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3,313,803

## HYDROXYALKYL STARCH ETHER PRODUCTS

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No Drawing. Original application Oct. 24, 1962, Ser. No. 232,864, now Patent No. 3,112,214, dated Nov. 26, 1963. Divided and this application Aug. 29, 1963, Ser. No. 305,531

4 Claims. (Cl. 260—233.3)

This application is a division of application Ser. No. 232,864, filed Oct. 24, 1962, which issued as Patent No. 3,112,214 on Nov. 26, 1963.

This invention relates to a new method of sizing cellulose sheets with starch. More specifically it relates to a novel process wherein paper and paperboard surfaces are pretreated with an aqueous solution of borax (sodium borate), and then sized with a gelatinized starch derivative bearing substituent vicinal (vic.)-glycol groups.

Surface-sizing agents are applied to paper and paperboard for the purpose of improving such properties as printability, abrasive resistance, erasability, and smoothness. Among the materials employed for this purpose are the modified starches and starch derivatives. The surface size is applied either by tub sizing, that is passing the paper through a water dispersion of the sizing agent, by the use of a size press, or at the calendar stack. When the sizing agent is starch, it is customary to apply it in pasted (gelatinized) state so that a film of starch paste is left on the surface of the sheet. Among the advantageous results obtained by surface-sizing are the binding of loose cellulose fibers, the improvement of sheet texture, the decreased tendency of the paper sheet to curl, the increased resistance to picking during printing, and the increased resistance to penetration of solvents, oils, greases and printing inks.

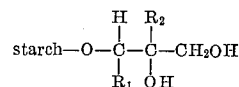
Although natural starches are sometimes used in surface-sizing, it is usually necessary to reduce the viscosity of the natural starches in order to incorporate into the size a sufficient amount of the starch to be effective. Thus, it is common to employ modified starches which possess low viscosities at high concentrations. Methods of modifying starches to obtain the desired low viscosity are well known in the art. These include dextrinization, acid hydrolysis, enzyme hydrolysis, and degradative oxidation. Each of these processes results in a decrease in the molecular size of the starch and a consequent reduction in viscosity.

An additional consequence of such modifications of starch for surface-sizing is increased penetration into the sheet by the smaller starch molecules. Since the effectiveness of a surface size is dependent upon the extent to which the size remains at the surface of the sheet, this increased penetration is undesirable; for with a given amount of size the greater the extent of penetration into the sheet, the smaller is the advantage gained by surface-sizing. With more porous cellulose sheets, such as paperboard, penetration occurs to an even greater extent. Penetration can be reduced by an increase in the viscosity of the size through the use of higher starch concentrations, but this practice is uneconomical. Penetration can also be controlled by varying the time of contact of the paper with the size. In tub sizing the contact time is relatively long and penetration is quite deep. In surface-sizing at the size press or at the calendar stack contact time is shorter and less penetration occurs. Even with a relatively short contact time, however, microscopic examination of the cellulose sheet reveals that considerable penetration of the starch occurs.

It is the main object of this invention to provide a process for surface-sizing cellulose sheets with a modified starch paste in which penetration of the modified starch

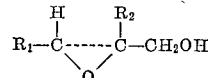
paste into the sheet is prevented. Another object of the invention is to provide a surface-sizing process in which the amount of starch required is reduced due to the lack of penetration of the starch paste into the sheet. A third object of the invention is to provide a process for imparting to the surface of paper or paperboard markedly increased resistance to penetration of inks, oils and greases. A further object is to provide a process for improving the printability of paper and paperboard. Still another object is to provide a process for imparting a smooth, abrasion resistant finish to the surface of cellulose sheets. A still further object is to provide a novel starch compositions which are especially suitable for use in a process of sizing cellulose sheets.

We have discovered that pretreatment of a cellulose sheet with an aqueous solution of borax, followed by surface-sizing the sheet with a starch derivative which carries substituent vic.-glycol groups, results in the retention of the size entirely on the surface of the sheet. Particularly suitable for this process are the di- (and poly-) hydroxyalkyl ethers of starch, which may be represented by the formula:

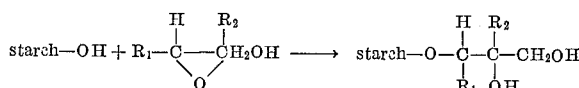


wherein  $\text{R}_1$  and  $\text{R}_2$  are taken from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, alkenyl, aryl and aralkyl.

