Li^+, and K^+ forms of Decalso and Dowex 50-x16—indicates qualitatively that the lithium ions contain less coordinated water in Decalso than in Dowex 50-x16. If the magnitude of the separation factor is dependent upon the differences in the degree of hydration of the lithium ion species in the two phases, which was the assumed model for the quantum mechanical estimation of α previously proposed (*8*), the higher value of 1.0047 for Decalso is reasonable.

The separation factor for lithium isotopes separated on zirconium phosphate was determined to be 1.0016. This value is not very different from the majority of the values found for other exchangers, but it does not compare with the value reported by Merz (*4, 9*). The conditions of the two experiments were considerably different. Perhaps the large difference in flow rates is the chief factor contributing to the discrepancy. Since the rate of exchange between lithium ions on zirconium phosphate and lithium ions in solution is slow (*1*), a fast flow rate could eliminate any isotopic separation. A difference in the procedures for preparing the zirconium phosphate could possibly produce precipitates that have divergent ion exchange properties toward lithium isotopes.

Very little is known about the structural homogeneity and ion exchange properties of the phosphonous and phosphonic acid resins. Therefore, it is difficult to explain the separation factors measured on these resins. Phosphonic acid resins have bifunctional groups. For the separation of lithium isotopes on Dowex Chelating Resin A-1, which has bifunctional groups, the separation factor was also an order of magnitude smaller than the factors determined for monofunctional exchangers (*6*). Whether this is characteristic of bifunctional groups is unknown. The separation factor on phosphonous acid resin was considerably larger than the factor for phosphonic acid resin, but much smaller than those found for other monofunctional exchangers. The only conclusion that can be made for the experiments performed on the Bio-Rex resins is that since the separation factors are small, the lithium ion species in the resin phase, more than likely, are not dehydrated in the primary hydration sphere.

SUMMARY

Carboxylic acid resins and inorganic exchangers produce separation factors for lithium isotopes which are comparable to the factors observed for sulfonic acid resins. However, column efficiencies are not as good as those for sulfonic acid resins. The separation factors on phosphonous and phosphonic acid resins are an order of magnitude smaller than the factors for other exchangers. It is postulated that the degree of hydration of the lithium ion in the resin phase will determine the magnitude of the separation factor, and any mechanism that will dehydrate that ion will increase the factor.

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Properties and Potential Uses of Sodium Cellulose Acetate Sulfate, A New Water-Soluble Cellulose Derivative

GEORGE P. TOUEY
Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

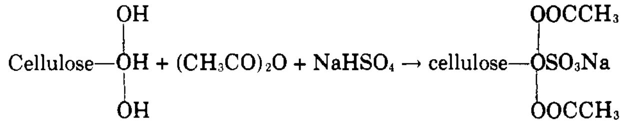
WILLIAM M. GEARHART
Eastman Chemical Products, Inc., Subsidiary of Eastman Kodak Co., Kingsport, Tenn.

WATER-SOLUBLE cellulose esters have been known for many years; however, in contrast to water-soluble cellulose ethers, the esters seem to have attracted little or no commercial interest.

This article describes a new type of water-soluble cellulose ester which has commercial potentialities. This derivative is a sodium cellulose acetate sulfate, conveniently referred to as SCAS.

The sulfation of cellulose to produce a water-soluble derivative is by no means a new reaction. In 1894, Stern (*8*) prepared a cellulose disulfate simply by dissolving cellulose in cold sulfuric acid. In 1928, Fulnegg (*3*) prepared a less-degraded product by allowing cellulose to react with chlorosulfonic acid dissolved in pyridine. During the past 10 years, several new methods for sulfating cellulose without degrading it excessively have been patented. Most of these patents (*4–7*) suggest alcohols and other sulfuric acid–miscible organic solvents as diluents for the reactants. Recently, at Eastman Kodak Co., a method (*1, 2*) was found for simultaneously sulfating and acetylating cellulose.

This reaction is given by the equation:



$$\text{Cellulose}\!-\!\underset{\text{OH}}{\overset{\text{OH}}{\text{OH}}} + (CH_3CO)_2O + NaHSO_4 \rightarrow \text{cellulose}\!-\!\underset{\text{OOCCH}_3}{\overset{\text{OOCCH}_3}{\text{OSO}_3\text{Na}}}$$

The method consists of treating cellulose with a solution of sodium sulfate and acetic anhydride in acetic acid. The products described in the article were prepared, with some modifications, according to this procedure.

