United States Patent Office

3,132,066

Patented May 5, 1964

3,132,066

PROCESS OF ADDING STARCH PHOSPHATES TO PAPER PULP CONTAINING TITANIUM DIOXIDE TO IMPROVE RETENTION THEREOF

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No Drawing. Continuation of application Ser. No. 808,925, Apr. 27, 1959. This application May 4, 1961, Ser. No. 107,651

1 Claim. (Cl. 162—175)

This invention relates to processes for making paper and more particularly to stages in these processes wherein the paper pulp is treated prior to the stage where the paper sheet is actually formed on the "wire." This invention is also, more particularly concerned with said treatments wherein certain adjuncts are added to the pulp, such as opacifiers or pigments, brighteners, and starch sizing agents, in order to improve certain wanted characteristics of the paper sheet being formed.

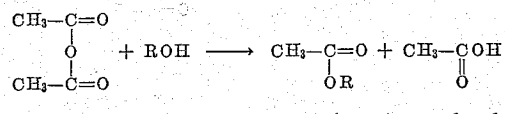
Various starch products have been used in the prior art as sizing agents for paper pulp in an operation broadly referred to as beater sizing. The starch is added to the pulp primarily to increase the strength of the sheet, as measured for example, by the Mullen test for bursting strength of the paper sheet after the sheet has been formed from the pulp. However, these sizing starches of the prior art are not satisfactory in several respects, most important of which are the following: (1) sizing efficiency of prior art starches in increasing strength of paper sheet is relatively low, per unit weight, compared to certain nonstarch sizing agents; (2) when pigments or opacifiers or whiteners, such as for example, titanium dioxide (TiO_2) are applied to the pulp, the added starch size acts to decrease the retention of the added TiO_2 by the paper pulp, which even with no other adjunct added, is already at a relatively low order, often being as low as 20 to 40 percent, only, of the total added TiO_2.

The situation described is aggravated by the fact that the addition of the most desirable pigments, e.g., TiO_2, to paper pulp very materially lowers the Mullen test of the paper to such unacceptably low levels as to require the addition of a sizing agent, even for pulps and in instances wherein the pulp by itself would not require the addition of a strength promoting size. Unfortunately, the defects noted for paper pulp sizing starches apply most particularly, and to the highest degree, to products made from starches which are most available and are made in greatest volume, as for example corn, grain sorghum and their so-called "waxy" varieties.

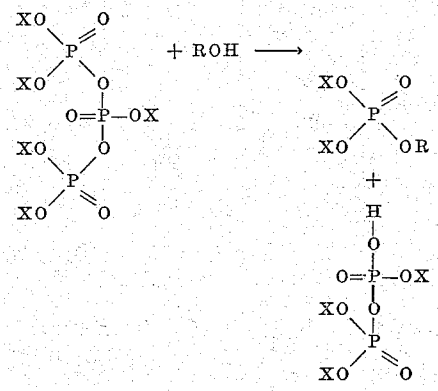
We have now discovered in accordance with this invention, that when certain starch phosphates are used to size paper pulp, their efficiency in increasing the strength of the paper sheet is of a surprisingly relatively high order, that these starch phosphates do not adversely affect the retention of TiO_2 by paper pulp; indeed under normal operating conditions they actually promote the retention of TiO_2 by the pulp to a most surprising degree, and that in spite of this very high TiO_2 retention, the starch phosphate size addition gives a paper sheet with exceptionally high and unanticipated strength.

In our U.S. patent application, Serial No. 576,524, now U.S. Patent No. 2,884,413, we have disclosed procedures for making starch phosphates, the products of which, among others, are suitable for carrying out our herein described invention on the use of starch phosphates for sizing paper pulp. The present application is a continuation of our pending U.S. patent application, Serial No. 808,925, filed April 27, 1959, now abandoned, which was a continuation-in-part of our U.S. patent application, Serial No. 576,524, filed April 6, 1956, now U.S. Patent No. 2,884,413, which was a continuation-in-part of application Serial No. 388,914, filed October 28, 1953, now abandoned. In our said patent we have disclosed that when starch in semi-dry state is heated under certain conditions in contact with an inorganic phosphate salt from the group consisting of metaphosphates, polymetaphosphates, pyrophosphates, tripolyphosphates, and mixtures thereof, the starch reacts with the phosphate to form a partial ester (simple ester), or the salt of a partial ester of the starch and orthophosphoric acid. Optionally, the starch ester may be cross-linked by continuing the heat treatment in the presence of certain alkaline substances.

There appear to be three types of reactions between starch and the phosphate salts specified. The first, such as may take place when tripolyphosphate is used under neutral to slightly alkaline conditions, may be considered analogous in some respects to esterifications using an organic acid anhydride, such as acetic anhydride. Thus, just as this condensed or polyacetic acid is presumed to react in an exchange with starch (ROH)



to give an acetic acid ester of starch and a molecule of acetic acid, so tripolyphosphate, for example, may react also in an exchange reaction involving one or more of the anhydro-phosphoric acid residues of the tripolyphosphate to form the orthophosphate ester of starch and leaving the corresponding acid:

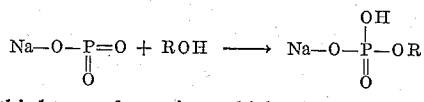


X represents H or monovalent metal.

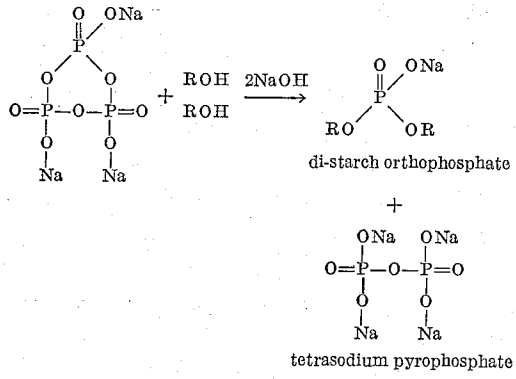
Starch may then conceivably react again in similar fashion with the acid dimer salt to give another starch orthophosphate ester group and a molecule of orthophosphate. In support of this theory, it has been noted that when sodium tripolyphosphate is heated with unbuffered starch, the pH value of the reaction mixture

drops progressively from about 8.5 to 9, to values less than 7. In further support of this interpretation, electrometric titration of the polyphosphate with acid and alkali gives two inflection points when plotted graphically against pH, one at pH 3.5 and the other at pH 9.75, whereas the mono-starch phosphate and the by-product phosphate salts, both give two inflections, or "neutralization" points identical to those of orthophosphate which are pH 4.0 and pH 9.2, using procedures given hereinafter. The latter result is convincing proof that the starch product formed according to procedures hereinafter described is a mono-starch orthophosphate ester.

