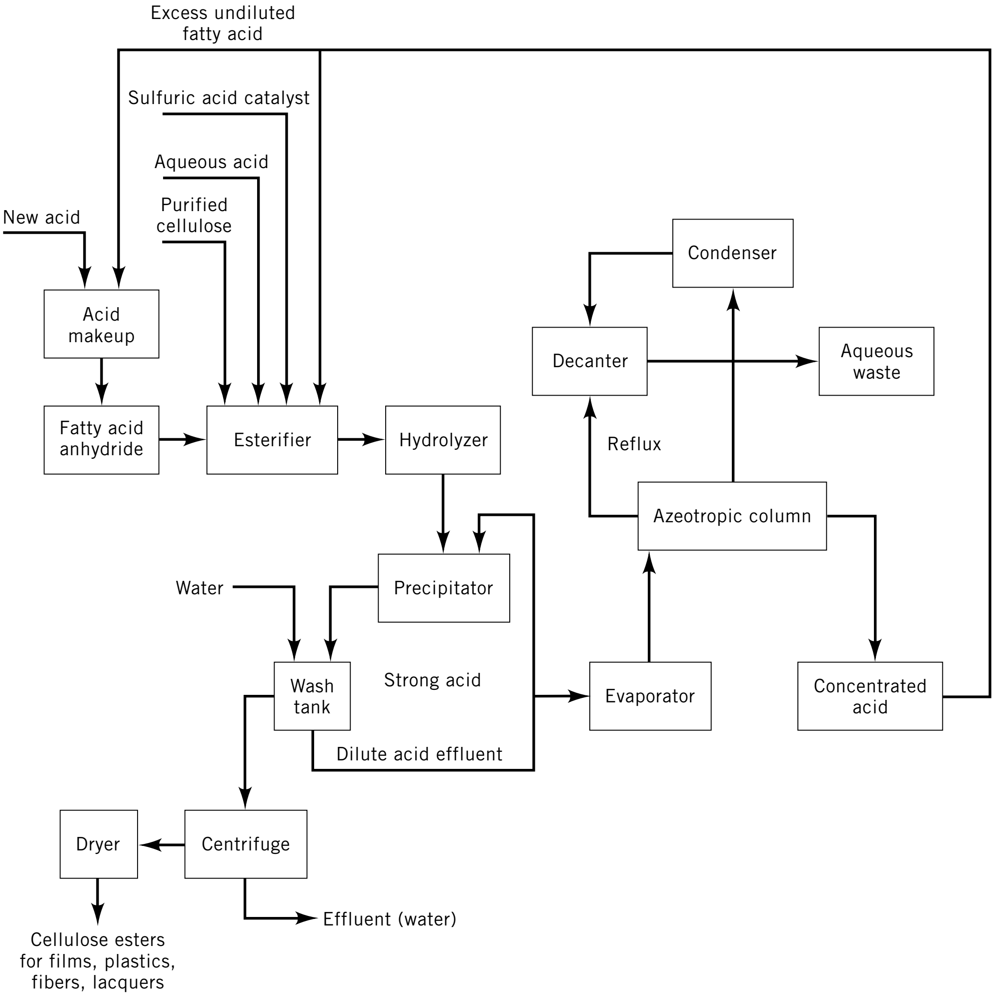


Fig. 8. Process flow sheet for cellulose esters.

rotates to cut the strands into granules (91). The granules are simultaneously slurried in dilute acetic acid to harden the particles for further washing.

Solution Process. With the exception of fibrous triacetate, practically all cellulose acetate is manufactured by a solution process using sulfuric acid catalyst with acetic anhydride in an acetic acid solvent. An excellent description of this process is given (85). In the process (Fig. 8), cellulose (ca 400 kg) is treated with ca 1200 kg acetic anhydride in 1600 kg acetic acid solvent and 28–40 kg sulfuric acid (7–10% based on cellulose) as catalyst. During the exothermic reaction, the temperature is controlled at 40–45°C to minimize cellulose degradation. After the reaction solution becomes clear and fiber-free and the desired viscosity has been achieved, sufficient aqueous acetic acid (60–70% acid) is added to destroy the excess anhydride and provide 10–15% free water for hydrolysis. At this point, the sulfuric acid catalyst may be partially neutralized with calcium, magnesium, or sodium salts for better control of product molecular weight.

The cellulose acetate is hydrolyzed in solution at 40–50°C for varying lengths of time (4–20 h) until the desired DS is obtained; at this point, the ester is precipitated with dilute aqueous acetic acid. The precipitate is hardened in 25–30% aqueous acetic acid, which is drained off and recovered.