PROPERTIES

General. SCAS is a neutral, white, granular, free-flowing powder containing a small amount of urea as a heat stabilizer; normally, its moisture content is 8 to 10%.

As shown in Table I, three viscosity types of the product have been evaluated. All are highly esterified, mixed esters containing both acetyl and sodium sulfo groups. They are soluble in hot or cold water and in water-miscible organic solvents containing as little as 10% of water; however, they are insoluble in organic solvents alone.

Table I. Viscosity Type of SCAS as a Function of Intrinsic Viscosity and Degree of Sulfation

	Sulfation, Amount		Acetylation, Amount			
Viscosity Type	Av. S, %	Av. D.S.[a] (sulfo)	Av. acetyl, %	Av. D.S.[a]	Av. [η]	Soln. Viscosity, Cp.[b]
High	6.6	0.6	25.6	1.8	2.0	5000-10,000
Medium	7.7	0.75	23.4	1.7	1.7	200-1,000
Low	9.2	0.9	20.9	1.6	1.5	50-100

[a] D.S. = degree of substitution.

[b] 2% solution at 25° C.; measured with Brookfield viscometer, Model RVT, using a speed of 5 r.p.m. and the appropriate spindle for this speed.

The solution viscosity of SCAS depends upon its intrinsic viscosity and the degree of substitution by sulfo groups (Table I). The high-viscosity sample has an intrinsic viscosity of 2.0 and a sulfur content of 6.6%. This amount of sulfur represents an average degree of substitution (D.S.) of 0.6 sulfo group for each anhydroglucose unit of the polymer. In contrast, the low-viscosity sample has an intrinsic viscosity of 1.5 and a sulfur content of 9.2% (D.S. of 0.9 sulfo group). The acetyl content of the samples decreases slightly as the sulfur content increases. The sample containing the highest sulfo content has an acetyl content of 20.9% (D.S. of 1.6); the one containing the lowest sulfo content has an acetyl content of 25.6% (D.S. of 1.8).

Stability to Heat and Storage. The three types of SCAS are stable to heat and storage. They did not discolor when heated in air for 5 hours at 150° C. Storage of products at 75° C. for 5 days did not affect their solution viscosities appreciably. They have exhibited no degradation after storage for over 2 years at room temperature.

Aqueous solutions of the three types of SCAS are stable to heat. The heat stability of a 2% solution of the medium-viscosity ester is shown in Figure 1. This solution was heated at 75° C. for 7 days. Aliquots were removed periodically and cooled to 25° C., and their viscosities were measured with a Brookfield viscometer. After 48 hours at 75° C., the viscosity of the solution was reduced by 20%; after 7 days, by about 50%. The other two types exhibited a similar viscosity decrease when tested in this manner.

Effect of Concentration and Heat on Solution Viscosity. As with other water-soluble cellulose derivatives, the viscosity of an SCAS solution depends upon its concentration. A 1% solution of the high-viscosity ester had a viscosity of 90 cp. (Brookfield viscometer), while a 2% solution had a viscosity of 9000 cp. (Figure 2). In contrast, an 8% solution of the low-viscosity ester was needed to obtain a viscosity of 9000 cp. In general, the high- and medium-viscosity esters gave thixotropic solutions, whereas the low-viscosity ester did not.

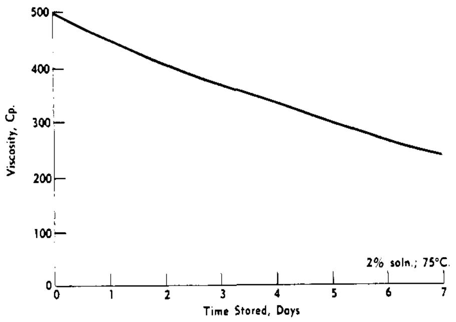


Figure 1. Stability of aqueous solutions of SCAS to heat

Figure 3 shows the effect of heat on the viscosity (Brookfield viscometer) of an aqueous solution of SCAS. The solution viscosities of the high- and medium-viscosity esters decreased over 80% when the temperature was raised from 23° to 50° C. The viscosity of the low-viscosity ester decreased 50% for this same temperature rise.

