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NEW CELLULOSE SULFATE DERIVATIVES AND APPLICATIONS*†

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ABSTRACT

The preparation of water-soluble cellulose sulfates having a degree of substitution (d.s.) of ~0.3–2.0 by a homogeneous method is reported. Instead of sulfating cellulose directly, a reactive intermediate, namely, cellulose nitrite, was used, thereby permitting sulfation to proceed under homogeneous conditions. Products obtainable via the homogeneous method differ substantially from those prepared via the heterogeneous method used at present for the production of water-soluble cellulose derivatives. Principal chemical differences are the uniform distribution of the substituents, the exceptionally high molecular weight of the sulfate esters, and in the location of the substituents on the glucosyl residues. The differences result in a number of chemical and physical properties that are unique and not exhibited by other cellulose derivatives. Performance in application areas, such as oil recovery, paints, paper, textiles, cosmetics, and the like, is indicated by these properties.

INTRODUCTION

All present methods of derivatizing cellulose are heterogeneous, that is, cellulose is substituted in the reaction medium as an insoluble, fibrous material. The fiber surface is generally exposed more readily to the reagent than the inner portion of the fiber, and, therefore, a substantially non-uniform distribution of the substituents over the macromolecule is typical of this method[1]. Products having low degrees of substitution are usually incompletely soluble; thus, aqueous dispersions contain significant amounts of transparent, highly swollen but insoluble particles. To approach complete solubility, the d.s. must be relatively high, particularly for celluloses having a high degree of polymerization (d.p.). Certain heterogeneous methods result in the production of mixtures of high-d.s. products and essentially unreacted cellulose, as the partially substituted fiber surface may become soluble in the reaction medium and peel off, then being further substituted[2] to a high d.s. Substitution under homogeneous conditions, where the cellulosic starting material is in a solubilized state prior

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to substitution, would be much preferred, and none of the disadvantages mentioned here would then be expected.

RESULTS AND DISCUSSION

The first, and at present, the only homogeneous method for making cellulose derivatives is the one used for preparing the cellulose sulfate products of this article. The reaction path has been shown and details have been reported previously[3,4].

The first step consists of nitrosation of the cellulose to form cellulose nitrite, a new cellulose ester that, owing to the lability of the nitrite groups, can be used as a chemical intermediate in transesterification reactions. The cellulose nitrite is solvated in the reaction medium, and consequently, the subsequent exchange of nitrite groups proceeds homogeneously. Up to about two nitrite groups per residue may be replaced by half-ester sulfate groups by employing an *N*,*N*-dimethylformamide–sulfur trioxide complex to form a mixed cellulose nitrite sulfate ester. Residual nitrite groups are removed by hydrolysis or alcoholysis, and the cellulose-sulfuric acid ester is neutralized with a base, usually sodium carbonate, to form sodium cellulose sulfate.

The homogeneous method affords products that are chemically different from those obtainable by heterogeneous methods in the following respects:

(*a*) The substituents are uniformly distributed, that is, a d.s. of 1 indicates essentially glucose monosulfate and a d.s. of 2 glucose disulfate residues. In contrast, the d.s. of a product obtained by a heterogeneous method refers to an average in which the d.s. of the individual residues usually lies between 0 and 3. Additionally, the average d.s. of the individual polymer molecules probably varies also.

(*b*) It has been shown previously that nitrosation proceeds without degradation[5]. The subsequent sulfation of cellulose nitrite is an ester exchange that produces relatively little heat of reaction, and the starting material is a fully substituted cellulose derivative that remains fully substituted until neutralization. Therefore, little or negligible degradation is expected, and the resulting products have exceptionally high molecular weights. Direct sulfations of hydroxyl groups are usually accompanied by severe degradation[6].