The ester is washed thoroughly in iron-free water to remove acid and any desirable salts; these wash liquids are sent for acid recovery. The final wash may contain some sodium, calcium, or magnesium ions to stabilize traces of sulfate esters remaining on the cellulose acetate.

Recent Developments. A considerable amount of cellulose acetate is manufactured by the batch process, as described previously. In order to reduce production costs, efforts have been made to develop a continuous process that includes continuous activation, acetylation, hydrolysis, and precipitation. In this process, the reaction mixture, ie, cellulose, anhydride, catalyst, and solvent, pass continuously through a number of successive reaction zones, each of which is agitated (92,93). In a similar process, the reaction mass is passed through tubular zones in which the mixture is forced through screens of successively small openings to homogenize the mixture effectively (94). Other similar methods for continuous acetylation of cellulose have been described (95,96).

Cellulose acetate with improved solubility properties can be prepared from low quality wood pulps by multistage addition of the components (97) or by interrupting the reaction in the early stages, filtering, and continuing the acetylation with fresh reactants (98,99).

In an integrated continuous process, cellulose reacts with acetic anhydride prepared from the carbonylation of methyl acetate withcarbon monoxide. The acetic acid liberated reacts further with methanol to give methyl acetate, which is then carbonylated to give additional acetic anhydride (100,101).

High temperature acetylation of cellulose above 50°C produces cellulose acetate from low purity wood pulp cellulose in shorter reaction times. In a high temperature method recently disclosed (102), cellulose reacts with 200–400% acetic anhydride in the presence of <5% acid catalyst at 68–85°C for 3–20 min. After the acid catalyst is neutralized with magnesium acetate, the cellulose acetate is hydrolyzed at 120°C for two hours (103). Several modified catalyst systems have been developed for acetylation of cellulose above 90°C (89,90).

4. Economic Aspects

From 1980 to 1988, annual cellulose acetate flake production in the United States showed a slight decrease in production from 392,000 t to 323,000 t with an annual decline of −0.4 to −0.1% (Table 6). World demand for cellulose acetate flake has also fallen. A modest recovery has occurred in recent years as a result of the increased demand for cigarette-filter tow; world consumption of cigarette-filter tow has risen about 2.5% per year since 1980 (Tables 7 and 8). In contrast, world demand for textile fibers and cellulose ester plastics decline 4.6% and 4.2% per year, respectively (Fig. 9).

Demand for cellulose acetate flake in the United States is projected to decline slightly from 1988 to 1993. Cigarette-filter tow for export is the only

Table 6. **U.S. Consumption of Cellulose Acetate Flake,[a] 10^3 t**

Year	Cigarette-filter tow	Textile fibers	Cellulose acetate plastics[b]	Total
1979	164	145	83	392
1980	175	145	48	368
1983	173	105	62	339
1988	205	68	50	323
1993	210–215	59	47	315–321
Average annual growth rate				
1988–1993	0.5–1.0%	−3.0	−1.1%	−0.4 – 0.1%

[a] Data are reported as cellulose acetate flake equivalents; plasticizers not included.
[b] Mixed esters (CAB and CAP) included. Courtesy of CEH Estimates.

Table 7. **World Consumption of Cellulose Acetate Flake,[a] 10^3 t**

Year	Textile fibers	Cigarette-filter tow	Plastics[b]	Total
1980	335	338	132	805
1985	241	335	172	710
1987	240	401	98	740

[a] Data for textile fibers and cigarette-filter tow include Eastern Europe and the People's Republic of China.
[b] Cellulose acetate ester plastics are produced largely in the United States, Western Europe, and Japan. World consumption is assumed to be approximately equivalent to production of cellulose ester plastics in these three regions. Courtesy of CEH Estimates.

Table 8. **World Capacity for Cellulose Acetate Flake,1988, 10^3 t**

Region	Capacity
North America	
Canada	30
United States	453
Central America	
Mexico	20
Western Europe	
Belgium	12
France	25
Germany (formerly FRG)	25
Italy	9
Spain	2
United Kingdom	68
Eastern Europe	
Germany (formerly GDR)	6
Russia	70
Asia	
Japan	112
Totals[a]	*832*

[a] In addition to the producers listed above, Victorio Ghisolfiwith state owned Gepi purchased the Taban SpA (a Mon-tedison subsidiary) plant in Pallanza, Italy in 1988 with plans to restart in 1989 (4).

