

1

2,903,391

PAPER SIZE AND METHOD OF PREPARATION

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Starch products have been used in the manufacture of paper for many years. Starch products have been used to size the paper pulp before it is cast into a sheet to improve the strength and the density of the sheet; they have been used to size the cast sheet by immersion of the sheet in a bath of the size, primarily to control ink penetrability of fine writing papers; starch products have been used to surface size paper board to provide an improved surface for printing, to lay surface fibers and to increase resistance to grease penetration; and starch products have been used as a binder for clays in surface sizing fine printing papers in order to provide suitable surfaces for detailed reproduction of printed illustrations and type characters.

Quite different starch products are required for these several distinctly different sizing operations, so that they may be used with different means of application at these different stations in a paper mill and so that they will impart the specific characteristic to the paper mentioned above. A starch product which is suitable for application in paper making machinery at one station and which very efficiently imparts one characteristic is not necessarily suited for use at some other station to impart a different characteristic.

This invention relates to an improved starch product eminently suited for use in sizing paper pulp at some stage prior to the formation of the paper sheet, that is, while the fibers are still in an aqueous suspension, in order primarily to increase the strength of the paper sheet to be formed from these pulp fibers.

In practice, starch is added to paper pulp primarily to control the strength of paper sheet within certain desired, specified limits. Most of the strength of the sheet will depend primarily on the inherent nature of the pulp being used at the time and the length of time allowable for beating the pulp in order to "hydrate" the fibers. At times, little or no starch may be added whereas at other times, when tests show that the strength of the finished sheet is dropping below specifications, an increased proportion of starch product may be added to the pulp either at the beaters themselves, or just before the Jordan disintegrators or at some other place before the wire mesh on which the sheet is formed.

A major problem in the use of starch to size paper pulp stems from the fact that because of the very nature of the application, a dry starch product, ready for instant, although intermittent, use is desired.

In the prior art of sizing paper pulp before the formation of the sheet, dry uncooked starch was added to the beaters; the heat and moisture present at the time the formed sheets were dried, as on heated rolls, was relied upon to gelatinize the starch. It was found that this application was highly inefficient in developing a bond between paper fibers for many reasons, most important of which are the relatively poor retention of uncooked starch by paper fibers and the lack of sufficient gelatinization of the starch at the paper dryers.

Gelatinization of starch, as by cooking with water, at the paper mill has been tried. This procedure has several

2

disadvantages. It adds another, and a bothersome step, in paper manufacture. Many paper mills are not even equipped with starch treating equipment. The cooked starch changes in characteristics in storage tanks. Most important, however, is the fact that the very tender starch particles of a cooked paste are very badly broken down by the cellulose fiber beating equipment so that the starch size is not very well retained by the paper fiber on the wire and so that the strength of the starch size is diminished due to mechanical forces.

A large number of mills have, accordingly, preferred to use a dry product which consists primarily of a starch which has been pregelatinized by the starch manufacturer, even in spite of the fact that use of these prepared starch powders, particularly those made from the less costly, domestic cereal starches has certain definite disadvantages, and presents certain new problems. It is almost impossible to gelatinize certain starches, and dry them to a powder so that the powder will function effectively and efficiently in a pulp sizing operation. Experience has shown that nondegraded starches impart the greatest strength to most pulps when the pulp is cast into sheets of average density and yet when some classes of unmodified starches, such as cereal starches, are gelatinized by the starch producer and dried to a powder, associative bonds are set up between the starch molecules which act materially to reduce the sizing value of the product for paper pulp. The net result observed for this poor redispersibility of starch substance is that although retention by paper pulp is greater than for uncooked raw starch or for starch freshly cooked at the paper mill, nevertheless, the sizing value of these products in pounds of starch per ton of paper pulp in increasing the strength of the paper sheet is of a disappointingly low order. Usually the addition of these prepared cereal starch products to pulp within the economically attractive range of 40 to 60 pounds per ton increases the sheet strength, as measured by the Mullen test, by only about 5 to 10 percent. Moreover, small undispersed particles of gel collect on the paper fiber which produce an effect on the finished sheet called "fish eyes" and render the paper an inferior grade.