The second type of reaction may be simply an addition reaction, similar to the addition of HOH to metaphosphate to form orthophosphate. With starch and sodium metaphosphate this would be:



The third type of reaction, which when desired, may be induced to proceed prior to, simultaneous with, or subsequent to the first two reactions and may be considered as an extension of these first two reactions although preferably it is induced by adding an alkaline metaphosphate. This reaction leads to the production of di-starch orthophosphate in which the orthophosphate ester group established a cross-link between starch molecules. The reaction is illustrated using sodium trimetaphosphate:



In carrying out our invention, the phosphate salt reagent is first added to starch. This addition may be effected in several ways. The simplest and one of the most effective ways is to add the phosphate to an aqueous starch slurry, at room temperature, and, when it is desired to produce a starch phosphate ester in granule form at a temperature insufficient to effect gelatinization of the starch, stir the slurry well and filter the same. If a phosphate salt is added to a starch slurry having a density between 17° Bé. and 22° Bé., which range has been found to cover practical operating conditions, the amount of such salt retained by the starch after filtration is about 10 to 75 percent of the salt originally added, depending upon conditions of addition and amount of washing. The filtrate, obtained from one such filtering operation and with appropriate additions of phosphate salt reagent to compensate for the amount retained by the filtered starch, may be used advantageously for starch to be treated subsequently.

Alternately, the slurry of starch in an aqueous solution of the phosphate reagent may be spray-dried or roll-dried, in which case all of the phosphate reagent added is incorporated with the starch. The starch may, or may not, be gelatinized during the spray-drying operation but is generally gelatinized by roll-drying. In fact, any desired method may be used for admixing the phosphate salt reagent and starch which tends to insure that the salt will be evenly distributed throughout the starch.

The amount of phosphate salt reagent admixed with

the starch during the heat treatment to be described subsequently may vary from about 0.5 to about 10 percent calculated on the anhydrous salt, based on the dry weight of the starch, and the pH of the mixture, as measured on a 20 percent aqueous dispersion of the mixture using a glass electrode, should be between 4 and 11.5, depending on the particular type of phosphate reagent employed and which of the three above described reactions is to be promoted. Use of pH levels less than about 4 promotes hydrolysis of the starch or starch product which is undesirable for many applications; use of pH levels higher than 11.5 makes possible alkaline degradation of the starch, hydrolysis of the meta- or polyphosphate and other side reactions all of which result in poor phosphorylation efficiency.

The second step of carrying out the present invention is to adjust the moisture content of the starch to 20 percent or below, a practical range being about 5 to about 20 percent, if, for example, the slurry method, which is the preferred method, has been used to admix the starch and phosphate salt. If it is desired to keep starch in granule form during the entire treatment, the starch-phosphate salt mixture may be dried satisfactorily in typical starch driers, e.g., those wherein heated air is forced through the drier. A drier of the continuous belt type sold by Proctor and Schwartz Company is satisfactory. Air temperatures of from 120° F. to 255° F., for example, are satisfactory in drying starch without gelatinizing it in this type of starch drying equipment. The temperature of the starch phosphate mixture during such drying should not exceed about 60° C. to 70° C. until the moisture content has been reduced to about 20 percent in order to insure the greatest beneficial effect from the added phosphate reagent in the production of mono-starch orthophosphate, and particularly if the starch granule form is to be preserved. It has been found that higher temperatures at higher moisture levels under such conditions of drying induce an undue amount of hydrolysis of the phosphate reagent and other undesirable side reactions involving the starch itself due to the long time of contact. However, when the drying is effected on heated rolls or by spray drying, the initial moisture content may exceed 20 percent since the removal of moisture is instantaneous, as will be explained more fully hereinafter.

The next step in the process of our invention is the heat treatment. This should be carried out at about 100° C. to about 160° C., i.e., the temperature of the starch-phosphate salt mixture should be within this range to effect the desired reaction. Temperatures lower than 100° C. would produce virtually no phosphorylation if indeed such a reaction does occur at all at these lower temperatures. Temperatures substantially above 160° C. are difficult to control and the products may become discolored and degraded, making them less suitable for many applications, although such temperatures may be used if the time is extremely short and care is exercised in handling the product. The preferred range is 120° C. to 140° C. The time will depend upon the type of product desired. The solubility of the simple ester increases as the time, temperature, and amount of phosphate reagent increase and is greatest when all three are at their maximum. The degree of cross-linking, when this reaction is to be promoted, also increases as the time, temperature, and amount of phosphate reagent increase, but is primarily influenced by pH control appropriate to the type of phosphate reagent employed. Under some conditions, cross-linking may reach the point where the starch cannot be gelatinized. It is not practical to set forth the exact time, temperature and amount of salt for each product possible of production. However, with the aid of the information set forth in the examples which follow and suitable preliminary tests, such as gelatinization characteristics, paste viscosity, paste clarity, and the results of electrometric titration, those skilled in the art will

be able to select conditions suitable to produce the product they desire.

The heat treatment of the starch-phosphate salt mixture at the temperature specified should be carried out in equipment which provides for removal of moisture. For example, one may employ a vacuum oven, infra-red heating of the material on a moving belt, etc.

It is also possible to effect the heat treatment on heated rolls or in a spray drier. In such cases, it is possible to effect gelatinization, drying and phosphorylation in one treatment provided the aforementioned conditions of pH and temperature are observed. Either a starch slurry or paste containing the phosphate may be roll or spray-dried. The moisture is reduced instantaneously by such methods to within the range heretofore specified and the phosphorylation reaction then can take place instantaneously also. In cases where roll or spray-drying of the material has been carried out at temperatures below those specified, it is possible to obtain the desired phosphorylation by subjecting the dried material to heat treatment at the proper temperatures.

After the heat treatment, the starch ester may be washed in appropriate solvents to effect purification and dried in conventional manner.

The process is applicable to any starch (corn (maize), wheat, grain sorghum, etc.) in raw or modified or derivatized form, in gelatinized or granule state. For example, in addition to raw starch, thin boiling starches, dextrins, derivatives of starch such as ethers and esters other than phosphate esters may be treated in accordance with the principles of our invention. The ethers and esters must contain at least one free hydroxyl group. The term "starch product," as used hereafter, is intended to include all of the aforementioned products.