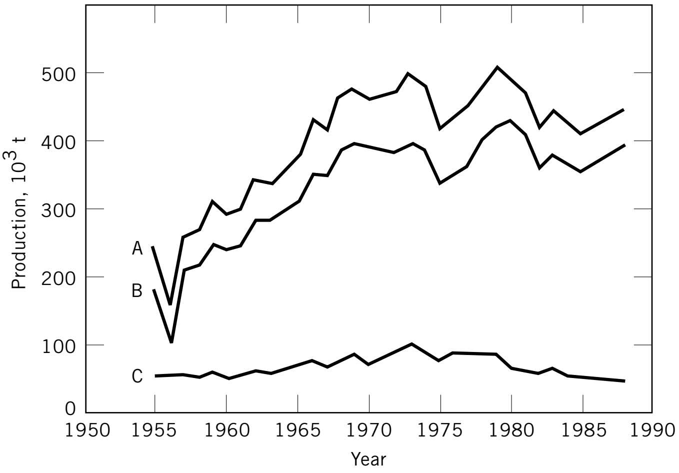


Fig. 9. U.S. production of cellulose esters; A, total cellulose esters production; B, cellulose acetate flake; C, other cellulose esters, ie, cellulose nitrate, cellulose acetate propionate, cellulose acetate butyrate (4).Courtesy of CEH Estimates.

market projected to grow. Cellulose acetate for textile fibers is expected to decline, as will flake demand for plastics, with the growth of photographic films somewhat offsetting declining markets in other plastics end uses.

The price of cellulose ester flake has generally increased with inflation and as of mid-1987 was estimated at ca \$3.64–\$4.71/kg for cellulose diacetate molding resin and from ca \$4.16–\$4.71/kg for the mixed esters molding resins depending on purity and the number of propionyl or butyryl esters (4).

From 1946 to mid-1987, Farbenfabriken Bayer AG in Germany was the European producer of cellulose acetate, cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP) before closing its facilities. Bayer's exit from the cellulose acetate mixed esters business leaves Eastman Chemical Co. in the United States as the sole producer of CAB/CAP resins.

In the United States, plastic and fiber grades of cellulose acetate and mixed cellulose ester flake, ie, acetate butyrate and acetate propionate, are produced by the Eastman Chemical Co.; Hoechst-Celanese manufactures a fiber-grade cellulose acetate flake suitable for plastics applications. Foreign producers of cellulose acetate flake include Gevaert and Fabelta in Belgium; Rhône Poulenc Chemie in France; British Hercules, Courtaulds, and Nelson in the United Kingdom; Mazzucchelli Celluliode SpA and Montedison in Italy; and Daicel and Teijin in Japan.

Cellulose ester flake production for nonfiber applications represents a small part of the total U.S. output. Cigarette-filter tow and cellulose acetate textile fibers consume more than 80% of flake production (104).

With the takeover of the American Celanese Corp. in mid-1986, the new Hoechst Celanese Corp., with Eastman Chemical Co. are the world leaders in cellulose acetate tow and flake production as of this writing. With confidence in both the acetate market and acetic anhydride supply (105), Hoechst Celanese recently announced an expansion that will double its tow and flake capacity from 35,750 metric tons to 60,500 metric tons by 1994 (106). The increased capacity will be achieved through expansions and productivity improvements at the U.S., Belgium, Canada, Mexico, and China operation centers.

In a similar announcement, Eastman Chemical Co. and Rhône-Poulenc S.A. have recently formed a 50/50 joint venture to make 59,090 metric tons/yr of cellulose acetate filter tow and fiber by the fourth quarter of 1993 (107). Eastman Chemical Co. announced a multimillion dollar expansion of its own filter tow capacity by approximately 11,363 metric tons/yr to be completed by mid-1991. The expansion brings the company's worldwide filter tow capacity up to 154,545 metric tons (108). Eastman Chemical Co. announced plans to expand the production of cellulose acetate butryates and cellulose acetate propionates by 20 and 40%, respectively, by mid-1991 (109).

5. Analytical and Test Methods

Standardized test methods for analyzing the chemical composition, viscosity, and physical properties of cellulose esters have been adopted by the ASTM and are described in substantial detail (110).

5.1. Degree of Substitution and DS Distribution. For cellulose esters, the substitution level is usually expressed in terms of DS; that is, the average number of substituents per anhydroglucose unit (AGU). Cellulose contains three hydroxyl groups in each AGU unit that can be substituted; therefore DS can have a value between zero and three. Because DS is a statistical mean value, a value of 1 does not assure that every AGU has a single substituent. In some cases there can be unsubstituted anhydroglucose units, some with two and some with three substituents, and more often than not the value will be a noninteger. The physical properties commonly associated with commercial cellulose acetates, cellulose acetate butyrates, and cellulose acetate propionates are, in many cases, directly related to the degree of substitution as well as the overall substitution pattern. The degree of substitution or acetyl content of cellulose acetate has traditionally been determined by saponifying a known amount of the ester with an excess of standard sodium hydroxide solution in the presence of swelling agent or solvent. The excess sodium hydroxide is back-titrated with a standard solution of hydrochloric acid to determine the total acetyl content. The relative amounts of acetyl, propionyl, and butyryl in cellulose mixed esters, however, are determined by partition analysis in butyl acetate–water mixtures. The esters are saponified in sodium hydroxide, and phosphoric acid is added to liberate the organic acids from their sodium salts. The acids are partitioned between butyl acetate and water and their mole ratios are determined by comparison to carefully prepared control standards.