(*c*) It has been published previously that, in cellulose, the most reactive hydroxyl groups are those at C-2 and C-6, which probably have similar reactivities whereas the C-3 hydroxyl group is the least reactive[7]. If one of the two ring hydroxyl groups is substituted, the reactivity of the other ring hydroxyl group is substantially decreased, particularly if the substituents have strong charges. Therefore, in cellulose derivatives, most of the substituents are at C-2 and C-6 and few at C-3. However, in the case of an ester exchange, that is in the removal of substituents and replacement by other groups, introduction of the new groups should proceed in the reverse order because substitution of the least reactive hydroxyl groups should produce substituents having the least stability. Considering then the effect on substitution at C-6, the net result would be (*i*) little or no substitution at C-6 in homogeneous reactions via intermediates of d.s. up to close to 1 and particularly at d.s. $\leqslant 1$, (*ii*) substantial

TABLE I

SUBSTITUTION AT C-6 AS DETERMINED BY PERIODATE OXIDATION

Product	*D.s.*	*Substitution at C-6 (% of total)*
Cellulose sulfate	0.45	0
Cellulose sulfate	0.73	13
Cellulose sulfate	0.95	14.4
Cellulose sulfate	1.05	17.8
O-(Carboxymethyl)cellulose	0.7	34.3
O-(Carboxymethyl)cellulose	0.9	40

substitution at C-6 in heterogeneous reactions via direct substitution of hydroxyl groups.

Table I shows the results of periodate oxidations of cellulose sulfates prepared via the nitrite and of *O*-(carboxymethyl)celluloses having various d.s. values. Periodate oxidation proceeds only if both the C-2 and C-3 hydroxyl groups are free, and from the d.s. and the degree of oxidation, the percentage of substitution at C-6 may be calculated. The data agree remarkably well with the considerations already made: in cellulose sulfate via nitrite, essentially no substitution at C-6 if the d.s. $\ll 1$ and relatively little substitution at C-6 if the d.s. approaches 1; in *O*-(carboxymethyl)-cellulose, substantial substitution at C-6 at d.s. values up to 1. The sodium cellulose sulfate having d.s. 0.95 was also analyzed by ^{13}C-n.m.r. spectroscopy. Similarly, the spectrum indicated a high percentage of free hydroxyl groups at C-6 and a minor percentage of 6-sulfate. A very rough estimate indicated ~19–20% of the sulfate groups at C-6, which correlates relatively well with the results from periodate oxidation.

As a result of these chemical differences, a number of the properties exhibited by cellulose sulfate obtained via nitrite ester are unique and are not exhibited by other cellulose derivatives. Discussed next are important chemical and physical properties that greatly determine the suitability of the products in various major application areas, namely:

TABLE II

VISCOSITY AND DEGREE OF PSEUDOPLASTICITY OF 1% SOLUTIONS OF CELLULOSE SULFATE

Degree of substitution	*Viscosity, centipoises (60 r.p.m.)*	*Viscosity at 6 r.p.m./ viscosity at 60 r.p.m.*
0.3–0.5	5000–7000	~3–3.8
0.6–0.9	2500–4000	~2.2–2.8
1.0–1.3	1500–2500	~1.7–2.2
1.4–1.6	800–1500	~1.2–1.7

(*a*) Products having a d.s. of above about 0.2–0.3 exhibit true solubility in water. If sufficiently diluted to avoid high viscosities, their solutions may be readily filtered through tight filter-paper without plugging and without the formation of an insoluble, gelatinous residue on the filter. Complete solubility at such a low d.s. is expected only if the distribution of the substituents is essentially uniform. A substantial degree of nonuniformity would result in a relatively large number of consecutive, nonsubstituted residues, which would probably retain enough hydrogen-bonding activity to render the product at least partially insoluble.

(*b*) Viscosities of 1% solutions are exceptionally high, as shown in Table II. This arises as a direct result of the high molecular weight of the products, indicating that essentially no depolymerization had occurred. The increase in viscosity on reducing the shear rate from 60 to 6 r.p.m. indicates pseudoplasticity, and the degree of pseudoplasticity increases greatly as the d.s. decreases.