The pH, as already mentioned, may vary from about 4 to about 11.5. At lower pH values the simple mono-starch phosphate esters are formed almost exclusively while at the higher pH values the cross-linked esters are formed. For example, at pH about 4 to 5 metaphosphates form substantially only simple esters. Above these pH values a very definitely larger proportion of di-starch phosphate (cross-linked esters) is formed. The pH values for the formation of simple esters when polymetaphosphates, pyrophosphates and tripolyphosphates are used are preferably from about 7 to 9, whereas from about 9 to 11.5, the cross-linked esters are formed to a very much larger extent. The degree of cross-linking increases with increase of pH. The pH may be increased by the addition of alkaline substances, such as sodium carbonate, sodium bicarbonate, sodium orthophosphate and sodium hydroxide, or other bases.

The end products of this invention will have a degree of substitution (D.S.) preferably up to 0.1 orthophosphate group per anhydro glucose unit, although obviously the degree of substitution (D.S.) may be increased substantially above this level by an extension of the procedures hereinafter described, and will be water soluble or insoluble depending upon the degree of phosphorylation and the manner of treatment. They have improved properties in respect of paste clarity, significantly higher hot paste viscosity and a marked reduction in the tendency of cold paste body to increase with age ("set-back") and their pastes or sols have "long" flow as compared with properties of the starches from which they were derived.

Thus, for example, corn starch and certain products derived therefrom form cloudy or opaque and relatively short bodies pastes when dispersed or gelatinized in water and form typical, non-reversible gels at higher concentrations on standing. However, when corn starch is partially esterified so as to contain as little as 0.03 simple mono-starch phosphate group per anhydroglucose unit (D.S.=0.03) the colloidal properties of the gelatinized starch ester are so profoundly altered as a result of esterification that the paste now resembles a potato starch sol (to which it is now closely related in chemical structure by virtue of phosphate ester groups).

When, and if, a relatively small number of di-starch phosphate cross-links are produced in the mono-starch phosphate ester either prior to, simultaneously with, or subsequent to production of the latter, then although in certain applications clarity of paste and freedom of set-back is preserved, the cross-linked, starch phosphate forms a relatively very thick, but very much less cohesive paste. Moreover, the cross-linked product forms pastes or sols with viscosity and body which are very much more stable to the effect of such agents or conditions as high temperature and pressure, shearing action, acidity, alkalinity or added soluble materials, such as sugars. In these improved characteristics, the mono-starch phosphate esters which are additionally cross-linked with a minor proportion of di-starch phosphate cross-links equal or excel the colloidal paste characteristics of waxy or non-cereal starches which are cross-linked by orthodox procedures such as by treatment with epichlorohydrin or by aldehydes. These partially cross-linked starch phosphates are accordingly particularly useful in applications where the starch pastes are subjected to destructive influences, such as, for example, to high temperature, pressure and shearing action.

From the foregoing it will now be apparent that a wide variety of products may be made for a large number of applications and that the number of mono-starch phosphate groups introduced as well as the proportion of di-starch phosphate cross-links may vary with the application.

Before description of the specific examples analytical procedures and method for comparison will be described.

Phosphorus was determined by an adaptation of the method described by Howk and De Turk, Ind. Eng. Chem. Anal. Ed., 4, 111 (1932). All products were first extensively washed either in aqueous alcohol, or in the case of water insoluble product, in distilled water prior to analysis. In several instances samples of the starch products of the examples subsequently given were additionally purified by dialysis against distilled water with no significant change in phosphorus content.

Clarity of paste was determined by gelatinizing one percent by weight of starch in water at pH 6.5 in a boiling water bath for 30 minutes after the paste temperature reached 90° C., cooling to 25° C. for one hour and measuring the percent light transmission at λ=650 mμ in a Coleman spectrophotometer, model 14.

Scott viscosity values were determined on hot pastes at pH 6.5 essentially as described by Kerr, "Chemistry and Industry of Starch," 2nd edition, Academic Press, Inc., New York (1950), pages 119 to 121. Because of the relatively high viscosity of some of the phosphate esters made from otherwise unmodified starch, a concentration of 5 grams, dry basis, in 280 ml. of water was used and the viscosity was reported as seconds for delivery of 50 ml. of the paste. Scott viscosity on the phosphate esters of acid modified starch (Table II) were determined at a concentration of 28.35 grams (at 12 percent moisture) in 280 ml. of water and viscosity was reported in seconds for delivery of 100 ml.

D.S. was calculated from the formula, D.S.=percent P of sample per percent P of a 1 D.S. starch phosphate which is, D.S.=percent P of sample per 12.8.

Stormer cold paste body, or consistency, was determined essentially as described by Kerr, "Chemistry and Industry of Starch," pages 123 and 124. Concentration of starch was varied from 5 to 15 grams per 280 ml. of water (as noted in Tables I and II) depending on the paste body and results were expressed as seconds per 100 revolutions.

The electrometric titration hereinabove referred to was run on 20 percent dispersions of the purified starch product in water into which was immersed the glass and secondary electrodes of a Beckman pH meter. The pH was

first adjusted to a value slightly less than 2.0 with hydrochloric acid and then with stirring 0.1 N sodium hydroxide was added in small portions and the resulting pH noted. Finally, observed pH values were plotted against amounts of alkali added.

These several types of starch phosphates were used in paper pulp sizing tests with results as shown in the examples, given hereinafter.

Mullen tests were performed using the accepted Mullen tester for measuring bursting strength and the values reported are the average for at least 15 tests on each paper sample. Tests were run under comparable conditions, that is, in any series given in the examples, conditions for preparing the sheet, such as, type and batch of pulp, charge of pulp treated, beating time and temperature, addition of standard additives such as rosin size and alum, pH values and weight of paper sheet produced were the same. Mullen test values were corrected for minor variations between samples such as, for example, sheet weight.

Titanium dioxide retention values were calculated from results obtained by ashing the paper pulp, the titanium dioxide, the starch samples, the "control" paper sheet and the experimental sample sheet.

The following are examples of the application of the invention to practice. These specific examples are to be regarded as merely informative and typical and not as limiting the invention in any way.

EXAMPLE 1

Reaction of Corn Starch With Sodium Metaphosphate at Neutral pH

Fifty-eight grams of commercial grade sodium metaphosphate was dissolved in 500 ml. of water. Then, one molar weight of corn starch (180 grams at 10 percent moisture) was stirred in. The pH of this mixture was adjusted to approximately 7 with NaOH. After 15 minutes, the starch was filtered by suction and the cake was air dried to approximately 12 percent moisture content. By analysis, it was found that 9 grams of sodium metaphosphate (0.09 mole) had been taken up by the starch, the balance being in the aqueous filtrate.