The acetyl content of cellulose acetate may be calculated by difference from the hydroxyl content, which is usually determined by carbanilation of the ester hydroxy groups in pyridine solvent withphenyl isocyanate [103-71-9], followed by measurement of uv absorption of the combined carbanilate. Methods for determining cellulose ester hydroxyl content by near-infrared spectroscopy (111) and acid content by nmr spectroscopy (112) and pyrolysis gas chromatography (113) have been reported.

With the advent of high resolution proton and carbon nuclear magnetic resonance spectroscopy, however, determining the DS and the DS distribution of mixed ester systems by aqueous saponification has become obsolete. Numerous studies have shown nmr to be a fundamental tool for probing the microscopic behavior of a wide variety of synthetic polymers and biomacromolecules (114). In the past, however, most spectral assignments required laboriously prepared derivatives containing a trideuterioacetyl or trideuteriomethyl group at a predetermined position or by comparison to spectra of mono- or oligosaccharides (115). These methods proved to be limited in detail because of line broadening and small differences in chemical shifts. Understanding the basic relationships between macroscopic properties and the microstructure of these biopolymer derivatives through nmr is the direction of much cellulose esters research.

Determining the degree of substitution using standard proton nmr relies on the integral ratio between the cellulosic ring protons ($\approx 5.0 - 2.9\delta$) and the ester alkyl protons ($\approx 1.2\delta$ for butyryl and propionyl and $\approx 2.0\delta$ for acetyl methyl groups). This simple procedure is used extensively to determine the extent of esterification and is currently the fastest, easiest way for determining the DS of mixed cellulose esters.

Standard proton nmr techniques provide information on the degree of substitution and ester ratios in mixed ester systems, but it has been the development of two-dimensional techniques that has allowed the greatest insight into the microstructure of the cellulosic polymer (116–119). The combination of ^{1}H and ^{13}C nmr spectroscopy has, for example, been applied to cellulose triacetate for determination of its configuration (120), identification of the chemical shifts of ring protons and carbons (117), and determination of the distribution of acetyl groups over C_2,C_3, and C_6 (118,121). More complex experiments such as insensitive nuclei assigned by polarization transfer (INAPT) and nuclear Overhauser exchange spectroscopy (NOESY) have been successfully applied toward the spectral assignments of most common triesters, the results of which are listed in Table 9. With INAPT, the lack of sensitivity that is commonly associated with two-dimensional nmr techniques is generally avoided. This increased sensitivity circumvents the need for ^{13}C enrichment and decreases the demand on instrument time.

Other two-dimensional techniques, such as COSY (122), DEPT (123), HOHAHA, solid state (124) etc. give varying degrees of success when applied to the structure-property relationship of cellulose triesters. The recent application of ^{1}H–^{13}C multiple-bond correlation (HMBC) spectroscopy for the unambiguous assignment of cellulose mixed esters has successfully demonstrated the utility of nmr for the structure elucidation of complex cellulose esters (125). It is this unique ability to provide detailed information on intermolecular interactions of cellulose esters in coatings (119) or in polymeric blends that continues to put nmr spectroscopy well ahead of other analytical techniques.

5.2. Viscosity. The viscosity of cellulose esters, a measure of the degree of polymerization, is determined by the falling-ball method. The time in Saybolt units (SU) required for an aluminum or stainless-steel ball of specified diameter to go through a specified distance in a solution of the cellulose ester is determined. The choice of solvents used to prepare the solutions for viscosity determination depends on the DS of the cellulose ester; the concentration of ester in the

Table 9. **^{1}H and ^{13}C Nmr Chemical Shifts, ppm, and Coupling Constants, J,[a] for Cellulose Triacetate, Cellulose Tripropionate, and Cellulose Tributyrate[b]**