(*c*) The compatibility with metal ions is outstanding, as shown in Table III and exceeds even that of neutral gums, such as *O*-(2-hydroxyethyl)cellulose (HEC) or guaran. Products having d.s. $\lesssim 1.3$ are compatible with all mono-, di-, and tri-valent metal ions tested, even at high concentrations of salt. Only products having an extremely low d.s. approaching ~0.3–0.4 can be salted out, but they still tolerate up to 5–10% of monovalent, and higher concentrations of polyvalent, metal salts. Products having d.s. $\gtrsim 1.3$ show incompatibility only with Ba^{2+}, Fe^{3+}, and Ce^{3+} ions, but may be saturated with salts of many other metals. One of the reasons for the unusual compatibility may be the uniformity of substitution, as it is known that highly substituted cellulose sulfate in which most residues are fully substituted[2] shows little compatibility, and that products having very low d.s. and a relatively large number of consecutive, unsubstituted residues are salted out relatively readily. A low-to-medium-d.s. product obtained by a heterogeneous reaction usually has significant proportions of nonsubstituted as well as highly substituted residues, both of which factors decrease compatability with metal ions. The major reason, however, may well be the fact that the substituents engage different hydroxyl groups. Precipi-

TABLE III

COMPATIBILITY WITH METAL SALTS

Metal ion	*Sodium cellulose sulfate*	
	D.s. $\lesssim$ *1.3*	*D.s.* $\gtrsim$ *1.3*
Na^+, K^+, NH_4^+	+	+
Mg^{2+}, Ca^{2+}, Sr^{2+}	+	+
Ba^{2+}	+	—
Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}	+	+
Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}	+	+
Al^{3+}	+	+
Ce^{3+}	+	—
Fe^{3+}	+	—

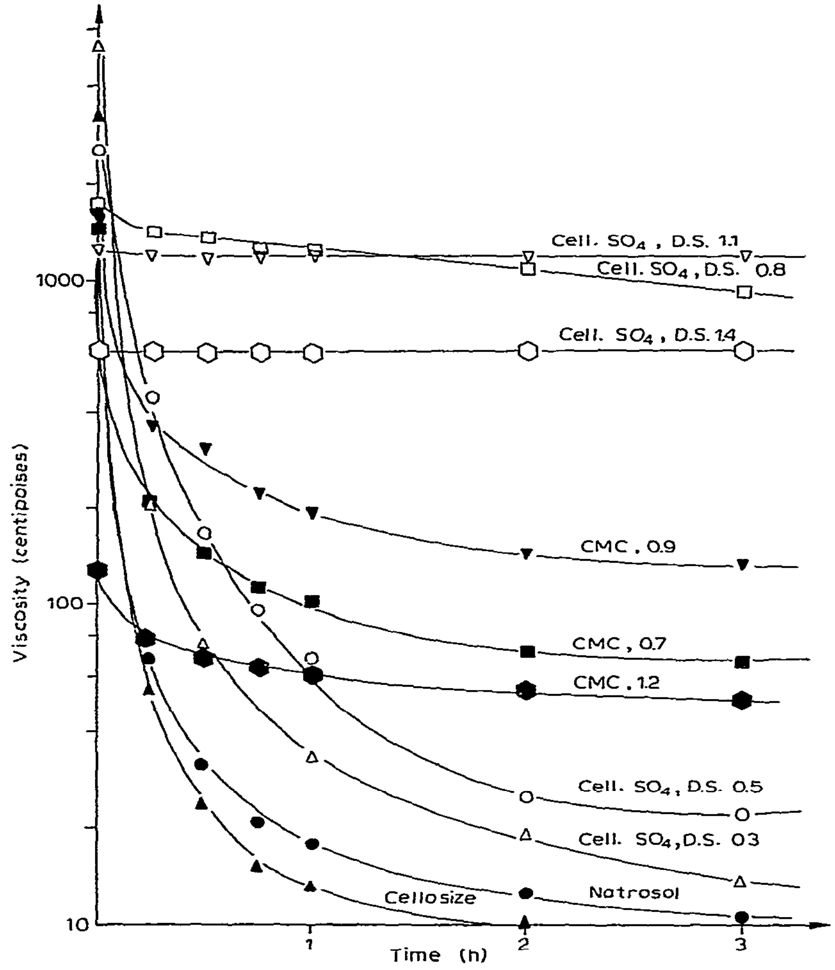

Fig. 1. Effect of cellulase on viscosity of 1 % solutions of cellulose gums.

tation of polysaccharides with polyvalent metal ions often arises as a result of chelate formation with the hydroxyl groups of polymer units in another chain[8]. Assuming that there exists a similar mechanism for the cellulose sulfates, a change in the availability of specific hydroxyl groups would definitely influence chelate formation with metal ions and the precipitation induced by such chelation.