On the other hand, some classes of prepared starches, such as the pregelatinized tuber or root starches, are very well suited for the sizing of paper pulp. Roll-dried potato and tapioca starches when added as a powder to paper pulp give two to three times the increase in strength to the paper that is given by the addition of an equal weight of a roll-dried cereal starch, such as corn or grain sorghum. However, the tuber and root starch products are either imported, their cost is higher per pound, or their supply is limited or uncertain; whereas corn starch is always readily available in the United States and is one of the lowest price starches.

It is a specific object of this invention to provide by a feasible, low cost procedure a pregelatinized and dried starch powder from cereal starches, such as corn and grain sorghum, which will increase the strength of paper to a very high degree; at least to the degree given by an equal proportion of pregelatinized tapioca and potato starch powders when added to paper pulp prior to formation of the paper sheet. A secondary object is to accomplish such a result by use of a cereal starch product which disperses so uniformly in the paper making operation that it will not give visual uneven sizing effects to the finished paper sheet.

Dispersibility of a starch powder, particularly a pregelatinized starch powder, is used by starch technologists in several senses. It is said that a starch product is dispersible if it readily mixes with water to form a transient, uniform suspension of the discrete powder particles in the solvent. Most all pregelatinized powdered products, both of cereal and tuber starches do not readily disperse in

this sense in water but tend to "ball up." Accordingly, wetting agents and other adjuncts, e.g., sodium carbonate, trisodium phosphate, borax, sodium sulphate, lauryl sulphate and the like are commonly added to the starch to promote this phase of dispersibility. Dispersibility is also used to describe the hydration of these discrete powder particles and their solution, or partial solution, in the solvent to form colloidal units approaching molecular dimensions. It is here that cereal starches in particular are lacking, due to the aforesaid, associative bonds between the starch molecules in the dried powder. Obviously, the development of an adhesive bond between cellulose fibers by the starch in an efficient manner depends upon both phases of dispersibility. The problem is quite complex inasmuch as it is to be recalled that retention of the starch size by the pulp fibers is probably due to a certain degree of nondispersibility in both of its hereinabove discussed phases.

I have now discovered, in accordance with this invention, a process for preparing a size for paper pulp prior to paper sheet formation in which cereal starches are employed, and the resulting products give at least the sizing efficiency of an equal proportion of tuber or root starches in the pregelatinized state. Broadly, this result is brought about by etherifying cereal starches by means of alkylene oxides to form hydroxyalkyl, partial ethers of starch, adding a relatively small proportion of borax to the starch ether and drying the gelatinized combination to form a powder.

It is not clearly understood why the particular combination of hydroxyalkylation and borax addition should give such unexpected high strength to the paper sheet when the pulp is sized with my product, particularly since, as will be shown hereinafter, the increased sizing effect due to hydroxyalkylation or of the borax, independently of each other, is insufficient to account for the combined effect of the two. However, it is presumed that the unanticipated effect is due to the fact that borax is able to form more readily a labile complex with an hydroxyl group on the end of a substituent chain, removed from the main carbohydrate chain by an alkyl group, than it is with hydroxyl groups directly on the carbohydrate molecule, and that it is the formation of this complex which is responsible for the improved physicochemical properties and the increased sizing value of the product for paper pulp.

In carrying out my invention an hydroxyalkyl starch ether is first prepared. The ether may be prepared in accordance with prior art methods, for example, U.S. Patents 2,516,633; 2,516,634; 2,733,238 and 2,801,241. The latter methods will be illustrated in Examples 1 and 2, respectively, which follow. The starch ether may be prepared from raw or modified starch, e.g., thin boiling starches, dextrins, made in conventional manner. The resultant starch ether, either in gelatinized or granule form, is then mixed with, for example, 0.25 to 15 percent of borax, based on the dry weight of the ether, and dried by passing the mixture over heated rolls in conventional manner. If the starch ether is not already gelatinized before the roll-drying operation, then sufficient water is incorporated into the starch ether-borax mixture to provide for gelatinization during the roll operation. The gelatinized starch ether-borax mixture may also be spray dried. The drying operation should be rapid and should permit free evaporation of water. Finally the product is ground to a powder and screened.