Effect of pH on Solution Viscosity. SCAS is not precipitated from solution by the addition of acids or bases. However, when solutions are made strongly acidic or basic their

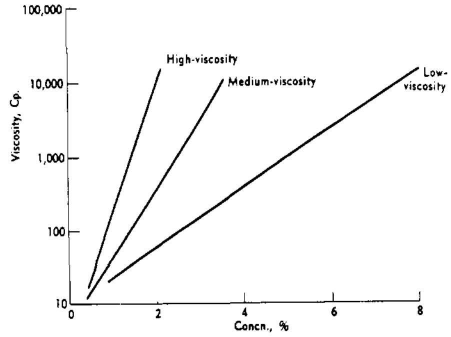


Figure 2. Effect of concentration on viscosity of aqueous solutions of SCAS

Samples were those described in Table I

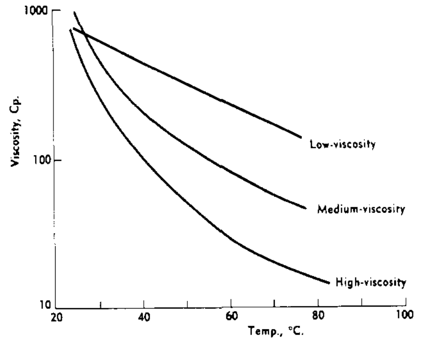


Figure 3. Effect of temperature on viscosity of aqueous solutions of SCAS

Samples were those described in Table I
Low-viscosity 5% concn.
Medium-viscosity 2% concn.
High-viscosity 1.5% concn.

Table II. Viscosity of an Aqueous Solution[a] of SCAS as a Function of pH

Immediate Effect		After 1 Week at 25° C.	
pH	Viscosity, cp.	pH	Viscosity, cp.
1.0	775	1.0	45
2.0	785	2.0	300
3.2	805	3.2	725
6.5	820	6.5	780
8.3	830	6.9	725
10.0	760	6.7	590
11.0	200	10.8	100

[a] 2.3% concn.; medium-viscosity SCAS.

viscosities decrease either immediately or upon storage. A 2.3% solution of the medium-viscosity ester was prepared and divided into a number of equal portions. Increasing amounts of concentrated hydrochloric acid were added to some of these solutions and increasing amounts of concentrated sodium hydroxide were added to others. Then the viscosity and pH of the solutions were recorded. After the solutions were stored for 1 week at 25° C. these properties were remeasured (Table II). Addition of acid had little immediate effect on the viscosities of solutions. However, those with a pH less than 3 exhibited an appreciable reduction in viscosity on storage. Solutions to which a small amount of alkali was added showed no marked change in viscosity. This was partly due to saponification of acetyl groups, with a resultant shift in pH back to the neutral point. However, the solution which was made strongly basic had a three fourths reduction in viscosity immediately and it underwent a further decrease on storage.

Table III. Compatibility of Aqueous Solutions of SCAS with Solutions of Metallic Salts[a]

	Appearance of Mixture	
Salt	Immediate observation	After 1 week at 25° C.
Sodium chloride	Compatible	No change
Manganese sulfate	Compatible	No change
Calcium chloride	Compatible	No change
Barium chloride	Slight precipitate	. . .
Zinc chloride	Compatible	No change
Cupric nitrate	Compatible	No change
Nickel acetate	Compatible	No change
Ferric sulfate	Compatible	No change
Basic aluminum acetate	Compatible	Hazy
Zirconium acetate	Heavy precipitate	. . .

[a] 5% solutions of SCAS and metallic salts used.

Compatibility with Salt Solutions. Unlike solutions of carboxy-containing polymers, those of SCAS are compatible with solutions of many metallic salts (Table III). Portions of a 5% aqueous solution of the low-viscosity ester were mixed with equal portions of various salt solutions. The mixtures were rated for compatibility immediately after they were prepared and after standing for 1 week. With the exception of the barium salt, which produced a slight precipitate due to the presence of some sodium sulfate, salts of monovalent and divalent metals were compatible with the ester solution. Salts of aluminum and trivalent iron also were compatible, although the aluminum salt produced a slight haze after 1 week. The zirconium salt produced a heavy precipitate. Solutions of the high-viscosity ester also did not give precipitates with most of these salt solutions. However, gelation occurred when excessive amounts of dissolved salts were present.