(*d*) Sodium cellulose sulfates having d.s. $\gtrsim 1$ are resistant to enzyme attack, and their solutions suffer no viscosity decrease in the presence of cellulase. Fig. 1 shows that products having d.s. ~ 1.1 and ~ 1.4 retain their viscosity, that there is a moderate decrease of viscosity for a product having a d.s. of 0.8–0.9, and that the viscosity losses become increasingly greater as the d.s. is further decreased. Other cellulose derivatives, such as HEC and *O*-(carboxymethyl)cellulose (CMC), depolymerize relatively fast, HEC being the most vulnerable and CMC becoming somewhat more

TABLE IV

SHEAR STABILITY (0.5% POLYMER SOLUTION WITH 0.5% SODIUM CHLORIDE)

Shearing time (min)	*Viscosity decrease (%)*					
	Cellulose sulfate					*HEC (Natrosol) (250 H)*
	D.s., 0.3	*D.s., 0.5*	*D.s., 0.8*	*D.s., 1.1*	*D.s., 1.5*	
1	13.3	5.8	11.0	9.0	13.2	13.6
5	23.3	20.4	18.8	23.0	24.5	43.8
15	34.0	23.4	34.0	33.0	37.7	58.6
	HEC (Cellosize) (100 M)	*Xanthan (Keltrol)*	*CMC 7H4F*	*Poly(acrylamide) (Pusher 700)*		
1	18.9	23.2	38.8	37.8		
5	35.8	26.4	51.4	71.3		
15	70.0	28.0	62.8	83.5		

resistant as the d.s. increases. It appears that, for complete enzyme resistance, each residue must have at least one sulfate group. This coincides with a d.s. of 1 only if the product is prepared under homogeneous conditions, and a considerably higher d.s. is probably required for similar products obtained under heterogeneous conditions.

(*e*) It was found that cellulose sulfate is significantly more shear resistant, that is, it depolymerizes to a much lesser extent under mechanical stress than other cellulose derivatives and most other gums. Table IV shows viscosity decreases of cellulose sulfates with various d.s. in comparison with a number of other hydrocolloids examined after various periods of shearing. It is remarkable that, after 15 min of mixing in a Waring Blendor at high speed, cellulose sulfate loses only about 30–35% of its viscosity, whereas the viscosity loss for such other cellulose derivatives as HEC and CMC is about twice that. It is unlikely that the substituent would have a substantial influence on the resistance of the cellulose chain to mechanical stress. However, it is conceivable that the homogeneity of substitution, and equal distribution of the weight over the polymer chain, may be responsible.

(*f*) The high temperature-stability of aqueous solutions appears to be excellent, as shown in Fig. 2 by the viscosity decreases observed on heating at 100°. In the presence of an oxygen scavenger to preclude oxidative depolymerization, the viscosity loss after 24 h at 100° is only about 25–50%, depending somewhat on the d.s. Most polysaccharides depolymerize more rapidly under these conditions.

(*g*) The stabilization of suspensions of titanium dioxide by cellulose sulfate is shown in Table V. All suspensions containing cellulose sulfate were quite stable and no separation at all was observed up to about 30 h and very little after storage for several weeks. Similar results were obtained with barium sulfate. In contrast, HEC