One method of preparation of suitable dihydroxyalkyl ethers of starch involves the reaction of starch with a 2,3-epoxyalcohol having the formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are identical with  $\text{R}_1$  and  $\text{R}_2$  in the preceding formula. The equation for the reaction may be written:



Examples of suitable 2,3-epoxyalcohols are glycidol, 2,3-epoxybutane-1,4-diol, and 2,3-epoxy-2-methylpropanol, which react with starch to form the 2,3-dihydroxypropyl, the 1-hydroxymethyl-2,3-dihydroxypropyl, and the 2-methyl-2,3-dihydroxypropyl ethers of starch, respectively. Other methods of preparing the necessary starch derivatives bearing vic.-glycol groups will be evident to those skilled in the art.

It is old in the art to use starch derivatives in the sizing of cellulose surfaces. Specifically, in the commercial manufacture of paper and paperboard it is common to use 2-hydroxyethylated starches. We have found that the use of a starch derivative bearing vic.-glycol groups instead of a 2-hydroxyethylated starch to surface-size an untreated cellulose sheet results in a sized sheet having superior surface properties, particularly with reference to ink- and oil-holdout. As will be shown in the examples below, little or no improvement in ink- and oil-holdout properties is obtained by pretreatment of the cellulose surface with borax before applying a 2-hydroxyethylated starch. It is a most surprising discovery, then, that an additional and far greater improvement in ink- and oil-holdout is obtained by pretreatment of the cellulose sheet with borax, followed by the application of a starch derivative bearing substituent vic.-glycol groups.

In explanation of the remarkable ink- and oil-holdout properties of paper and paperboard sized by the process of this invention, we believe that a chemical reaction takes place between the borax and the vic.-glycol groups on

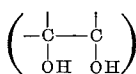
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the starch derivative to form a cross-linked gel structure. We further believe that this reaction is instantaneous and occurs only at the surface of the cellulose sheet. The cross-linked gel which forms cannot penetrate into the sheet, and in turn it prevents penetration of any additional size into the sheet. Consequently, all of the size remains on the surface of the sheet to provide a continuous barrier to ink and oil penetration.

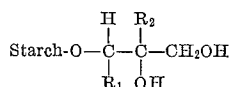
Although the starch molecule contains vic-glycol groups, these are in a rigid cyclic configuration, and are incapable of forming the necessary borax complex. On the other hand, the acyclic structure of the substituent vic-glycol groups on the starch derivatives which are essential to the practice of this invention permits the formation of the necessary borax complex.

In the process of this invention the concentration of the borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , applied to the cellulose sheet may vary from about 1 percent to that of a saturated solution. However, since the maximum effect appears to be produced when the concentration is 5 percent or greater, a borax concentration of 5 percent is preferred. Because it is the borate ion which is required for the process of this invention, any soluble alkali salt or alkaline earth salt of boric acid may be used. Furthermore, boric acid may replace borax if sufficient alkalinity is present in, or is added to, the cellulose sheet to convert the boric acid to borate ion.

It is essential to the practice of this invention that the starch used to size the borax pretreated cellulose sheet contain an acyclic vic-glycol



group. The linkage between the vic-glycol group and the starch is not critical and may consist of an ether, ester, glycosidic, or direct carbon-carbon linkage. For reasons of economy and stability we have preferred to attach the vic-glycol group to starch through an ether linkage to form derivatives having the general formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are taken from the group consisting of hydrogen, alkyl, substituted alkyl, cyloalkyl, alkenyl, aryl and aralkyl. The number of substituent vic-glycol groups may be between 0.01 and 3.0 per anhydroglucose unit; excellent results, however, are obtained with from 0.1 to 0.2 substituent vic-glycol groups per anhydroglucose residue. Any available starch may be used to prepare the starch derivative, including native starches from corn (maize), potato, wheat, rice, tapioca, sorghum, waxy corn, waxy rice, high amylose corn, etc., and including any of the said native starches which have been modified either by acid hydrolysis, enzyme hydrolysis, oxidation, dextrinization or derivatization, as well as the amylose and amylopectin fractions of said starches.

The invention is illustrated by the following examples which are intended to be informative only and in no way limiting.

#### EXAMPLE I

This example illustrates the resistance to printing ink penetration imparted by a starch glycerol ether (a 2,3-dihydroxypropyl ether of unmodified corn starch), degree of substitution (D.S.) of 0.2, when applied to a borax pretreated cellulose sheet.

Sheets of Whatman No. 1 filter paper were treated as shown in Table I. The sheets were dried in air, conditioned at room temperature and humidity for 24 hours, and then tested for resistance to printing ink by TAPPI Butyl Carbitol Test RC18. The results are shown in Table I.

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TABLE I

Treatment:	Time (sec.) required for penetration <sup>a</sup>
None	0
Impregnated with 5% borax solution	0
No pretreatment, sized with 4% starch glycerol ether paste	6
Impregnated with 5% borax solution, dried, and sized with 4% starch glycerol ether paste	45

<sup>a</sup> A penetration time of 45 seconds indicates excellent resistance to printing inks.

#### EXAMPLE II

This example illustrates the oil-holdout property imparted to paper by pretreatment with borax followed by sizing with glycerol ethers of acid-modified corn starches.

Pastes containing 6 percent of the corn starch derivatives (60-80 fluidity) listed in Table II were prepared by heating the starch slurries for one-half hour on a steam bath. The pastes were then cooled to 110° F. and applied to 55-pound offset paper with a No. 4 Mayer rod. Half of the paper had been pretreated with a 5 percent solution of borax. The sheets were tested, after conditioning overnight at room temperature and humidity, by measurement of the rate of oil penetration using a Vanceometer Absorption Tester (Hillside Laboratory, Chicago, Illinois). The results are shown in Table II together with the values obtained using a commercial 2-hydroxyethylated acid-modified starch.

TABLE II

Starch Used in Size	Percent Loss in Reflectance <sup>a</sup>			
	No Pretreatment		Borax Pretreated	
	After 10 sec.	After 50 sec.	After 10 sec.	After 50 sec.
Acid-modified 0.10 D.S. starch glycerol ether	45	61	28	34
Acid-modified 0.044 D.S. starch glycerol ether	58	72	11	33
Acid-modified 0.05 D.S. 2-hydroxyethyl starch	68	73	55	66

<sup>a</sup> Percent Loss in Reflectance is directly proportional to the amount of oil penetration into the sheet.

#### EXAMPLE III

This example illustrates the use of sizes containing corn starch glycerol ethers, acid-modified to a lesser extent than those in Example II, on borax pretreated paper.

The test was carried out as described in Example II, except that the starches used were in the 20-40 fluidity range. The amounts of oil penetration as measured by percent loss in reflectance are given in Table III together with the values obtained on paper which had not been pretreated.

TABLE III

Starch Used in Size	Percent Loss in Reflectance <sup>a</sup>			
	No Pretreatment		Borax Pretreated	
	After 10 sec.	After 50 sec.	After 10 sec.	After 50 sec.
Acid-modified 0.10 D.S. starch glycerol ether	29	47	31	34
Acid-modified 0.18 D.S. starch glycerol ether	22	47	16	20

<sup>a</sup> Percent Loss in Reflectance is directly proportional to the amount of oil penetration into the sheet.

#### EXAMPLE IV

Sheets of paperboard were impregnated with 5 percent borax solution and allowed to dry at room temperature

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overnight. A film, 0.0015-inch thick, of each of the pastes described in Table IV was applied both to the treated and to untreated sheets, and the sheets were again air-dried overnight. The resistance of the sized sheets to penetration by printing ink was determined as in Example I.

The results in Table IV are the average of 15 determinations in each case. The 2-hydroxyethyl starch is typical of some sizes in use in the art, and was included for comparison.

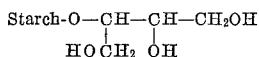
TABLE IV

Size Composition	Average Time (Seconds) Required for Penetration	
	No Pretreatment	Borax Pretreated
10% 2-hydroxyethyl Starch 0.1 D.S. 80 fluidity		
4% 1-methyl-2,3-dihydroxypropyl Starch, 0.025 D.S.	4½	2
4% 1-hydroxymethyl-2,3-dihydroxypropyl Starch, 0.1 D.S.	4	80
	7	470

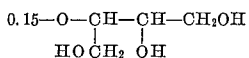
The foregoing tabulated results show that the process for sizing a cellulose sheet consisting of pretreatment of the cellulose sheet with an aqueous solution of borax, followed by the application of a size prepared by pasting a starch derivative carrying a vic-glycol grouping affords a major increase in the resistance of said sheet to penetration by oils and printing inks.