The starch was heated for one hour at 120° C. in a vacuum oven and then cooled. The product was washed three times by suspension in 250 ml. of water followed by filtration by suction. The pH of the first suspension was 5.4, indicating that phosphorylation took place between pH 7 and 5.4. The pH of the third wash was 6.0. The washed product was dried for analysis with results as shown in Table I. These results indicate a phosphorus content of 0.35 percent equivalent to a D.S. of 0.03 as orthophosphate groups. When this starch phosphate was gelatinized by heating in water, a paste was formed of very much greater viscosity (as indicated by Scott viscosity value) and body (as indicated by Stormer consistency values) which did not increase materially with age and with greatly improved clarity as compared with the untreated corn starch. Pastes showed no tendency to gel with age.

Comparing the characteristics of this product, such as percent phosphorus, clarity and viscosity of paste, with characteristics of products described in the following examples, particularly Examples 3 and 4, it is obvious that a portion of the phosphate groups introduced into the starch were di-starch phosphate cross-linkages. The initial phases of the phosphate cross-linking reaction produces an abnormally higher viscosity and a smaller increase in paste clarity for any given percentage of phosphorus introduced into the starch than does simple esterification.

TABLE I.—PROPERTIES OF STARCH PRODUCTS MADE IN EXAMPLES 1 TO 8 AND 10 TO 12

Product	Reagent	Amt. reagent per molar wt. starch, g.	Reaction time at 120° C., hrs.	D.S. as orthophosphate groups	Clarity as percent L.T.	Scott viscosity, 5 g./280 ml., sec. per 50 ml.	Stormer consistency tests, 5 g. product in 280 ml. H_2O, 75 g. wt., sec./100 revolutions	
							1 hr. at 25° C.	24 hrs. at 25° C.
Example 1	Metaphosphate (pH 7)	3	1	0.03	59	121	[a] 102	[a] 67
Example 2	Metaphosphate (Carbonate pH 8.5).	9	1	.06				
Example 3	Metaphosphate (pH 4)	11	1	.03	86	15	34	33
Example 4	Tripolyphosphate	9	1	.03	74	30	214	232
Example 5	do	10	2	.04	78	45	[a] 52	[a] 26
Example 6	do	5	2	.03	65	21	62	49
Example 7	do	3	2	.02	58	21	72	53
Example 8 [b]	do	8	1	.04	77	28	122	130
Example 10	Hexametaphosphate	7	1	.03	60	21	57.3	57.3
Example 11	Pyrophosphate	5	1	.015	61	17	58.0	57.3
Example 12	Tripolyphosphate / Metaphosphate	9 / 5	1	.05	76	570	[a] 590	[a] 540
Corn starch	None				25	11	[c] 34	[c] 220
Grain sorghum	do				35	11	[c] 126	[c] 422
Potato starch	do				85	61	142	129
Potato starch	do				90	24	50	48

[a] 175 g. wt.
[b] Grain sorghum starch used; in all other examples, used corn starch.
[c] Used double the concentration of unmodified corn and grain sorghum starches because using 5 grams in 280 ml. of water, Stormer values were about 10 secs. of very nearly that of water.

EXAMPLE 2

Reaction of Corn Starch With Sodium Metaphosphate and Added Sodium Carbonate

This example illustrates how cross-linking may be obtained to an extent that the product can not be gelatinized in water. The procedure outlined in the preceding example (Example 1) was repeated with the exception that approximately 12.5 grams of a 4:1 mixture of sodium bicarbonate and sodium carbonate was added to the slurry of starch in the metaphosphate solution prior to the first filtration step. The pH of this mixture was 8.5. Analysis of the washed product, as shown in Table I, indicates that it contained 0.7 percent phosphorus.

When 5 grams of this starch phosphate was heated in 100 ml. of water at 95° C. for 20 minutes, the granules failed to gelatinize and settled from suspension when the cooked mixture was allowed to stand, indicating that the starch was highly cross-bonded with phosphate groups.

EXAMPLE 3

Reaction of Corn Starch With Sodium Metaphosphate Under Acidic Conditions

The procedures outlined in Examples 1 and 2 were repeated with the exception that nothing was added to the mixture of corn starch and sodium metaphosphate in water. The pH of the starch slurry before filtration was 4.0.

After the dried starch cake had been heated for one

hour at 120° C., it was thoroughly washed in water, at the same time the pH of the product being adjusted to 6.5 with dilute sodium hydroxide. The pH of the first aqueous suspension of the heated product was 4.1.

Characteristics of this product are shown in Table I. Pastes made from this starch phosphate were "long" in flow characteristics and of very high clarity. These properties, together with the lower paste viscosity of this product compared with the product of Example 1, indicate that there was much less cross-linking in the product of this example, than in the product of Example 1, and, of course, very considerably less cross-linking than in the product of Example 2.

These first three examples indicate that at lower pH values metaphosphate reacts with starch to form simple phosphate ester groups with little or no phosphate cross-linkages between starch molecules, but as the pH of reaction is raised, cross-linking becomes more pronounced.

EXAMPLE 4

Reaction of Corn Starch With Sodium Tripolyphosphate for One Hour at 120–130° C.

One molar weight of corn starch (180 grams at 10 percent moisture) was stirred into 215 ml. of water into which had been dissolved 15.5 grams of sodium tripolyphosphate. The pH was approximately 8.5. The starch was filtered by suction to form a cake of approximately 45 percent moisture content. This was dried at 60° C. to approximately 12 percent moisture content. By analysis, 9 grams of the polyphosphate (0.08 mole calculated as a sodium monophosphate) was retained by the starch, the balance being in the aqueous filtrate.

This starch was now heated with stirring, and with provision for moisture removal, at temperatures between 120 and 130° C. and then cooled. The starch product suspended in 250 ml. of water, now showed a pH of 7.0. It was filtered and washed twice more by suspension in 250 ml. of water followed by filtration with suction. The starch was then dried to a commercial moisture content of approximately 10 percent for a powdered starch.

Analytical values shown in Table I indicate that the product contained 0.37 percent phosphorus, equivalent to a starch phosphate ester with a D.S. of 0.03 as orthophosphate groups. The starch when gelatinized by heating in water formed a very viscous sol (as indicated by Scott viscosity value) with little or no tendency to gel or increase in viscosity with age (as indicated by Stormer consistency values). The sol had very high clarity compared with untreated corn starch (both measured at pH 6.5) and had "long" flow characteristics similar to tuber or waxy starches.

EXAMPLE 5

Reaction of Corn Starch With Sodium Tripolyphosphate for Two Hourse at 120° C.

The procedure essentially as described in the previous example (Example 4) was repeated with the exception that the heating period at 120° C. was extended to 2 hours.