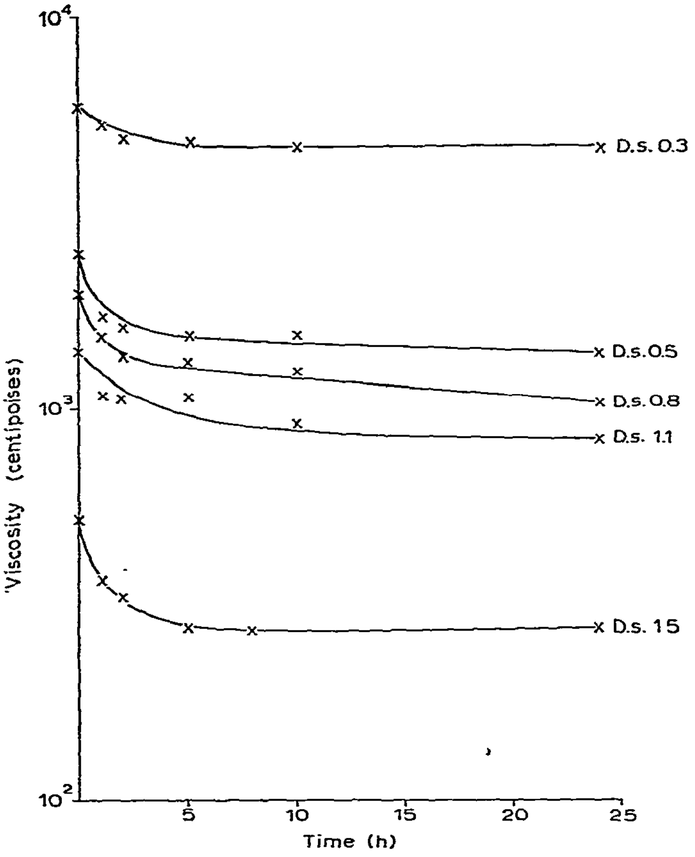

Fig. 2. High-temperature stability at 100°.

TABLE V

STABILITY OF TITANIUM DIOXIDE SUSPENSIONS IN THE PRESENCE OF HYDROCOLLOID (0.5%)

Polymer	*Separation of TiO_2, %, after (h)*				
	3	*20*	*60*	*150*	*300*
Cell. SO_4, d.s. 0.3	0	0	0	0	0
Cell. SO_4, d.s. 0.5	0	0	0	0	2
Cell. SO_4, d.s. 0.8	0	0	0	0	0
Cell. SO_4, d.s. 1.1	0	0	0	0	0
Cell. SO_4, d.s. 1.5	0	0	0	0	0
HEC (Natrosol 250 H)	2	24	48	70	80
HEC (Cellosize 100M)	0	7	18	36	65

TABLE VI

TOLERANCE OF ORGANIC SOLVENTS

Solvent	*Volume of solvent tolerated*			
	D.s., 0.3	*D.s., 0.7*	*D.s., 1.1*	*D.s., 1.5*
Methanol	<4	>4	>4	>4
Ethanol	<1.2	1.6	2–2.2	1.2
2-Propanol	<1.2	1.2–1.4	1.2	1–1.2
Acetone	<2	2.4	2.6–2.8	2.2–2.4
Glycerol	<10	10	sol.	sol.
Ethylene glycol	sol.	sol.	sol.	sol.

showed signs of separation within the first few h and essentially complete separation after a few days. As a number of the sulfate esters used had viscosities lower than the HEC, this stability effect is obviously not the result of the high viscosity but, more likely, of the high negative charge of the substituents.

(*h*) All cellulose sulfate esters, irrespective of d.s., form strong and clear films similar to those obtainable from other cellulose derivatives. These films may be crosslinked and readily insolubilized easily with such common crosslinking agents as melamine–formaldehyde, glyoxal, and the like. The reason is obviously the availability of the reactive C-6 and C-2 hydroxyl groups, in contrast to all other cellulose derivatives obtained by heterogeneous methods.

(*j*) The cellulose sulfates are protein-reactive, that is, they associate with protein by the formation of ionic bonds between the negative sulfate groups and the positive sites in the protein, resulting in crosslinkage. This reaction is indicated by a significant increase in viscosity when cellulose sulfate and protein solutions are combined. Data reported previously^4 show viscosities of solutions containing both 0.5% cellulose sulfate and 5% sodium caseinate in comparison with solutions containing 0.5% cellulose sulfate only. Solutions containing both cellulose sulfate and caseinate have substantially higher viscosities than the corresponding controls containing cellulose sulfate only. The viscosity of a 5% caseinate solution is about 5 centipoises and does not contribute significantly to any viscosity increase unless there is an interaction with the cellulose sulfate. Similar results were obtained when, instead of caseinate, soy-protein isolate was used. In the case of gelatin, a substantially higher gel strength was measured when relatively small amounts of cellulose sulfate were present. As expected, the protein reactivity increases with increasing d.s., obviously because more sulfate groups become available for crosslinkage.