Such product may be added directly to the beater in beater sizing operations at the rate of at least about 3 pounds per 1000 pounds of dry pulp. The Mullen value increases with increased amounts of starch ether but above about 3 percent (dry basis) the increase in Mullen value is not sufficient to offset added cost. Direct addition of the size to the beater is a distinct advantage since no cooking of the starch ether is required at this point. In addition the product gives unexpectedly superior re-

sults (shown in the examples) as revealed by tests on the finished paper as compared to raw starch, which requires cooking prior to its use, or even to pregelatinized, dry cereal starch products.

Another advantage for the product of this invention, in addition to requiring no cooking, is that the size is so readily dispersible in aqueous medium that it may be added to the pulp at some place in the paper making operation following the beaters, e.g., at the Jordon disintegrators. Size is added to paper pulp not only to contribute certain properties, such as density and "rattle," but also to improve the strength of the finished sheet (Mullen test) particularly the abnormally low strength of some batches of pulp, as mentioned hereinabove. That is, starch size is added in variable amounts depending on the batch, in order to provide a constant level of strength during use of a series of batches. Inasmuch as beaters are operated for several hours time, then abnormalities cannot be corrected on any particular batch until after paper has been produced for several hours, if additions are made at the beater. However, if the size may be added subsequent to the beater operation, then obviously irregularities may be corrected in the stock by proper addition of size after paper has been produced for only a very relatively short time, possibly within 15 minutes.

The following examples will further illustrate the invention but are not intended to limit the invention in any way. The values set forth in parentheses are practical operating ranges, not critical unless so stated.

Example 1

An aqueous slurry of raw grain sorghum starch having a density of 20 Bé. (10 to 24) was treated in the presence of 2.4 percent of calcium hydroxide (1 to 3), with 2.4 percent of ethylene oxide (1 to 3), both based on the dry weight of the starch. The reaction was allowed to proceed at 96° F. (80 to 130) with agitation for 12 hours (5 to 15). Thereafter the pH of the reaction mixture was adjusted to 5.6 (5 to 8) with an acid, such as hydrochloric. The hydroxyethyl starch was washed and reslurried in water. Then 4 percent of borax, based on the dry weight of the hydroxyethyl starch, was added to the slurry (20° Bé.) and the slurry was passed over steamheated rolls (160 p.s.i.) to gelatinize and dry the starch ether. The final product was ground to desired particle size.

The analysis of the finished product was as follows:

Moisture	9.4% (4 to 12)
pH	9.0% (7 to 10)
Soluble material	38.2% (10 to 100)
Ash	2.3% (0.2 to 9.0)
Degree of substitution	0.05 (0.01 to 0.1)

Example 2

Two hundred and twenty pounds of corn starch was charged to a closed reactor provided with a stirrer, an external jacket for heating by steam and with valves for introduction of other materials and for air-exhaust. Then 4 gallons of a 1 percent solution of wetting agent (Tween-20) was sprayed onto the starch followed by 5 pounds of 50 percent triethanolamine. Stirring was continuous in all operations. After thorough mixing, 8 pounds of propylene oxide was added to the starch. The reactor was then closed and the temperature was raised to 55 to 60° C. and maintained at this level for 7 hours. The temperature was then raised to 100° C. for 30 minutes during which time a stream of air was drawn through the reactor.

After cooling, the starch ether was suspended in water and 5 pounds of borax was added. The slurry, adjusted to approximately 20° Bé., was fed to double rollers, heated with steam at 120 p.s.i. The gelatinized and dried starch ether leaving the rolls was ground to a powder and screened.

Example 3

A starch ether produced in accordance with Example 1 was used as a beater size at the rate of 5 and 10 pounds per 1500 pounds of dry pulp and compared with 10 pounds of untreated starch and a run with no starch. The results are as follows:

Characteristics of Paper Produced	Pounds Starch Added to Beater per 1,500 lbs. Dry Pulp			
	No Starch	10 lbs. Raw Starch	5 lbs. Starch Ether	10 lbs. Starch Ether
Weight, per ream, lbs.	60	60	60.2	60.1
Mullen Test, lbs. per sq. in.	48	52	54	59
Mullen Factor ¹	0.800	0.867	0.898	0.982
Increase in Mullen Factor, percent		8.4	12.3	22.8
Porosity (Densometer):				
B Size Press, seconds		10-15	25	50
A Size Press, seconds			90	140

¹ Mullen factor = $\frac{\text{Mullen test, lbs per sq. in.}}{\text{Ream weight in pounds}}$

The above example shows that the addition of as little as 10 pounds of the pregelatinized hydroxyethyl grain sorghum starch ether borax complex powder to 1500 pounds of paper pulp in the beater (or about 0.7 percent cereal starch product, based on pulp) increased the Mullen factor approximately 23 percent. This is a highly unanticipated result and represents a higher increase in strength of paper formed than has been reported in the prior art for any starch product made from cereal grain, and indeed is a greater increase than has been reported for tuber or root starch products when used at a comparable level of percentage of starch to pulp. In comparison, the unetherified starch product, and containing no borax addition, showed a Mullen factor grain of only 8.4 percent when added at a ratio of 0.7 percent to the paper pulp.

Moreover, the results of densometer tests show that the porosity of the formed sheet was only half that of the sheet using the unetherified and unborated starch product even when twice the amount of the latter was used compared to the etherified, borated starch complex.

The following examples show the results for changes in the Mullen test factor brought about by starch products pregelatinized by roll-drying when, singly, either the starch products contained small percentages of borax or when the cereal starch was hydroxyalkylated. An additional example compares the relative increase in Mullen strength provided by root or tuber starches, such as potato or tapioca starch with a cereal starch, such as corn starch, at several levels of addition to pulp, when these starch products have been simply pregelatinized and dried by roll-drying. This latter example will show the very highly efficient beater sizes that can be prepared from the former class of starches without any chemical modification and will show the disadvantage to which domestic cereal starches have been subjected heretofore when used in this particular application.

It is to be pointed out that in all of these tests, one lot of bleached sulfite pulp was used and this was always beaten to the same degree of freeness; that is, the pulp and the degree of hydration were the same in all tests. Unless otherwise specified, 2 percent of starch size, based on pulp, dry basis, was added to the beaters after the addition of 1.5 percent rosin, since this is the normal procedure in paper mills.

Again it is to be pointed out that in the following examples, Mullen test factor is the actual Mullen test observed in p.s.i. (an average of 20 determinations in each case) divided by the ream weight of paper produced, since it is appreciated that the strength of the paper as measured by Mullen test usually varies with the weight of paper being produced; a thicker or more dense sheet may

have considerably greater strength, even with no added starch size whatsoever, than a thinner or less dense sheet.

Example 4

The following example illustrates the increased sizing effect for paper pulp at the beaters (as measured by the increase in Mullen test factor) when a cereal starch, such as corn starch, is hydroxyalkylated prior to gelatinization and drying, and added as a dried powder to paper pulp at the beaters. This product contains no borax.

Corn starch was etherified by the procedures given in Example 1, using a ratio of propylene oxide to starch to give a purified starch ether which analyzed D.S.=0.04 as hydroxypropyl groups. After neutralizing the reaction mixture, filtering and washing the product in water (but before the addition of borax), the wet filter cake of the starch ether at 45 percent moisture content was fed to the valley between double rolls heated with steam at 160 p.s.i. to gelatinize and dry the product. After drying, the product was ground to a powder which was then added to paper pulp at the beaters.

A wet filter cake of untreated corn starch at 45 percent moisture content was similarly gelatinized and dried on the heated rolls and tested.

The results are given below for Mullen tests on paper produced.