The characteristics of the purified product as shown in the table indicate that phosphorylation was increased so that the starch product contained 0.47 percent P (equivalent to D.S. 0.04 as orthophosphate groups). This resulted in a product which when gelatinized by heating in water gave a sol of higher viscosity, higher clarity and heavier body when cold than the product of the preceding example. The colloidal properties of this product compared favorably with those of two randomly selected commercial potato starch samples, as shown in Table I.

EXAMPLES 6 AND 7

Reaction of Corn Starch With Different Amounts of Sodium Tripolyphosphate at 120° C.

The procedures given in Example 5 were repeated essentially as described wth the exception that preliminary conditions were so adjusted that lesser amounts of sodium tripolyphosphate were taken up by starch for reaction in the dry state at 120° C. for 2 hours.

In Example 6, a molar weight of starch took up 5 grams of the polyphosphate, and in Example 7, 3 grams. As shown in Table I, the finished products formed pastes with progressively less clarity, less viscosity and body than corn starch which had been similarly treated with 9 grams of the salt.

EXAMPLE 8

Reaction of Grain Sorghum Starch With Sodium Tripolyphosphate

The procedure given in Example 4 was repeated with the exception that grain sorghum starch was used instead of corn starch. After one hour reaction period at 120° C., the washed product had a phosphorus content of 0.44 percent equivalent to a D.S. of 0.04 as orthophosphate groups, as shown in Table I. This starch phosphate ester formed a sol with exceptionally high clarity and high viscosity and which showed practically no tendency to retrograde or to set to an irreversible gel on standing. The flow of this paste was long and stringy, resembling pastes of the tuber and waxy starches.

EXAMPLE 9

Reaction of Acid-Modified, Thin Boiling Corn Starch With Sodium Tripolyphosphate

An acid-modified, thin boiling corn starch (having an alkali fluidity of 50 and a 28.35 grams Scott test approximately 40 seconds per 100 ml.) was treated with sodium tripolyphosphate in a variety of ways. The object was to show not only that it is feasible to phosphorylate a modified starch product by our process in order to improve its colloidal properties but also to show:

(1) That the amount of modification in properties is dependent on the amount of sodium tripolyphosphate used, other conditions being the same.

(2) And that simply adding the tripolyphosphate to the starch in an aqueous slurry does not materially improve the colloidal properties of the starch. That is, the polyphosphate does not act as a plasticizer or dispersing agent or other type of adjunct sufficiently to modify the paste properties, per se, but rather the decided improvement which results in paste properties when starch is treated with tripolyphosphate in our process is the result of an esterification reaction and the creation of a starch phosphate, as claimed, such as takes place almost entirely in the dry-heating phase of our process.

(A) Approximately 30 grams of sodium tripolyphosphate was dissolved in 400 ml. of water to which was added with stirring 180 grams of a commercial 50-fluidity grade of corn starch at 10 percent moisture content. The starch was filtered, the cake was air-dried to approximately 12 percent moisture content and then the starch was heated for one hour at 120° C. It was found that the starch had taken up approximately 6 grams of the tripolyphosphate. The starch product was triple washed with water and dried to 10 percent moisture content as detailed in Example 1.

(B) The experiment was repeated using only 15 grams of the tripolyphosphate to 180 grams starch in aqueous suspension.

(C) The experiment was repeated using only 7.5 grams of the tripolyphosphate to 180 grams of starch in aqueous suspension.

(D) Part A was repeated in every detail except the heating period at 120° C. was omitted.

The characteristics of the treated starch products are

compared with those of the untreated, 50-fluidity corn starch in Table II below:

TABLE II.—CHARACTERISTICS OF TREATED AND UNTREATED 50-FLUIDITY CORN STARCH

Product	Sodium tripolyphosphate retained per 180 g. of starch, g.	D.S. as orthophosphate groups	Paste clarity as percent L.T.	Scott vis., 28.35 g./280 ml., sec. per 100 ml.	Stormer consistency, 15 g./280 ml. conc. and using 75 g. wt., sec./100 revolutions	
					1 hr. at 25° C.	24 hrs. at 25° C.
A	6	0.031	88	43	34	41
B	3	0.019	83	42	30	80
C	1.5	0.016	82	40	32	94
D (not heated)	6		61	41	35	214
50-F starch, untreated			58	40	43	178

From these results it will be seen that the properties of a premodified starch, such as clarity of paste and consistency stability on standing, are improved in the same manner as a native starch is improved by phosphorylation. It will also be observed that the extent of improvement depends on the amount of tripolyphosphate added to the starch before the reaction period. It will be noted further that simply treating starch with sodium tripolyphosphate in aqueous solution, without providing more optimal conditions for phosphorylation to take place does not materially alter the characteristics of the starch.

EXAMPLE 10

Reaction of Corn Starch With Sodium Hexametaphosphate

One molar weight of corn starch was stirred into 215 ml. of water containing 12.8 grams of sodium hexametaphosphate. The pH was 7.4. The starch was filtered by suction and air-dried. By analysis it was found that the starch had taken up approximately 7 grams of the phosphate (0.07 mole as sodium metaphosphate).

The air-dried starch was heated for one hour whereupon it was cooled and washed three times by suspension in 250 ml. water and filtering by suction. The final pH was 6.7.

Data on this product set forth in Table I show that a starch phosphate ester formed with a D.S. of 0.03 as orthophosphate groups and that the ester formed a sol in water which had higher viscosity and clarity than untreated corn starch and no tendency to set up to a gel on standing.

EXAMPLE 11

Reaction of Corn Starch With Tetrasodium Pyrophosphate

The procedure given in Example 10 was repeated, using tetrasodium pyrophosphate instead of sodium hexametaphosphate and dissolving 10 grams of the salt in the water used to slurry the starch. The pH of this phosphate-starch slurry was 8.5. Approximately 5 grams of the phosphate was taken up by the molar weight of starch. The purified final product had a phosphorus content of 0.18 percent equivalent to a D.S. of 0.015 as orthophosphate groups. As shown in Table I, this product formed a sol when heated with water which had somewhat higher viscosity and clarity than untreated corn starch. Pastes made from the starch showed no tendency to thicken on standing.

EXAMPLE 12

Reaction of Corn Starch With a Combination of Sodium Tripolyphosphate and Sodium Metaphosphate

The following example is given to illustrate how both cross-linking and simple phosphorylation may be simultaneously controlled by use of a combination of different phosphates. In this example sodium tripolyphosphate at pH 7.9 was used to effect substantially simple mono-starch phosphate production and a lesser addition of metaphosphate was added which at this pH produces substantially only distarch phosphate cross-linkages.