(*k*) Aqueous solutions of cellulose sulfate tolerate high concentrations of water-miscible, organic solvents. Table VI shows the approximate number of volumes of organic solvent that may be added to a 1% solution without separation of the polymer. The products dissolve in ethylene glycol at all d.s. levels and in glycerol at d.s. $\gtrsim 1$. It is remarkable that the tolerance of organic solvents is relatively high, particularly at a d.s. near 1. This appears to be the result of the uniformity of substitution, as

TABLE VII

RELATIONSHIP BETWEEN CERTAIN PROPERTIES AND APPLICATIONS

	Viscosity	*Pseudoplasticity and yield point*	*Solubility*	*Compatibility*	*Enzyme resistance*	*Shear resistance*	*Temperature stability*	*Suspension stability*	*Film formation*	*Crosslinking film*	*Crosslinking solution*	*Protein reactivity*	*Solvent tolerance*
Tertiary oil-recovery	+		+	+		+							
Oil-well drilling	+	+		+		+	+	+			+		
Paints		+	+		+			+					
Paper			+	+				+	+	+		+	
Textiles	+							+	+	+			
Explosives	+			+							+		
Photography	+		+	+				+				+	
Cosmetics	+		+					+				+	+
Toothpaste	+				+			+					
Food	+	+	+	+			+	+				+	

highly substituted residues, as well as a large number of consecutive, unsubstituted residues obviously decrease solvent tolerance of the polymer.

The properties indicated here suggest a variety of uses, and Table VII shows the principal relationships between the properties discussed and a number of application areas.

One application that is immediately suggested is use as a thickener in tertiary oil-recovery. Properties required are high viscosity to permit the use of low concentrations of polymer, complete solubility and filtrability to avoid plugging of the formations, and shear resistance to avoid significant viscosity-losses during injection of the polymer solution. Plugging of the reservoir has, of course, serious consequences, and the suitability of a polymer as regards injectivity is usually tested by passing the polymer solution through fine Millipore filters and determining the decrease of the flow rate. Table VIII shows the results of such filtrations and the

TABLE VIII

VISCOSITY OF 0.1% CELLULOSE SULFATE SOLUTIONS AND RATE CHANGE OF FILTRATION THROUGH MILLIPORE FILTERS (1.2 μm)

D.s.	*Time ratio*	*Viscosity, centipoises*
0.5–0.6	1.57	~16
0.8–0.9	1.42	~14
1.1–1.2	1.38	~10
1.4–1.5	1.30	~ 8

corresponding viscosities of the solutions. The time ratios are indicative of the decrease in flow rate, and a factor of 1 indicates no decrease, namely, perfect injectivity, and a factor of 2, a decrease of 50%. All products tested had factors significantly below 2 and viscosities of ~8–16 centipoises, depending on the d.s. The factors were similar when up to 8% of sodium chloride and up to 0.8% of calcium chloride were present in the solutions. The viscosity, however, was then somewhat lower, and the concentration of the cellulose sulfate had to be increased about 1.3–1.6 times to maintain the viscosity indicated in Table VIII.

In drilling muds and related applications, temperature stability, suspendability, shear stability, and pseudoplasticity combined with yield point are desirable characteristics. All of these characteristics are present in the cellulose sulfates, particularly those having a d.s. within the range of about 0.5–1.0. The degree of pseudoplasticity may be varied by the degree of substitution. Additionally, the cellulose sulfate solutions can be saturated with such salts as sodium or calcium chlorides, without separation, even at alkaline pH values. Most polymers currently used have compatibility problems when calcium chloride is present at alkaline pH. It implies that the cellulose sulfate may have fewer limitations in this use than the products now used.

Water-based paints is an application in which the gum functions as a levelling agent, thickener, and suspending agent, properties exhibited by the cellulose sulfate discussed. Also, enzyme resistance is of great importance and, therefore, products having d.s. $\gtrsim 1$ may be more suitable than those having a d.s. < 1. When, in a standard formula for an interior emulsion-paint, the 2% of HEC was replaced by 1.5% of cellulose sulfate having a d.s. of ~0.5–0.6, the viscosity and appearance were similar to those of the control containing the HEC. After storage for about one year, the control showed separation, whereas the sample containing cellulose sulfate was still in perfect condition.