Compatibility with Other Water-Soluble Polymers. Table IV illustrates the compatibility of SCAS with other water-soluble polymers. Equal portions of a 5% solution of the low-viscosity ester and a 5% solution of the polymer were mixed and allowed to stand for 24 hours. After being rated for compatibility, the mixtures were cast into films. In solution, all of the polymers tested were compatible with SCAS. However, as films, two cases of slight incompatibility were observed: sodium carboxymethylcellulose and poly(vinyl alcohol).

Table V. Effect of Plasticizer Content on Elongation, Flexibility, and Tensile Strength of SCAS Films[a]

Glycerol Content, %	Tensile Strength, P.S.I.	Elongation at Break, %	Flexibility, M.I.T., Double Folds
0	8900	8	25
15	5100	19	60
20	3800	27	73
25	3200	36	100
30	2400	47	150

[a] Low viscosity-type SCAS; film thickness 5 mils; 73° F., 45% relative humidity.

Film Properties. Clear, flexible, oilproof films of SCAS can be prepared from solutions in water or in organic solvent-water mixtures. Table V shows some properties of glycerol plasticized and unplasticized films of the low-viscosity ester. Plasticized films had lower tensile strengths, but better elongations and flexibilities. Addition of a plasticizer also makes the films heat-sealable at 120° C. or above.

Table IV. Compatibility of SCAS with Other Water-Soluble Polymers[a]

Polymer			Appearance	
Material	Designation	Source	Solution	Film
Methylcellulose	Low viscosity, 25 cps. at 2%	Dow Chemical Co.	Clear	Clear
Hydroxyethylcellulose	Cellosize, WP-09, low viscosity	Union Carbide Chemicals Co.	Clear	Clear
Gelatin	Cat. No. 1099, pract. grade	Distillation Products Industries	Clear	Clear
Guar gum[b]	Jaguar A-20-D	Stein, Hall, and Co.	Clear	Clear
Poly(vinylpyrrolidinone)	NPK-30	Antara Chemical Co.	Clear	Clear
Dextrin	Cat. No. 1297, Eastman grade	Distillation Products Industries	Clear	Clear
Sodium carboxymethylcellulose	Low viscosity	Hercules Powder Co.	Clear	Slight haze
Poly(ethylene glycol)	Polyox, WSR-205	Union Carbide Chemicals Co.	Clear	Clear
Poly(vinyl acetate), 88% hydrolyzed	Elvanol 51-05	Du Pont	Clear	Clear
Poly(vinyl alcohol)	Elvanol 70-05	Du Pont	Clear	Slight haze

[a] 5% solution of polymer and SCAS used.

[b] 2% concentration.

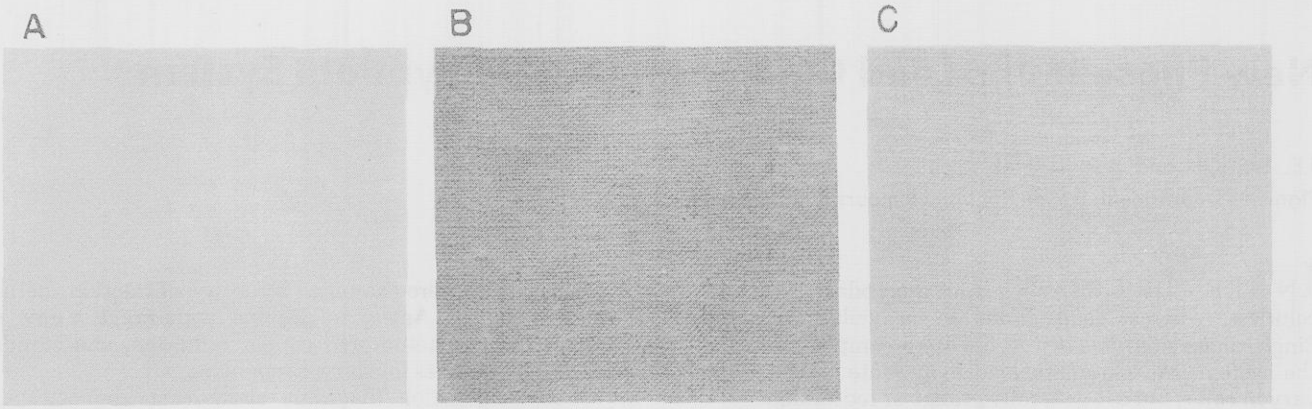


Figure 4. Effectiveness of SCAS in preventing soil deposition during laundering of cotton fabrics