The procedures given in Example 4, using tripolyphosphate and corn starch, were repeated essentially as described with the exception that sufficient commercial sodium metaphosphate was added to the aqueous starch slurry so that the filtered starch cake took up 5 grams of the sodium metaphosphate as well as 9 grams of sodium tripolyphosphate per 162 grams, dry basis corn starch. The pH of the final slurry was 7.9.

After drying the filtered starch cake to approximately 10 percent moisture content, it was heated for one hour at 120° C., cooled and suspended in water (162 g. in 265 ml.). The pH was 6.5. The starch product was filtered, washed twice more by suspension in water and filtering, and then air-dried to a moisture content of 10 percent.

Analytical results on the purified product, shown in Table I, are typical for a mono corn starch orthophosphate ester of about 0.03 to 0.04 D.S. which has also been cross-linked with a limited amount of di-starch phosphate groups.

EXAMPLE 13

Production of Starch Phosphate by Spray-Drying Starch and Pyrophosphate

Grain sorghum starch was stirred into water into which had been dissolved 0.5 lb. of sodium pyrophosphate for each 100 lb. of starch treated. The starch concentration in the slurry was approximately 10 percent. Equal quantities of tetrasodium pyrophosphate and disodium dihydrogen pyrophosphate were employed so as to adjust the pH level to 7.0. This slurry was then heated with stirring to approximately 210° F. and after it had become sufficiently fluid, it was fed to the atomizing nozzle (Spray Systems Company) of a parallel air flow, spray drier at an atomization pressure of 6,000 to 7,000 p.s.i. gauge. The inlet air temperature was 340° F. and the outlet temperature was 230° F. During this cycle, the starch was gelatinized and dried to a moisture content of approximately 5 percent.

The product from the spray drier was a white powder which readily dispersed in cold water to form a relatively heavy bodied, homogeneous, smooth, collodial system.

A 25 gram sample of this product was prepared for analysis by extraction with 250 ml. of 50 percent by volume aqueous methanol for 72 hours. The product was filtered by suction and washed on the filter with two 100 ml. portions of 50 percent aqueous methanol. The cake was then extracted for 24 hours with 200 ml. of 50 percent aqueous methanol, filtered by suction and again washed on the filter with two, 100 ml. portions of 50 percent aqueous methanol. The product was then dehydrated by successive washes with absolute methanol during a period of 24 hours and air-dried.

Analysis for phosphorus by the Parr bomb method described previously showed 0.091 percent, which is equivalent to a phosphate content of 0.273 percent, dry basis.

EXAMPLE 14

Production of Starch Phosphate by Spray-Drying a Mixture of Starch and Pyrophosphate and Additionally Heating the Product From the Spray Drier

Starch was treated as in Example 13 and the dry powdered product from the spray drier at 5 percent moisture content was fed as a thin layer to the belt of a continuous heater. Heating of the starch on the belt was accomplished by infra-red radiation. Movement of the starch on the belt was at such a rate, and the radiation was of such intensity that the starch product of Example 13 was heated to approximately 350° F. in 60 to 90 seconds and maintained at this temperature for 90 seconds. At the end of the belt, the starch product was cooled to room temperature in about 5 seconds.

During this heating, the moisture content of the starch product was reduced to the level of approximately 1 percent.

The product of this example formed a much more viscous collodial mass when stirred into cold water than the product of Example 13. Moreover, the paste or sol was exceptionally homogeneous and smooth.

A sample of this starch phosphate was purified for analysis by the procedure given in Example 13. The content of phosphorus found was 0.102 percent, which is equivalent to a phosphate content of 0.306 percent, dry basis.

For comparison, grain sorghum starch, purified by aqueous methanol and absolute methanol extraction, in the manner used to purify the products of Examples 13 and 14, showed a phosphorus content of 0.031 percent, which is equivalent to a phosphate content of only 0.093 percent, dry basis.

From these comparisons it is obvious that some phosphorylation of the starch occurred during the spray-drying operation, under the conditions, temperature and time, employed in Example 13; 0.273—0.093=0.180 percent phosphate groups were introduced by these procedures, which it is believed accounts for the improved colloidal properties and the improved odor and taste of the product compared to untreated starch which is merely spray-dried or roll-dried.

During the secondary heating stage, employed in Example 14, phosphorylation by the added pyrophosphates was further increased, 0.306—0.093=0.213 percent phosphate groups, now having so been introduced into the starch product. It is believed that this further increase in phosphate ester groups introduced, accounts for the further improvement in colloidal properties of the product, particularly the excellent homogeneity of a cold water dispersion of the powdered product.

EXAMPLE 15

Spray-Drying and Heating Mixtures of Corn Starch and Pyrophosphates

Corn starch was wet blended with 0.5 percent pyrophosphate and the mixture spray-dried according to the procedures outlined in Example 13. The dried powdered product was additionally heated by the method given in Example 14. The final corn starch phosphate was quite comparable to the product obtained in Example 14. Compared to corn starch which had merely been spray-dried and heated, the product of Example 15 dispersed very much more readily in cold water and formed a much more homogeneous and viscous aqueous system.

EXAMPLE 16

Higher Ratio of Pyrophosphate to Starch

The procedures given in Examples 13 and 14 were reepated using a ratio of 2.5 percent added tetrasodium pyrophosphate and 2.5 percent disodium dihydrogen pyrophosphate to starch. The final product formed a very viscous, homogeneous mass when mixed into cold water.

Other proportions of the sodium pyrophosphate to the acid sodium pyrophosphate have been employed, with resulting pH levels of the reaction mixture being different from the level employed in Example 13, which is pH 7.0. When higher proportions of the acid sodium pyrophosphate are used and when pH levels lower than about pH 6.0 are used, the end products are comparable to those obtained in Examples 13 and 14 except that cold water dispersions are of higher clarity and the viscosities are lower. This is due no doubt to the acid hydrolysis of the glucosidic linkages in the starch polymer, brought about by the acidity present at the temperatures employed. When higher proportions of the tetrasodium pyrophosphate were used, and when the pH value of the reaction mixture was higher than about pH 8.0, then the product developed a yellowish to brownish color, and a slight caramelized odor, due quite likely to an atmospheric oxidation of the starch molecule at the alkalinity and the temperatures employed.

Accordingly, although starch may be phosphorylated with condensed phosphates, such as pyrophosphate and tripolyphosphate, using make-up pH values over a wide range of from about pH 4 to pH 11, and using a spray-drying technique illustrated in Example 13, preferably followed by an additional heating period, or using a conventional roll-drying operation followed by a heating period at appropriate temperatures and times, the preferred operating pH make-up range is between about 6.0 and 8.0, for reasons above outlined.