## EXAMPLE V

This example illustrates the preparation of 1-hydroxymethyl-2,3-dihydroxypropyl starch,



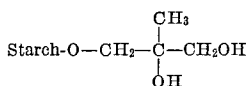
To 100 ml. of an aqueous solution containing 13.2 grams of 2,3-epoxy-1,4-butanediol, 2 grams of 2-butene-1,4-diol, and 0.7 gram of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , prepared from 2-butene-1,4-diol by a known process (U.S. 2,833,787), was added with vigorous agitation 20 grams of  $\text{Na}_2\text{SO}_4$ , 93 grams of corn starch containing approximately 12 percent  $\text{H}_2\text{O}$ , and 21.5 ml. of 1.65 N NaOH. The mixture was heated with stirring at 50° C. overnight. The resulting slurry was neutralized with 2 N HCl to pH 4.7, filtered, and the cake was washed free from sulfate ions with water and aqueous methanol. The product was further washed with acetone and dried at 60° C. It contained 0.86 meq. per gram  $>\text{COH}-\text{CH}_2\text{OH}$ , determined by measurement of the HCHO evolved upon oxidation with sodium periodate. This value is equivalent to



groups per anhydroglucose unit. The Scott viscosity was 10 grams per 59 seconds, and the resulting paste was stable but set to a gel upon the addition of borax.

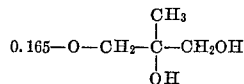
## EXAMPLE VI

This example illustrates the preparation of 2-methyl-2,3-dihydroxypropyl starch,



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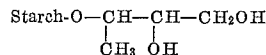
Example V was repeated using 150 ml. of an aqueous solution containing 15 grams of 2,3-epoxy-2-methylpropanol-1, 7.5 grams of methallyl alcohol, and 1 gram of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , similarly prepared from methallyl alcohol. At the end of the reaction period the starch had become partially gelatinized and it was necessary to dilute the mixture with water before neutralization. After neutralization to pH 5.7 the slurry was dialyzed against deionized water until free from sulfate ions, and precipitated with methanol containing a small amount of  $\text{CH}_3\text{CO}_2\text{Na}$ . The precipitate was collected on a filter, washed with methanol and acetone, and dried. It contained 0.98 meq. per gram  $>\text{COH}-\text{CH}_2\text{OH}$ , equivalent to



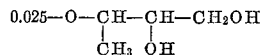
groups per anhydroglucose unit. The Scott viscosity was 11 grams per 43 seconds and the resulting paste was stable but gelled upon the addition of borax.

## EXAMPLE VII

This example illustrates the preparation of 1-methyl-2,3-dihydroxypropyl starch.



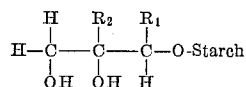
Example V was repeated using 40 grams of  $\text{Na}_2\text{SO}_4$ , 43 ml. of 1.65 N NaOH and 200 ml. of an aqueous solution containing 13.5 grams 2,3-epoxybutanol-1, 7.2 grams of 2-butene-1-ol, and 1.6 grams of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , similarly prepared from 2-butene-1-ol. The product contained 0.15 meq. per gram  $>\text{COH}-\text{CH}_2\text{OH}$ , equivalent to



groups per anhydroglucose unit, and it had a Scott viscosity of 10 grams per 43 seconds. The paste was stable and became gelatinous upon the addition of borax.

We claim:

- 1-hydroxymethyl-2,3-dihydroxypropyl starch having a degree of substitution between about 0.01 and 3.0.
- 2-methyl-2,3-dihydroxypropyl starch having a degree of substitution between about 0.01 and 3.0.
- 1-methyl-2,3-dihydroxypropyl starch having a degree of substitution between about 0.01 and 3.0.
- Composition of matter corresponding to the formula



wherein  $\text{R}_1$  and  $\text{R}_2$  are selected from the group consisting of H, methyl, and hydroxymethyl, and  $\text{R}_1$  and  $\text{R}_2$  are not identical having a degree of substitution between about 0.01 and 3.0.

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