	CTA DMSO-d$_6$, 25°C	CTA DMSO-d$_6$,[c]	CTA CDX$_3$,d[d]	CTP CDX$_3$,[d] 25°C	CTB CDX$_3$,[d] 25°C
			^{1}H Values		
H-1	4.65 (d, $J_{1,2}$ = 7.9 Hz)	4.65 (d, $J_{1,2}$ = 7.9 Hz)	4.42 (d, $J_{1,2}$ = 7.9 Hz)	4.35 (d, $J_{1,2}$ = 7.9 Hz)	4.65 (d, $J_{1,2}$ = 7.9 Hz)
H-2	4.52 (t, J = 7.3 Hz)	4.55 (t, J = 8.6 Hz)	4.79 (t, J = 8.6 Hz)	4.77 (t, J = 8.6 Hz)	4.76 (t, J = 8.6 Hz)
H-3	5.06 (t, J = 9.2 Hz)	5.04 (t, J = 9.2 Hz)	5.07 (t, J = 9.0 Hz)	5.07 (t, J = 9.1 Hz)	5.06 (t, J = 9.2 Hz)
H-4	3.65 (t, J = 9.2 Hz)	3.68 (t, J = 9.2 Hz)	3.71 (t, J = 9.2 Hz)	3.66 (t, J = 9.1 Hz)	3.61 (t, J = 9.2 Hz)
H-5	3.81 (m)	3.77 (m)	3.53 (m)	3.47 (m)	3.48 (m)
H-6$_s$	4.22 (d, $J_{6s,6r}$ = 10 Hz)	4.26 (d, $J_{6s,6r}$ = 10 Hz)	[e]	[e]	[e]
H-6$_r$	3.98 (m)	4.04 (m)	4.06 (m)	4.03 (m)	4.03 (m)
			^{13}C Values		
C-1		99.8 (d, J = 167 Hz)	100.4 (d, J = 165 Hz)	100.3 (d, J = 163 Hz)	100.1 (d, J = 163 Hz)
C-2		72.2 (d, J = 152 Hz)	71.7 (d, J = 153 Hz)	71.7 (d, J = 150 Hz)	71.4 (d, J = 150 Hz)
C-3		72.9 (d, J = 151 Hz)	72.5 (d, J = 148 Hz)	72.2 (d, J = 148 Hz)	71.8 (d, J = 147 Hz)
C-4		76.4 (d, J = 151 Hz)	76.0[f]f	75.8 (d, J = 153 Hz)	75.8[f]f
C-5		72.5 (d, J = 146 Hz)	72.7 (d, J = 139 Hz)	73.0 (d, J = 138 Hz)	73.1 (d, J = 143 Hz)
C-6		62.8 (t, J = 151 Hz)	61.9 (t, J = 151 Hz)	61.9 (t, J = 147 Hz)	61.9 (t, J = 145 Hz)
C-2 acetyl			169.1[g]		
C-3 acetyl			169.6[g]		
C-6 acetyl			170.7[g]		

[a] Digital resolution for ^{1}H was 0.20–0.26 Hz; For additional information see Ref.116. For ^{13}C the digital resolution was 0.52 Hz.

[b] All solutions are 30 mg/mL.

[c] At 80°C for ^{1}H; and 90°C for ^{13}C.

[d] X = Cl for ^{1}H; X = I for ^{13}C. 25°C

[e] H-6$_r$ overlaps with H-1.

[f] The coupled resonance overlaps with the solvent peaks. For additional information see Refs. 116 and 117.

[g] Doublet, coupling constant unavailable.

solution is normally 20 wt%. Dilute-solution viscosity (intrinsic viscosity) is determined by using a solution of 0.25-g ester dissolved in 100 mL of solvent. The flow time of the solution through a specially designed capillary viscometer is compared to that of the pure solvent. Methods of calculating molecular weight from intrinsic viscosity of cellulose esters have been reported (126).

5.3. Thermal Properties. The thermal stability of cellulose esters is determined by heating a known amount of ester in a test tube at a specific temperature a specified length of time, after which the sample is dissolved in a given amount of solvent and its intrinsic viscosity and solution color are determined. Solution color is determined spectroscopically and is compared to platinum–cobalt standards. Differential thermal analysis (dta) has also been reported as a method for determining the relative heat stability of cellulose esters (127).

The thermal transitions of a cellulose ester such as the glass-transition temperature and the melting point are usually determined by differential scanning calorimetry (dsc) (Fig. 10), which measures the flow of heat into and out of a sample. Generally a first heating run is necessary in order to erase any previous thermal processing characteristics, ie, regions of crystallinity. A slow cool followed by a reheat above the melt temperature provides information on the glass-transition temperature, crystallization temperature (exothermic), and the melting temperature (endothermic). This information is essential for the development of new thermoplastics.

Similar information can be obtained from analysis by dynamic mechanical thermal analysis (dmta). Dmta measures the deformation of a material in response to vibrational forces. The dynamic modulus, the loss modulus, and a mechanical damping are determined from such measurements. Detailed information on the theory of dmta is given (128).