EXAMPLE 17

Spray-Drying and Heating Mixtures of Starch and Tripolyphosphates

The procedures given in Examples 13 and 14 were repeated with the exception that instead of the added pyrophosphates, 1 percent of sodium tripolyphosphate was added to the starch and the slurry make-up was pH 8.0.

A starch phosphate resulted, quite comparable to the product obtained in Example 14.

EXAMPLE 18

Use of Starch Phosphate in Beater Size

The following data will show that a corn starch phosphate as made in Example 4 of U.S. Patent 2,884,413 produces an unanticipated result in greatly increasing the Mullen test when added at the rate of 2 percent, based on weight of pulp, as beater size for bleached sulfite pulp, when compared to one of the best commercial paper sizes, made from potato starch.

Starch	Mullen test (427 lb. sheet basis) p.s.i.	Percent increase in Mullen test over blank
Blank (no starch)	13.1	----------
Gelatinized potato starch [a]	24.4	86.3
Starch phosphate product of Example 4	29.9	128.5

[a] Sold under trademark "Tufjel."

EXAMPLE 19

Example 18 was repeated wherein cooked paste of starch was added to the beaters containing bleached sulfite pulp at a ratio, dry basis, of 2 pounds of starch per 100 pounds of pulp, with the exception that a grain sorghum starch phosphate, made in accordance with procedures given in Example 8 of U.S. Patent 2,884,413 was used instead of the corn starch phosphate, made in accordance with procedures given in Example 4 of U.S. Patent 2,884,413.

Mullen tests for bursting strength, run on the paper produced, gave increases in bursting strength over the control with no added starch, quite comparable to the increase shown in Example 18 for 2 percent addition of corn starch phosphate.

EXAMPLE 20

The sizing value of corn starch phosphate, as prepared in Example 4, of U.S. Patent 2,884,413 was compared directly against the parent corn starch from which it was made, and against a waxy variety of starch known commercially as white milo, which is known to be a very superior sizing agent for paper pulp, compared to other varieties of starch. Cooked pastes of each starch were added to identical charges of sulfite pulp and hand sheets were made and tested under carefully controlled conditions. Results obtained are as follows.

Added starch:	Mullen test for bursting strength
None (control)	115
Corn starch phosphate	163
Corn starch	126
White milo starch	136

The results conclusively demonstrate the superior sizing efficiency of a starch phosphate over the parent, underivatized starch. The effect of 2 percent added corn starch is an increase in Mullen test of 126—115=11; for corn starch phosphate an increase of 163—115=48. Therefore, the starch phosphate is more than 4 times as effective in increasing the strength of the paper sheet compared to the parent starch and is at least twice as effective as one of the most superior varieties of paper sizing starches on the market. These results are the more surprising and unanticipated when they are considered along with the values determined for the percentage of added starch size actually retained by the pulp in forming the sheet. Whereas under the test conditions used, 96 percent of the added white milo starch was retained by the pulp, 69 percent of the starch phosphate was retained, demonstrating the inherent superiority of the starch phosphate structure in promoting a strong bond between the paper pulp fibers.

EXAMPLE 21

Corn starch phosphate was compared directly against untreated potato starch, a very superior starch size for paper which is used in countries where potato starch is available for paper sizing at a competitive price. Cooked pastes of both starches were added to charges of bleached sulfate pulp, adding 2 percent starch dry basis, based on pulp. Hand sheets were made and tested for bursting strength under strictly controlled conditions. Results were as follows:

Starch added:	Mullen test for bursting strength
None (control):	93
Potato starch	167
Corn starch phosphate	185

The results show that whereas 2 percent addition of potato starch (reported to be the best variety of starch for paper beater sizing) increased the bursting strength of bleached sulfate pulp nearly 80 percent, a similar addition of the corn starch phosphate increased the bursting strength 100 percent, a significant and surprising increase over the potato starch.

EXAMPLE 22

Paper beating sizing tests were run as given in Example 18 with the following changes. The starches added to the pulp were water dispersions of a corn starch phosphate made in accordance with procedures given in our copending U.S. patent application, Serial No. 560,902, filed January 23, 1956, and a water dispersion of the parent, untreated corn starch. (Application Serial No. 560,902, now U.S. Patent 2,961,440, covers a process for making starch phosphates by heating starch containing less than 5 percent of moisture with a water soluble acid salt of an inorganic polybasic oxyacid in the ortho form at temperatures within the range of about 160° C. to about 200° C.). This above mentioned phosphated starch was made by suspending corn starch granules in a solution of sodium acid orthophosphate at pH 5.5, filtering and drying the cake and then heating the dried reaction mixture for 2 hours at 160° C. This product was found to give an ash analysis of 6.3 percent dry basis. A small sample, purified for further analysis, was found to contain 1.18 percent bound phosphorus as phosphate.

Paper sheets produced were found to give Mullen tests for bursting strength as shown:

Starch added:	Mullen test (427# sheet basis), p.s.i.
None (control)	13.1
Corn starch	13.8
Corn starch phosphate	22.9

EXAMPLE 23

A series of paper pulp sizing tests were run using bleached sulfite pulp in the beaters and to which were added in all cases the usual adjuncts of 2 percent rosin size and alum addition to pH 5.5. In all cases but one, a control, 5 percent TiO_2 based on pulp was added also. Cooked pastes of various corn starch products, as listed in the table below, were added at a ratio of 2 percent dry basis based on pulp, except in two beater tests, the control above mentioned, and one beater to which 5 percent TiO_2 had been added to the pulp.

The starch products compared, as shown in the table, were: a commercial, hypochlorite oxidized corn starch, used in practice in paper sizing; a starch sulfate of D.S. 0.03, made by reacting corn starch in granule form in aqueous alkaline slurry with trimethylamine sulfur trioxide; a starch phosphate made by reacting corn starch in accordance with the procedures given in Example 12 of U.S. Patent 2,884,413 and a corn starch phosphate made in accordance with procedures given in Example 4 of U.S. Patent 2,884,413. The first starch phosphate (Example 12) contains distarch phosphate groups as well as the monostarch phosphate groups that are the sole substituent of the second product (Example 4). Both products were about D.S. 0.03 to 0.04 in respect to phosphate groups.

Beating and sheet formation conditions were such that in the beater to which no starch had been added, only 28 percent of the 5 percent added TiO_2 was retained at the wire by the paper pulp, as shown in the table below, and the Mullen test of this sheet with 5 percent added TiO_2, but no starch, fell to a value of 25, compared to a Mullen test of 32 for the control.