The principal paper applications that are suggested by a number of properties are (*i*) paper coatings, (*ii*) sizings, and (*iii*) specialty papers, such as erasable paper. Paper coatings appear to be by far the largest area, and the properties required, such as suspension stabilization, film formation, complete solubility resulting in smooth solutions without the presence of insoluble gelatinous particles, crosslinkability, and so on, are all exhibited by cellulose sulfate. In sizings and other similar applications, the products having an extra-low d.s. that still show hydrogen-bond activity may be able to associate with the cellulose fiber and, therefore, result in exceptional strength and smoothness of the paper.

Applicability in textiles is in backcoatings, such as carpet backing, as a dye antimigration agent, as a latex stabilizer to prevent roller build-up, as a thickener in printing pastes, and so on. There is also the possibility of its use as an antistatic agent because of the high negative charge and the fact that it may be readily cross-linked and insolubilized to result in a permanent finish. Work to establish the suitability in these areas is in progress, and preliminary results are positive.

Potential applicability is also in explosives, specifically, slurry explosives. The requirements are solubility in high concentrations of inorganic nitrate, high viscosity, and gel formation by crosslinkage. These properties are provided best by cellulose sulfates having a d.s. of about 0.5–1.0. They have high viscosities, dissolve directly in, for example, saturated solutions of ammonium nitrate, and, in view of the reactive C-6 and C-2 hydroxyl groups, should be relatively easily gellable.

Photographic applications are suggested by such properties, as high viscosity, film formation, suspension stabilization, complete solubility, compatibility with polyvalent metal ions, and protein reactivity. The use of cellulose sulfate as a gelatin extender or thickener, for example, is one among several potential photographic applications.

In cosmetics, high viscosity, complete solubility combined with clarity, emulsion and suspension stabilization, and tolerance to organic solvents are desirable characteristics depending on the specific use, whereas, in toothpaste, viscosity, suspension stabilization, and, for certain parts of the world, enzyme resistance, are of importance. Cellulose sulfate having d.s. $\sim$0.6 was tested as a replacement for Carbopol in a vanishing-cream formula, for *O*-(carboxymethyl)cellulose at about one third of its concentration in a clear-gel hair conditioner, and for *O*-methylcellulose in a clear-gel shampoo. The three formulations containing cellulose sulfate were at least equal to the controls in appearance, viscosity, flow characteristics, and shelf life. In a toothpaste formula, relatively low levels of cellulose sulfate performed as well as, or better than, *O*-(carboxymethyl)cellulose (CMC) or carrageenan, and definitely better than CMC in the presence of enzymes.

Another most promising application is in food, and many specific uses may be suggested by relating properties with functional requirements. However, a detailed discussion of this area would go beyond the scope of this article.

The application areas thus far discussed are those that are obvious candidates for cellulose sulfates and that are directly indicated by certain properties. It must be realized, however, that it is difficult to establish valid property–application relationships, because of interactions that may occur with the various ingredients of a formulation. Such interactions are difficult to predict and may result in a beneficial or a detrimental effect on the performance of the colloid in a particular system. Therefore, the areas discussed are probably not the only applications for the cellulose sulfates, nor do they necessarily constitute the best examples. Only additional, extensive testing in actual formulations will, in time, establish the performance and the value of these new products.

EXPERIMENTAL

Preparation of sodium cellulose sulfates. — Cotton-linter pulp (50 g) is suspended in *N*,*N*-dimethylformamide (1.5 L) in a 3-L, three-neck, round-bottom flask equipped with a mechanical stirrer, calcium chloride tube, and dropping funnel. About 75 g of dinitrogen tetraoxide dissolved in 100–150 mL of *N*,*N*-dimethylformamide is slowly added during a period of 30–45 min and stirring is continued until a clear highly viscous solution is obtained. A saturated solution of *N*,*N*-dimethylformamide–sulfur trioxide complex prepared as described previously[2] is then slowly added to the solution of nitrite ester during a similar period of time, with continuous stirring and cooling in an ice bath to maintain the temperature at $\sim$10–15°. The amount of sulfur trioxide is calculated stoichiometrically to afford the desired degree of sulfation. The mixture is then mixed with $\sim$50 mL of methanol or water, transferred to a large beaker, and neutralized with aqueous sodium carbonate. During neutralization, strong agitation and cooling are required. The sodium cellulose sulfate is precipitated by the addition of methanol, washed with 70% aqueous methanol, and dried. The yield is quantitative.

As reported previously[4], the preparation of cellulose sulfate having d.s. $\gtrsim$1.1 requires a cellulose nitrite having d.s. $<$3 such that the combined d.s. (degree of nitrosation plus degree of sulfation) is about 3. The cellulose nitrite intermediate having d.s. $<$3 is obtained similarly by using correspondingly smaller, stoichiometrically calculated amounts of dinitrogen tetraoxide. The further procedure for sulfation and neutralization is the same as already described.

Viscometry and ^{13}*C-n.m.r. spectroscopy.* — Viscosity measurements were conducted with a Brookfield Viscometer, LVT Model, at 60 r.p.m. and 20° unless stated otherwise. The ^{13}C-n.m.r. spectrum was obtained with a Bruker 90-MHz spectrometer operating at 22.628 MHz at 75° with hexafluorobenzene as external reference and lock signal. The spectrum was taken with complete proton-decoupling and obtained from 44,640 scans. All chemical shifts were calculated by using tetramethylsilane as reference standard. The C-6 region showed peaks at 61.2 and 66.7 p.p.m., the first being in the region of unsubstituted C-6-hydroxyl groups and the latter indicating C-6-sulfate[9].

Periodate oxidation. — An aliquot of cellulose sulfate was dissolved in distilled water, an excess (about twofold) of M sodium periodate solution added, and the solution kept for 48 h at room temperature. The excess of periodate was then reduced with 0.1M sodium arsenite and the excess of arsenite was titrated with 0.1M iodine, with starch as the indicator.

Enzyme resistance. — To 100 mL of a 1% aqueous solution of hydrocolloid was added 5 mg (7 units) of cellulase (from *Aspergillus niger*) at pH 7 and 22°. The viscosity was determined initially, and after various periods of time. A decrease in viscosity was considered indicative of enzymic degradation.

Shear resistance. — Aqueous solutions (1%) of cellulose sulfate containing 0.5% of sodium chloride were mixed in a Waring Blendor at high speed. The viscosity was measured initially and after 1, 5, and 15 min of shearing. A viscosity decrease was indicative of depolymerization by mechanical stress.

High-temperature stability. — Solutions (1%) were heated at 100° and the viscosity determined initially and after various periods of heating. All solutions contained 0.5% of sodium acetate as a buffer to maintain the pH at 6.5–7.5. To minimize oxidative degradation, the experiments were conducted under exclusion of oxygen, or the solutions contained an oxygen scavenger, such as a sulfite or thiosulfate.

Suspension stabilization. — Titanium dioxide or barium sulfate (10 g) was suspended in 100 mL of a 0.5% solution of cellulose sulfate. The suspension was homogenized for 2 min in a Virtis 45 homogenizer at 20,000 r.p.m. and transferred to a 100-mL graduated cylinder. The products were observed for 2 weeks, and any separation at the top recorded (in mL) after various periods of time.

Solvent tolerance. — To 1% aqueous solutions of cellulose sulfate were added with strong agitation increasing amounts of water-miscible solvent. The amount of solvent required to cause separation combined with a significant decrease in viscosity was determined and is recorded in Table II in vol per vol of aqueous cellulose sulfate solution.

Millipore filtration. — Cellulose sulfate was dissolved in tap water (~250 p.p.m. of sodium chloride, ~50 p.p.m. of calcium chloride) and the solution was sheared for three min in a Waring Blendor at high speed, diluted with tap water to 0.1%, and filtered through Whatman No. 1 filter paper. A volume of 1 L was then passed at 40 lb.in^{-2} through a 1.2-μm Millipore filter of 5.1-cm diameter. The sum of the flow times of the 16th, 18th, and 20th 50-mL portions was divided by the sum of the flow times of the 2nd, 4th, and 6th 50-mL portions. The resulting factor is a measure for the flow-rate decrease. After passage through the Millipore filter, the viscosity was measured at 6 r.p.m. by using a UL adaptor, an attachment designed for determining low viscosities with the Brookfield viscometer. Similar flow-rate ratios were measured when 0.8-μm Millipore filters were used and/or the solution contained 1000–2000 p.p.m. of calcium chloride.

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