Determination of the thermal decomposition temperature by thermal gravimetric analysis (tga) defines the upper limits of processing. The tga for cellulose

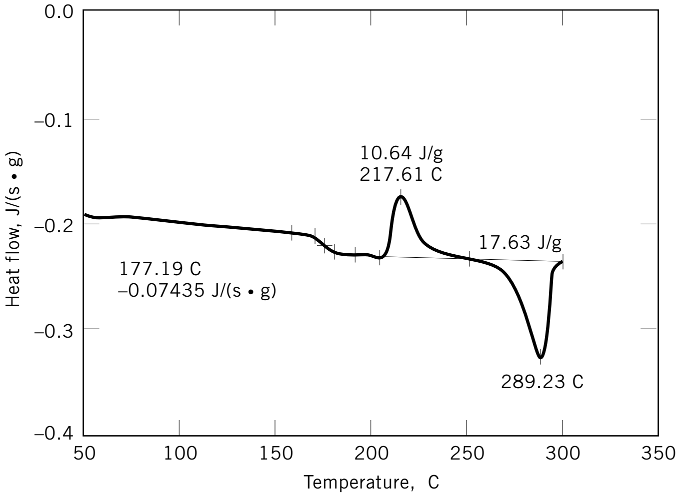


Fig. 10. Differential scanning calorimetry of cellulose triacetate. Second heating at 20°C/min.; glass-transition (T_g) temperature = 177°C; crystallization on heating (T_{ch}) = 217°C; melting temperature (T_m) = 289°C. To convert J to cal, divide by 4.184.

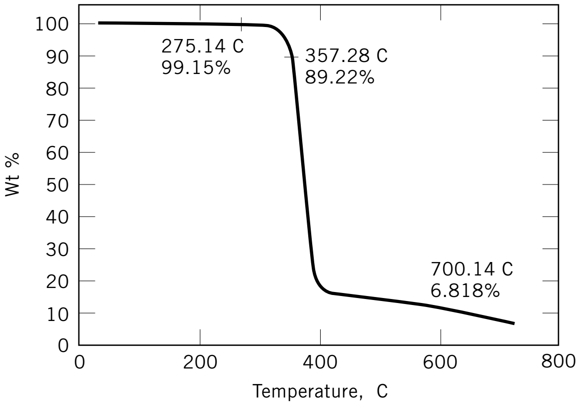


Fig. 11. Thermogravimetric analysis of cellulose triacetate. Method: 20°C/min to 700°C, in (N_2) at 40 mL/min purging rate.

triacetate is shown in Figure 11. Comparing the melt temperature (289°C) from the dsc in Figure 10 to the onset of decomposition in Figure 11 defines the processing temperature window at which the material can successfully be melt extruded or blended.

5.4. Molecular Weight. The molecular-weight distribution of cellulose esters is normally determined by gel-permeation chromatography (129) in which the ester, dissolved in a suitable solvent, is eluted through a column of porous cross-linked polystyrene. The elution profiles are compared to narrow molecular-weight polystyrene standards to obtain the molecular weight or DP distribution. Other methods, such as fractional precipitation and fractional extraction, although considerably more laborious, may be used to determine DP and DS distribution of cellulose esters (130). The DP of cellulose triacetate has been determined by gpc using a styrene–divinylbenzene copolymer column with an assigned peak molecular weight of approximately 60,000. Other solvents such as THF and NMP have also been shown to solvate secondary cellulose acetates and mixed esters for gpc analysis (131).

6. Health and Safety Factors

The vapors of the organic solvents used in the preparation of cellulose ester solutions represent a potential fire, explosion, or health hazard. Care should be taken to provide adequate ventilation to keep solvent vapor concentrations below the explosive limits. Mixing equipment should be designed to ensure that solvent temperatures do not approach their flash point during the mixing cycle. All equipment must be electrically grounded to prevent static discharge, and appropriate precautions should be followed as recommended by the manufacturer of the solvents.

Mixing cellulose esters in nonpolar hydrocarbons, such as toluene or xylene, may result in static electricity buildup that can cause a flash fire or explosion. When adding cellulose esters to any flammable liquid, an inert gas atmosphere should be maintained within the vessel (132). This risk may be reduced by the use of conductive solvents in combination with the hydrocarbon or by use of an antistatic additive. Protective clothing and devices should be provided.

Cellulose esters, like most dry organic materials in powder form, are capable of creating dust explosions (133). The explosion at Bayer's cellulose acetate plant at Dormagen, Germany in 1976 can attest to the explosive potential of dust. Damage to the plant was estimated at between DM 5–10 million (134).

Cellulose esters are considered nontoxic and may be used in food-contact applications. However, since cellulose esters normally are not used alone, formulators of coatings and films for use in food packaging should ensure that all ingredients in their formulations are cleared by the United States Food and Drug Administration for such use.

7. Uses

The cellulose esters with the largest commercial consumption are cellulose acetate, including cellulose triacetate, cellulose acetate butyrate, and cellulose acetate propionate. Cellulose acetate is used in textile fibers, plastics, film, sheeting, and lacquers. The cellulose acetate used for photographic film base is almost exclusively triacetate; some triacetate is also used for textile fibers because of its crystalline and heat-setting characteristics. The critical properties of cellulose acetate as related to application are given in Table 10.

Large quantities of secondary cellulose acetate are used worldwide in the manufacture of filter material for cigarettes. Because of its excellent clarity and ease of processing, cellulose acetate film is widely used in display packaging and extruded plastic film for decorative signs (see PACKAGING MATERIALS). Injection-molded plastics of cellulose acetate are used in toothbrush handles, computer brushes, and a large variety of other applications (7).

Low viscosity cellulose acetate is used in lacquers and protective coatings for paper, metal, glass, and other substrates and as an adhesive for cellulose photographic film because of its quick bonding rate and excellent bond peel strength (135) (see COATINGS). Heat-sensitive adhesives for textiles have also been prepared from cellulose acetate (136). Extruded cellulose acetate film

Table 10. **Uses and Critical Properties of Cellulose Acetate**[a]

	Use[b]			
Property	Yarn	Photographic film	Plastics	Lacquers
color, absence of haze	I		C	I
			I	I
false viscosity[c]	I	I		I
filterability	C	I	I	I
adhesion		C		
radioactivecontamination				

[a] Ref. 62.

[b] I = important; C = critical.

[c] Concentrated solution viscosity higher than predicted for the intrinsic viscosity.

makes an excellent base for transparent pressure-sensitive tape (137) (see ADHESIVES).

Cellulose acetate films, specially cast to have a dense surface and a porous substructure, are used in reverse osmosis to purify brackish water (138–141) in hollow fibers for purification of blood (artificial kidney) (142), and for purifying fruit juices (143,144) (see MEMBRANE TECHNOLOGY).

Compaction of cellulose acetate desalination membranes, causing reduction in throughput and performance with time, can be significantly reduced by irrigation grafting of styrene onto the membrane (145).

Eyeglass frames made of cellulose acetate plasticized with diglycerol esters do not exhibit opaqueness at the frame-lens junction with polycarbonate plastic lenses (146,147).

Biodegradable film (148), foam-molding compositions, eg, sponges (149), tobacco substitutes (150), and microencapsulated drug-delivery systems (151) are potentially new and useful applications for cellulose acetate esters.

With the renewed interest in environmentally friendly products, cellulose esters are being re-evaluated as a natural source of biodegradable thermoplastics. Cellulose acetates are potentially biodegradable (152). Films prepared from a cellulose acetate with a DS of 2.5 were shown to require only a 10–12 day incubation period for extensive degradation in an *in vitro* enrichment assay. Similarly, films prepared from a cellulose acetate with a DS of 1.7 saw 70% degradation in 27 days in a waste water treatment facility, whereas films prepared from a cellulose acetate with a DS of 2.5 required approximately 10 weeks for similar degradation to occur. The results of this work demonstrate that cellulose acetate fibers and films are potentially environmentally nonpersistant.

Cellulose acetate propionate and butyrate esters have numerous applications, such as sheeting, molding plastics, film products, lacquer coatings, and melt dip coatings. The properties of propionate and acetate propionate esters ordinarily lie between those of cellulose acetate and acetate butyrate. The acetate propionate mixed esters have traditionally covered a narrow composition range compared to the range of acetate butyrate esters. Table 11 shows uses and a range of commercial compositions of cellulose acetate butyrate esters. Through proper variation of acetyl and butyryl contents, the esters can be adapted to a broad range of applications. Cellulose acetate propionate and acet-

Table 11. **Application and Characteristics of Commercial-Grade Cellulose Acetate Butyrate**[a]

			Degree of esterification[b]			
Acetyl, %	Butyryl, %	Hydroxyl, %	Acetate	Butyrate	Hydroxyl	Application
29.5	17	1	2.1	0.7	0.2	lacquers
20.5	26	2.5	1.4	1.1	0.5	lacquers
13	37	2	0.95	1.65	0.4	plastics, lacquers
6	48	1	0.5	2.3	0.2	melt coatings

[a] Ref. 153.

[b] Ratio of ester groups to glucose residues (see Fig. 6).

ate butyrate are thermoplastic; properly formulated, these esters are processible by methods such as injection molding and extrusion and can be dissolved and cast into films from a variety of solvents (see FILMS). The mixed esters are generally more compatible with various plasticizers and synthetic resins than the acetates, and their films possess excellent clarity and toughness. For example, cellulose acetate butyrate is compatible with polyester, acrylic, vinyl, andalkyd resins (qv), depending on the amount of butyryl substitution and the degree of hydrolysis of the esters.

Cellulose acetate butyrates with high butyryl content and low viscosity are soluble in inexpensive lacquer solvents. They are widely used in lacquers for protective and decorative coatings applied to automobiles and wood furniture.

Higher butyryl esters, formulated with acrylic polymers, provide coatings with excellent weather resistance, good color fastness and dispersibility, and good flow properties (154). Formulations for a typical automotive refinishing lacquer and a wood furniture lacquer are given in Tables 12 and 13, respectively. Low viscosity, high butyryl cellulose esters tolerate substantial amounts of alcohol solvent without appreciable increase in solution viscosity. An alcohol-soluble cellulose acetate butyrate containing ca 50% butyryl and ca 4.5% hydroxy is available commercially.

Low viscosity cellulose propionate butyrate esters containing 3–5% butyryl, 40–50% propionyl, and 2–3% hydroxyl groups have excellent compatibility with oil-modified alkyd resins (qv) and are used in wood furniture coatings (155). Acetate butyrate esters have been used in such varied applications as hot-melt adhesive formulations (156), electrostatically spray-coated powders for fusible, non-cratering coatings on metal surfaces (157–159), contact lenses (qv) with improvedoxygen permeability and excellent wear characteristics (160–162), and as reverse-osmosis membranes for desalination of water (163).

In a relatively new decorative-coating technique called wet-on-wet coatings, cellulose acetate butyrate ester as the pigmented basecoat provides good pigment

Table 12. **CAB–Polyester Automotive Refinishing Lacquer**[a]

Components	Wt %
polyester	11.5
CAB 381-20[b]	11.4
CAB 381-0.5b	5.7
phosphoric acid, 85%	0.3
TiO_2 pigment	4.2
toluene	34.4
xylene	6.1
MIBK	5.0
isopropyl alcohol	9.3
acetone	7.5
n-butyl alcohol	3.2
Ektasolve EB acetate[c]	1.4
Total	*100.0*

[a] Ref. 154.

[b] CAB = cellulose acetate butyrate.

[c] Eastman Kodak Co.

Table 13. **CAB-Based Clear Topcoat Formulation for Wood Furniture**

Components	Wt %
CAB ester[a]	16.1
Unirez 7003 maleic resin[b]	17.4
DOP[c]	4.0
toluene	35.3
isopropyl alcohol	14.0
acetone	4.5
xylene	7.7
SF-69[d]	1.0
Total	*100.0*

[a] CAB = cellulose acetate butyrate.

[b] Union Camp Corp.

[c] DOP = dioctyl phthalate.

[d] Slip aid; 1% xylene (General Electric Co.)

and metal-flake control before applications of the clear topcoat (164,165). Such coatings provide good appearance and excellent resistance to weathering and are expected to find broad use in automotive decorative coatings.

Because of certain properties, such as a high melting point, high tolerance for alcohol solvents, low odor, and excellent surface hardness, cellulose acetate propionates are used in printing inks (flexographic and gravure) (166) (Table 14). Alcohol-soluble cellulose acetate propionate ester tolerates substantial quantities of water in the solvent blend and thus provides an environmentally desirable system for flexographic ink coatings (167).

Acetate propionate esters are nontoxic, exhibit excellent clarity and high tensile strength, and can be formulated into hot-melt dip coatings for food (168). Alternatively, they may be dissolved in volatile solvents and applied to foods in the form of a lacquer coating (169).

Desalination membranes with improved, rigid, and stable surfaces have been prepared from cellulose acetate propionate (170). These films are generally more resistant to hydrolysis than those from cellulose acetate.

Table 14. **Flexographic Ink Formulation Containing Alcohol-Soluble Cellulose Acetate Propionate**

Components	Wt %
cellulose acetate propionate[a]	6.1
sucrose acetate isobutryate (SAIB)	1.5
Kodaflex DOP plasticizer[b]	4.1
Uni-Rez 710 maleic resin[c]	8.2
pigment	5.1
isopropyl alcohol, 99%[a]	56.3
water	18.7
Total	*100.0*

[a] Alcohol-soluble propionate (ASP) CAP 504-0.2.

[b] DOP = dioctyl phthalate (Eastman Kodak Co.)

[c] Union Camp Corp.

Cellulose esters, especially acetate propionate and acetate butyrate mixed esters, have found limited use in a wide variety of specialty applications such as in nonfogging optical sheeting (171), low profile additives to improve the surface characteristics of sheet-molding (SMC) compounds and bulk-molding (BMC) compounds (172,173), and controlled drug release via encapsulation (174).

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