As controls, paper was made from the pulp and tested, by adding no starch to the beater, by adding 2 percent (based on pulp) of a boiled suspension of untreated corn starch and by adding the same proportion of a boiled suspension of the purified hydroxypropyl corn starch.

Type of Starch Addition (2 Percent Based on Pulp)	Mullen Test, p.s.i.	Mullen Factor	Percent Increase in Mullen Factor Over Unsized Sheet
None	39.85	0.797	
Cooked, Untreated, Corn Starch	41.88	0.838	5.1
Cooked, Hydroxypropyl Corn Starch	42.20	0.844	5.9
Roll-Dried Corn Starch	42.70	0.854	7.2
Roll-Dried, Hydroxypropyl Corn Starch	43.25	0.865	8.5

The above results show that, whereas 2 percent addition of roll-dried cereal starch increased the Mullen factor for sheets made from the base pulp by 7.2 percent, hydroxyalkylation of this cereal starch prior to roll drying gave a product which increased the Mullen factor of sheets made from the sized pulp by 8.5 percent. That is to say, hydroxyalkylation, within the limits as set forth in this invention, was able to increase the Mullen factor of pregelatinized corn starch by an additional 1.3 percent; not a very significant value, compared to the relatively very large increase indicated for the product of this invention, as shown by the results given in Example 3.

The same conclusion may be drawn as to the value of hydroxyalkylation, when the Mullen factors are compared on sheets produced when corn starch and the corn starch ether, which had merely been cooked, were added in paper pulp sizing tests. Here, only an 0.8 percent rise in Mullen factor can be attributed to the hydroxyalkylation.

The above results show, additionally, the gain in sizing value for paper pulp that can be obtained when a cereal starch is pregelatinized and dried before adding to the beater. This gain, at a level of 2 percent addition of starch product to pulp, is from an increase in Mullen factor from 5.1 percent, to an increase of 7.2. That is to say, roll-drying corn starch gave an additional increase in Mullen factor of 2.1 percent, at a level of 2 percent addition of starch size to the pulp.

Example 5

The following example shows the results obtained by adding small percentages of borax to unmodified starches in a roll-drying operation.

Potato, corn and sweet potato starches were made into aqueous slurries of approximately 20° Bé. and the slurries were roll-dried in a "liquid-feed" operation. The dried products were ground to powders which were then added to paper pulp at the beaters in a ratio of 2 percent, based on pulp. In replicate tests, small additions of borax were made to these slurries before roll-drying and in another series of tests potato starch was roll-dried, using for this operation a wet filter cake at only about 45 percent moisture content, in a "cake-feed" operation, to show, incidentally, the measurable difference in sizing results when, as is often the case in practice, starch is pregelatinized under conditions which are not conducive to obtaining a high degree of swelling.

Roll-Dried Starch Added as Beater Size	Borax in Product, Percent	Mullen Factor	Percent Increase In Mullen Factor Due to Added Product	Percent Increase In Mullen Factor Due to Borax in Product
None	None	0.797		
Potato (Cake-feed)	0	0.984	23.5	
Do	1	0.994	24.7	1.2
Do	2	1.015	27.2	3.7
Potato (Liquid-feed)	0	0.991	24.4	
Do	1	1.025	28.6	4.2
Corn (Liquid-feed)	0	0.899	12.8	
Do	1	0.917	15.0	2.2
Do	4	0.922	15.7	2.9
Sweet Potato (Liquid-feed)	0	0.972	21.9	
Do	2	0.978	22.6	0.7

The above results show that the addition of small amounts of borax does not, in itself, materially improve the beater sizing efficiency of a pregelatinized starch, whether it be tuber or cereal starch and would do little to account for the extraordinarily high beater sizing effect of the cereal starch product produced in accordance with this invention and as shown in Example 3. Even under highly favorable conditions for roll-drying corn starch in granule form to obtain a pregelatinized, dried product, a 2 percent addition of this product to the pulp at the beaters led to a paper sheet with 12.8 percent increase Mullen factor over the control sheet with no added starch size. Adding as high as 4 percent borax to the starch prior to roll-drying gave an additional increase of only 2.9 percent in the Mullen factor.

Indeed, it will be seen that even in the case of non-cereal starches, such as potato and sweet potato starches, the addition of small amounts of borax to the starch prior to roll-drying, increased the efficiency of the product as a paper pulp size by a relatively very small percentage.

Therefore, it will be plainly seen by comparison of the results given in Examples 4 and 5 that the sum of the individual effects of hydroxyalkylation, addition of relatively small proportions of borax in the pregelatinization step and the process step of roll-drying cannot account for the unexpectedly high pulp sizing value demonstrated in Example 3, wherein a 23 percent increase in Mullen factor was obtained by adding to pulp less than one percent of a cereal starch product which had been prepared by a combination of hydroxyalkylation, addition of borax and roll-drying.

Example 6

The following example is given additionally to show the inherent superiority of the tuber and root starches, compared to cereal starch, for use in preparing a paper pulp size, when these starches are simply roll-dried to pregelatinized, dry powders and these powders are added

at ratios of 1, 2 and 3 percent, respectively, to paper pulp at the beaters.

The results for the comparative strengths of the paper sheets produced from these sized pulps are given below. The Mullen test factors show that the strength imparted by the addition of 3 percent of the corn starch product (or 60 lbs. per ton of pulp) could be obtained by the addition of about only one percent of either the potato or tapioca starch products.

Roll-Dried Starch Added	Percent Added Starch Size Based On Dry Pulp	Mullen Test Factor
Corn Starch	1 2 3	0.802 0.821 0.876
Potato Starch	1 2 3	0.851 0.939 1.08
Tapioca Starch	1 2 3	0.905 0.993 1.100

That is to say, pregelatinized and dried potato and tapioca starch powders, without any other treatment whatsoever, are approximately three times as effective in increasing the strength of paper as is the pregelatinized and dried corn starch powder. This result, coupled with the results shown in the previous example for products made with no borax addition (which show that at the 2 percent starch size addition level potato starch imparts about twice the increase in strength that can be attributed to a corn starch product, even when made under very favorable conditions of liquid-feed) clearly shows the very unfavorable economic position for prior art pulp sizes made from domestic cereal starches.

Example 7

An hydroxyethyl corn starch product was made by the procedures as given in Example 1. The borated dried powder was tested at several addition levels as a size for paper pulp at the beaters and the results were found to be substantially the same as those shown in Example 3 for the hydroxyethyl grain sorghum starch.

Example 8

The hydroxypropyl corn starch product made in Example 2 was tested as a size for paper pulp and the results were found to be substantially the same as those shown in Example 3 for the hydroxyethyl grain sorghum starch.

This application is a continuation-in-part of application Serial No. 396,767, filed December 7, 1953, now abandoned.

I claim:

1. The process of sizing paper pulp which comprises adding to the pulp at a stage in the manufacture of paper prior to formation of the paper web, at least about 0.03 percent of a starch ether, based on dry weight of ether and pulp, which has been gelatinized and dried in contact with about 0.25 to 15 percent of borax, based on the dry weight of the starch ether; said ether being from the group consisting of hydroxyethyl and hydroxypropyl corn starch and hydroxyethyl and hydroxypropyl grain sorghum starch.

2. Paper pulp which has been sized prior to the formation of the web with at least about 0.03 percent of a starch ether which has been gelatinized and dried in contact with about 0.25 to 15 percent of borax based on the dry weight of starch ether; said ether being from the group consisting of hydroxyethyl and hydroxypropyl corn starch and hydroxyethyl and hydroxypropyl grain sorghum starch.

3. The process of making a starch product for sizing paper pulp which comprises etherifying starch from the group consisting of corn and sorghum grain with an etheri-

5 fying agent from the group consisting of ethylene oxide and propylene oxide and gelatinizing and drying the starch ether in contact with borax, the borax being added at some stage in the process prior to drying and the amount being 0.25 to 15 percent, based on the dry weight of the ether, said drying step being carried out rapidly while permitting free evaporation of water.

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