A. Unwashed control, light reflectance 87%
B. Washed in detergent-soil solution, light reflectance 35%
C. Washed in detergent-soil solution containing SCAS, light reflectance 70%

APPLICATIONS

Based on Thickening, Suspending, and Emulsion-Stabilizing Properties. Like the commercial water-soluble cellulose ethers, this new cellulose ester has pronounced thickening, suspending, and emulsion-stabilizing characteristics. Water paints were produced simply by suspending powdered pigments, such as Cadmium Red or zinc oxide, in a 6% solution of the low-viscosity ester. A latex paint was formed by diluting a 45% emulsion of poly(vinyl acetate) with a 2% solution of the high-viscosity ester and adding a pigment. Liquid cleansing creams, hand lotions, and other cosmetics were prepared by using published formulations and substituting SCAS for the designated thickening agent. Stable olive oil emulsions were formed by rapidly mixing the oil with a 2% solution of the medium-viscosity ester containing a surface active agent. An emulsion polymerization of vinyl acetate was carried out by using a small amount of the low-viscosity ester to disperse monomer in water during the polymerization step.

Based on Film-Forming and Bonding Properties. Extensive studies revealed that the low-viscosity ester is a warp size for cellulose acetate yarn. It adheres strongly to filaments, protecting them from abrasion during weaving. In addition, it is soluble in hot or cold water, somewhat mold-resistant, and possesses a low biochemical oxygen demand. This latter property is desirable from the standpoint of reduced stream pollution.

Paper coated with a film of SCAS was highly resistant to penetration of a number of oils and greases. Such a coating, therefore, should be of value in producing grease- and oilproof containers or in controlling penetration of printing ink on paper.

Water-soluble unit packages for powders of detergents, dyes, and bleaches were prepared by heat-sealing the edges of plasticized SCAS films. These films were prepared from solutions in either water or mixtures of organic solvents and water.

SCAS is a good adhesive for paper. The low-viscosity ester can be used alone for this purpose, or the high-viscosity ester can function as a thickener for aqueous solutions of cheaper glues.

Examples of both suspending and bonding properties of the ester are illustrated in its potential use as a sticking agent in insecticide sprays and as a dye-dispersion stabilizer in textile printing pastes.

Miscellaneous Uses. SCAS has shown promise in uses which are not directly related to its thickening, suspending, bonding, and film-forming properties.

The water-retaining qualities of the product suggest its utility as an additive for oil well driling muds or oil well cements. In these applications it should function like other water-soluble polymers now being used to prevent water loss from mud or cement on contact with clay formations.

The medium-viscosity ester is a creaming agent for natural rubber latex. When 0.3% of the ester, based on the rubber content, was dissolved in a latex of 30% solids, two layers formed. The top layer contained the rubber, whereas the bottom layer was mostly water. Concentrating latex in this manner would enable a manufacturer to reduce shipping costs.

SCAS has also given indications of being an effective detergent additive for preventing soil redeposition during the laundering of cotton fabrics. This was illustrated by using a modification of a "whiteness retention" test (9) often used for the initial evaluation of a water-soluble polymer for this purpose (Figure 4). A clean swatch of cotton cloth was washed in a solution containing a detergent, a builder, and colloidally suspended carbon. Another clean swatch was washed in another equal portion of this solution to which 3% of SCAS (based on the weight of detergent and builder) had been added. The two solutions were placed in a Launder-Ometer and shaken for 30 minutes at 140° F. After the swatches had been rinsed and dried, their light reflectance values were obtained. The swatch on the left is an unwashed control. The one in the center was washed in the solution containing no detergent additive, whereas the one on the right was washed in the solution containing SCAS. The effectiveness of SCAS in preventing the carbon soil from depositing on the cloth is clearly shown. Similar results were obtained with several other detergent formulations with and without SCAS.

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