Data obtained for this series of tests are summarized in the table below:

Starch added	TiO_2 retention, percent	Opacity, percent	TAPPI brightness, percent	Relative Mullen test
None (No. TiO_2 added), control	0	57.8	79.1	32
None	28	64.8	83.4	25
Oxidized corn starch	6	59.6	82.4	41
Starch sulfate	2	57.9	82.0	32
Starch phosphate (Ex. 12)[a]	24	63.2	82.6	52
Starch phosphate (Ex. 4)[a]	28	63.2	82.8	90

[a] Examples of U.S. Patent 2,884,413.

These results show further that addition of the oxidized corn paper sizing starch very greatly reduced TiO_2 retention by the pulp from 28 to 6 percent while increasing the Mullen test value from 32 to 41, or an increase over the control of only about 30 percent. The addition of 3 percent corn starch sulfate drastically reduced TiO_2 retention almost to the vanishing point, from 28 to 2 percent, while giving no increase whatsoever in Mullen test value over the control.

Quite in contrast, addition of the corn starch phosphates did not so adversely affect TiO_2 retention by the pulp and moreover increased the Mullen test value of the sheets to unexpectedly high levels. With starch phosphate as made in Example 12 of U.S. Patent 2,884,413 the increase over

the control amounted to about 65 percent and with the starch phosphate as made in Example 4 of U.S. Patent 2,884,413 the increase from 32 to 90, is equal to the surprising high percentage increase of about 190 percent in bursting strength. This result is the more amazing when it is considered that the amount of retained TiO_2 present in this sheet reduced the Mullen test value of the control from 32 to 25.

It is significant also that the effects accomplished by the starch phosphates resulted with no adverse effects on the action of added TiO_2 in increasing the brilliance and opacity of the control sheet.

When hypochlorite acts on starch it is known to oxidize starch hydroxyl groups to acidic, carboxyl groups, thus producing an anionic polyelectrolyte. Sulfating a starch to form a partial ester of sulfuric acid likewise produces an anionic polyelectrolyte even more analogous in structure to the anionic, polyelectrolyte, starch phosphate, particularly the product of Example 4 of U.S. Patent 2,884,413. Therefore, the effects above noted for starch phosphates are entirely unanticipated on the basis of the action of other anionic polyelectrolyte derivatives of starch, such as the carboxylated starch and the sulfate partial ester, both of which by their presence seriously reduced TiO_2 retention by the pulp and imparted a relatively low order of increase, if any, in bursting strength to the formed sheet.

EXAMPLE 24

The effect of various starch phosphates on the retention of added TiO_2 to paper pulp at the beaters was more critically studied by adding cooked pastes of each to a charge of bleached sulphite pulp at a ratio of 2 percent starch, dry basis, to pulp at the beater, and an addition of 5 percent TiO_2 based on pulp, but adding no rosin size. Alum was added to adjust pH to 5.5.

For comparison, 2 percent of cooked corn starch and of white milo starch (waxy grain sorghum) was also used and a control was run in which no starch was employed.

Corn starch phosphate (A) was made in accordance with Example 4, of U.S. Patent 2,884,413. Corn starch phosphate (B) was made in accordance with Example 12, of U.S. Patent 2,884,413 and corn starch phosphate (C) was made in accordance with procedures given in Example 3 of U.S. Patent 2,801,242, using 0.25 gram of sodium trimetaphosphate per 180 grams of starch. The white milo starch phosphate was made in accordance with procedures as given in U.S. Patent 2,801,242, Example 8. Titanium dioxide retention values for these hand made sheets were as follows.

Starch added:	TiO_2 retained by pulp (percent of added TiO_2)
None (control)	40.1
White milo starch	36.3
White milo starch phosphate	49.2
Corn starch	39.4
Corn starch phosphate C	63.5
Corn starch phosphate B	63.6
Corn starch phosphate A	74.6

These results show the outstanding effect of starch phosphates in promoting TiO_2 retention in paper sheets, an effect herein above demonstrated as independent of rosin size.

EXAMPLE 25

Beater sizing tests as described in Example 24, above, were repeated with the following alterations: To each beater was added 2 percent rosin size, based on dry weight pulp. In addition, in each series of tests the "white water," or effluent from the "wire," was recirculated and used as make-up water for a succeeding batch of pulp at the beater, using the same starch product. In this manner, 15 successive beater sizing tests were made for each starch shown in the table below. Filler retention was calculated from hand sheets and values are shown below for the second, tenth and fifteenth successive beater sizing operation from these "closed systems." Again, the superiority of starch phosphate is demonstrated, even in a paper sizing process wherein the "white water" is continuously returned to the system.

Starch added	Percent retention of added TiO_2 at beater No.—		
	2	10	15
None (Control)	38.4	53.0	60.0
Milo starch	50.6	54.6	64.7
Corn starch	49.6		69.3
Corn starch phosphate (A)	66	70	75

(See Example 24.)

We claim:

In the process of sizing paper pulp before formation of the sheet in the manufacture of paper wherein titanium dioxide is added to the pulp to increase the opacity, brilliance and whiteness of the paper sheet, the improvement consisting of adding to the paper pulp, as sizing agent, with the titanium dioxide, a starch phosphate in an amount sufficient to improve the retention by the pulp of said titanium dioxide, said starch phosphate being selected from the group consisting of mono-starch phosphates, di-starch phosphates and starch phosphates having both mono- and di-starch groups, the mono-group predominating; thereby improving the percentage of titanium dioxide retained by the pulp and improving the strength of the paper sheet to at least the level of strength when the sheet is formed from paper pulp alone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,105,052	Oltmans	Jan. 11, 1938
2,171,796	Kelling	Sept. 5, 1939
2,337,458	Edson	Dec. 21, 1943
2,590,912	Yarber	Apr. 1, 1952
2,680,072	Marrone	June 1, 1954
2,692,824	Yarber	Oct. 26, 1954
2,801,242	Kerr et al.	July 30, 1957
2,884,412	Neukom	Apr. 28, 1959
2,884,413	Kerr et al.	Apr. 28, 1959
2,993,041	Sietsema et al.	July 18, 1961

OTHER REFERENCES

Casey: "Pulp and Paper," vol. 1, 1952, Interscience Publishers, New York, N.Y., pp. 370, 468, 469 and 491.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,132,066 May 5, 1964

Ralph W. Kerr et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 68, for "bodies" read -- bodied --; columns 7 and 8, in the table, third column, line 1 thereof, for "3" read -- 9 --.

Signed and sealed this 8th day of September 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents