TREATMENT OF A PAPER PULP SUSPENSION WITH A COMPOSITION OF ROSIN AND A STARCH PHOSPHATE

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Abstract

Treatment of a paper pulp suspension with a unitary composition of rosin and a starch phosphate whereby the resultant paper article is rendered relatively impermeable to water.

11 Claims, No Drawings
TREATMENT OF A PAPER PULP SUSPENSION WITH A COMPOSITION OF ROSIN AND A STARCH PHOSPHATE

This application is a continuation-in-part of pending application Ser. No. 661,817 filed Aug. 2, 1967, now abandoned.

Paper is manufactured for the most part from wood pulp. A small amount of high grade paper is manufactured from rag pulp. There are five different kinds of wood pulp: mechanical pulp (ground wood), semichemical pulp, sulfite pulp, sulfate or kraft pulp, and soda pulp. The first is prepared by purely mechanical means, the second by a combination of mechanical and chemical means, and the others by chemical means. The mechanical pulp contains substantially all the wood except the bark and that lost during storage and transportation. Semichemical pulps are partially free of lignin. Chemical pulps, however, are essentially cellulose, the unwanted lignin and other non-cellulosic components of the wood having been dissolved away by the cooking and bleaching treatment. Because of this, chemical pulps are much superior to mechanical and semi-mechanical pulps for fine paper making. However, because of the special processing required, they are too expensive to serve as the main source of fiber for the cheaper grades of paper such as newsprint. It is understood, of course, that the primary constituent of each paper pulp is cellulose in form of an aqueous suspension of cellulosic paper fibers.

Pulp stock is prepared for formation into paper by two general processes, beating and refining. Mills use either one or the other alone or both together. The most generally used type of beater is that known as the Hollander. Beating the fibers makes the paper stronger, more uniform, more dense, and less porous. It is in the beater that many paper additives are added. The standard practice in making the final grades of paper is to follow the beaters with the refiners, the latter being continuous machines.

Paper additives may be added to the beaters, prior to the Jordan or to a combination of points in the system or subsequent to the beating operation but prior to the refining step. The order in which paper mill wet end additives are added to the pulp may vary with different mills and also depends upon the type of additive involved.

In order to actually form the paper sheet, two general types of machines are utilized, the Fourdrinier Machine and the cylinder machine. The basic principles of operation are essentially the same for both machines. The sheet is formed on a traveling bronze screen or cylinder, dewatered under rollers, and the wet matted paper dried by heated rollers and then finished by calendar rolls. As the Fourdrinier moves along, it has a sidewise shaking motion which serves to orient some of the fibers and give better felting action and more strength to the sheet. While still on the Fourdrinier wire, the paper passes over suction boxes to remove water and then under a dandy roll which smooths the top of the sheet.

In the cylinder machine, there are several parallel vats into which similar or dissimilar paper stocks are charged. At this point, the stocks are generally in a dilute form, containing 1-5 percent by weight of fibers as measured in the bone dry state. A wire-covered rotating cylinder rotates in each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder revolves further, the paper stock reaches a point where the wet layer of fibers comes in contact with and adheres to the moving felt. This felt and paper, after removal of some water, come into contact with the top of the next cylinder and pick up another layer of wet paper. Thus, a composite wet sheet or board is built up and passed through press rolls and on to the drying and smoothing rolls.

The pH of the paper pulp prior to adding of the various additives used to improve the resultant paper article generally falls within the range of about 4.5 to about 5.5. Adjustment of pH within this range is usually effected by adding sulfuric acid. Coincident with or subsequent to addition of paper additives, an aluminum salt such as alum is also added for various purposes.

Without benefit of addition of certain treatment agents, a paper sheet is generally water adsorbing. Thus, sizing materials are added to the wet end of the paper process, such as to the beaters, whereby water repellency or water resistance of the finally cured paper article is achieved. Sized papers are particularly used for wrapping and writing paper. Some paper articles, such as blotting paper and facial tissue are, of course, unsized. If, for example, a writing paper does not have the proper water repellency, a water-based ink imprinted thereon would tend to "feather," that is, the drawn lines would spread out upon the writing paper to an undesirable enlarged degree.

A number of materials have been proposed as sizing agents for paper. Among these may be listed rosin, various hydrocarbons and natural waxes, sodium silicate, synthetic resins, and rubber latex. The most widely used sizing agent is rosin, which can be refined from pine chips or stumps. The extracted rosin is partially saponified with caustic soda and processed to yield a thick paste. The paste is diluted at the paper mill and then added to the stock. Aluminum sulfate (alum) is also added before or simultaneously with the rosin. Alum tends to precipitate or affix the rosin on the fibers. The sized sheet then inhibits penetration by water. While rosin and the other materials listed above are suitable in the relative sense, there is a continuing need to improve water repellency or water resistance of paper articles in a number of situations. Also, cost of many of the above listed additives such as rosin is somewhat high, particularly considering the dosage level necessary to achieve the desired effect.

A number of chemical additives other than those set out above have been proposed for use as reagents to impart sizing or water repellency to a treated paper sheet. In some instances these are meant to replace one or more of the above conventional sizes in toto, or to be used in conjunction with these. However, while these added reagents have sometimes enhanced the water repellency of the so-treated paper product they often have the tendency to adversely affect other desired properties such as by reducing the wet and/or paper dry strength, by inhibiting retention of such other additives as coloring agents, fillers, and the like, etc. In some other instances, while water repellency is increased, conversely the flexibility of the paper product is decreased whereby it cannot be molded or shaped into the desired form. Such paper products are often extremely stiff or hard. In addition to the above problems created by addition of certain chemical additives employed to increase water repellency, there is often a
tendency for these additives to measurably decrease the porosity and permeability of the paper product to the point where it cannot "breathe." In view of the above, it therefore becomes an object of the invention to provide a composition useful in treating a variety of paper pulps whereby the resultant paper article has measurably improved repellency to water and water-based inks.

Another object of the invention is to provide the above method of treating paper pulp to improve its relative impermeability to water without adversely affecting other desired paper article properties such as wet and dry strength.

Still another object of the invention is to provide a unique sizing composition which may be suitably utilized in the conventional paper process by addition to the wet end without resort to special manipulative techniques, and without calling upon special feeding devices.

A still further object of the invention is to provide a sizing composition comprising rosin in combination with a particular starch derivative, which composition is readily dispersible in water, and can be suitably added in a single addition step to the paper pulp in form of aqueous dispersions of varying solids content.

Other objects will appear hereinafter.

GENERAL DESCRIPTION

In accordance with the invention we have discovered a novel and unique method of improving the water repellency of paper articles. This achievement is realized without at the same time adversely affecting other desired properties of paper, such as their wet and dry strength. The process of the invention broadly comprises the steps of treating an aqueous suspension of cellulosic paper fibers comprising a paper pulp with rosin and a starch phosphate. These additives are adsorbed upon the fibers of the pulp and remain firmly affixed to the fibers after addition to the pulp. The thus treated paper pulp is further processed by draining the suspended water therefrom to produce a matted product. The matted product is then dried in a conventional manner to yield the desired improved paper article which is thus rendered relatively impermeable to water.

ROsin

Rosin is a well-known paper additive which has been used for sizing purposes for a long period of time. This material is a solid resinous substance obtained from the oleo-resin or stump wood of pine trees or from gum tapped from living pine, and chiefly contains resin acids as well as lesser amounts of nonacid compounds. It is chiefly composed of abietic-type acids, and may be further characterized as containing monocarboxylic acids of alkylated hydroxyphenanthrene nuclei.

When utilized as a paper additive, rosin is generally added to the pulp in form of the sodium salt. The sodium resinate is commercially available as a powder or in form of a 70-90 percent aqueous dispersion or paste. This paste is further diluted prior to addition of the pulp at the paper mill site. As well, the powder is dispersed in water in a relatively dilute form prior to addition to the pulp stream.

Fortified rosins are also useful here and are a particularly preferred rosin species for use in the invention.

Fortified rosin sizes are made from the partial adduct of 4-7 percent maleic anhydride and rosin.

STARCH PHOSPHATE

Starch phosphates likewise are well-known materials, and are commercially available. The starch phosphate esters are usually formed by heating starch with an inorganic phosphate salt, such as an alkali metal phosphate salt. A typical salt of this type is a sodium phosphate salt. The salt is usually chosen from among metaphosphates, polyphosphates, pyrophosphates, tripolyphosphates, or mixtures of these or other phosphates. The starch reacts with the phosphate to form an ester or salt of an ester. Starch phosphates preferred for use in the present invention are monophosphate starches (mono-starch phosphates). Di-starch phosphates may also be utilized wherein di-starch phosphate cross-linkages are present. However, starch monophosphates are the preferred additives for use in the present invention, though these may contain some cross-linked starch phosphate, say in the amount of 0.1-20 percent. An excellent reference to various starch orthophosphate esters, and their method of preparation, is set out in U.S. Pat. No. 2,884,413, dated Apr. 28, 1959, assigned to Corn Products Company, as invented by Robert W. Kerr and Frank C. Cleveland, Jr. The disclosure of this patent is herein incorporated by way of reference. Materials set out therein have been found admirably suited for this invention.

Any type of starch material may be phosphated to produce suitable starch phosphate esters. The starch reactant may be derived from vegetable sources, such as, for example, corn, wheat, potato, tapioca, rice, sago, and grain sorghum such as red and white milo. Waxy starches may also be used. The term "starch" is used broadly herein and encompasses unmodified starch and tailings, and, as well, starch that has been somewhat modified by treatment with acids, alkali, or enzymes. Soluble or partially soluble modified starches, dextrins, pregelatinized products, and starch derivatives are also suitable here. Typical starch sources are those starches derived from corn and red and white milo.

Most preferred starch phosphate esters such as orthophosphate esters of starch are those wherein the bound phosphorous content expressed as P ranges from about 0.08 up to about 0.5, and more often ranges from about 0.15 to about 0.3 percent.

TREATMENT OF PAPER PULPS

The above additives may be added to the paper pulp at almost any step in the wet end of the normal paper mill process. It is greatly preferred that they be added subsequent to the refining step. However, they may perform their role of increasing water repellency by addition to the paper stock at any point prior to sheet formation. That is, they may be added to the "slush" stock at any point from the beater to points prior to the head box or cylinder vat. By application via this method, uniform distribution of the additives throughout the pulp is achieved, resulting in uniform water repellency of the paper article. For example, the pulp may be treated with the additives by addition at the beaters, consistency regulator, Jordan discharge lines, screen, fan pump, cylinder vat or head box. One preferred site of addition is the machine chest. Another practical application point is at the fan pump where the pulp is simul-
taneously diluted with white water to the proper consistency and pumped to the head box. It has been determined that the paper additives described herein, particularly when utilized with alum as further described become strongly attached to the fibers, and are held when the sheet is formed. The additives are not separated from the fibers by the vigorous conditions of washing which are imposed by sheet formation.

The rosin and starch phosphate additives may be added to the pulp in concentrated form or as further diluted solutions, and either via a single batch addition or in incremental additions. The required amounts of these agents may be added by gravity flow or by means of pumps, preferably with some type of metering guide. Flow rates for the diluted treating solutions may be controlled with rotometers or other suitable flow measuring devices such as orifices and weirs. Likewise, the rosin and starch phosphate in aqueous solution form may be supplied to the pulp in controlled amounts by means of reciprocating, proportionately or gear metering pumps.

Again, the rosin and starch phosphate may be added separately and at different areas of treatment of the pulp in the overall pulp processing system. It is greatly preferred that the two ingredients be added simultaneously to the pulp as a single or unitary composition. For some unexplained reason, superior results are realized when the simultaneous mode of pulp treatment is effected. Thus, a greatly preferred method of application involves addition to pulp of a relatively dilute solution or dispersion of rosin and starch phosphate. For example, a 0.25–5 percent total solids dispersion of the two ingredients comprising the novel blend may be added to the paper pulp.

When a single composition comprising the above discussed materials is added to the pulp, it is greatly preferred that the composition contain 20–80 percent by weight of rosin and 20–80 percent by weight of starch, each of the foregoing percentages being based on total weight of rosin and starch phosphate solids. Most preferred is a composition which comprises 40–80 percent by weight of rosin and 20–60 percent by weight of a starch phosphate. When the additives are separately added to the pulp the ratio of rosin to starch phosphate should also range as stated above, that is from about 1:4 to about 4:1, and most preferably from 4:1 to 2:3.

For best results the paper pulp prior to treatment with the above discussed materials should have a pH ranging from about 4.0 to about 6.0. Usually, the pH of the pulp is around 5.0. This corresponds to normal practice wherein the pH of paper pulps is adjusted within the above range by addition of acids such as sulfuric acid.

In order to more firmly affix the rosin and starch phosphate to the fibers of the pulp, an aluminum salt such as alum (aluminum sulfate) is added subsequently to or simultaneously with addition of the rosin and starch phosphate composition. In case of separate addition of rosin and starch phosphate it is greatly preferred that the aluminum salt be added after addition of the last-added water-repellent reagent, or simultaneously with the last addition of these materials. By far the most preferred method of treatment involves addition of rosin and starch phosphate in a blended solution, followed by addition to the pulp of alum.

The amount of rosin and starch phosphate to be added to the pulp will widely range depending upon the particular pulp involved and the extent of water repellency desired. In the usual case the total amount added of rosin and starch phosphate will range from about 0.3 percent to about 3.0 percent by weight based on bone dry fiber weight, and more often is 0.3–1.0 percent.

The compositions of the invention are useful in imparting water repellency of a wide variety of papers derived from varying paper pulps. Such pulps as ground wood, unbleached kraft, unbleached sulfite, semi-bleached kraft, bleached sulfite, alpha-sulfite, rag, unbleached soft wood pulp, bleached hard wood sulfite pulp, or any pulp derived from a mechanical, chemical or semi-chemical process may be treated with the water repellent compositions of the invention. They are particularly useful in treating bleached sulfite or bleached sulfate pulps or mixtures of these or kraft pulps.

The following examples particularly illustrate typical compositions of the invention and their effectiveness in improving water repellency of paper articles derived from thus treated paper pulps. These examples are meant solely to illustrate specific compositions of the invention, and their various methods of employment. It is understood, of course, that the invention is not to be limited thereto.

**EXAMPLE I**

First, a starch monophosphate was prepared. This material was generally made according to the directions of the Kerr et al patent cited above. In this particular instance a red milo starch was phosphated as set out therein to produce a starch monophosphate having a bound phosphorus level of 0.21 percent. After gelatinization the starch monophosphate was diluted with water to a 0.25 percent solids content and then blended with a 0.25 percent solution of a fortified rosin size, specifically one marketed by Hercules Inc. under the tradename PEXOL. Various preparations of starch phosphate and rosin were blended together to give a number of desired combinations.

The above blends were then added to a 60 percent bleached softwood sulfite–40 percent bleached hardwood sulfate pulp mixture at numerous total size levels. The pulp mixture had previously been Jordanized to 300–350 Canadian Standard Freeness. After addition to the pulp of the starch phosphate–rosin compositions, alum was subsequently added to the pulp in a level of 2.0 percent based on bone dry fiber weights. The starch monophosphate–resin combinations were metered into the pulp slurry at the mixing chest of the pilot paper machine utilized in the instant work. The alum was metered into the head box as a 0.5 percent solution.

Paper made from the starch phosphate–rosin treated pulp was then evaluated for its ink hold-out character. Specifically, an Ink Flotation Test was used to measure this property (TAPPI Routine Control Method RC-14). Here, the treated paper in a one inch square piece was placed in a dish containing ink. The paper floated on the ink, and was observed for ink penetration. At the time when 50 percent of the surface of the paper was covered by ink, that is the ink penetrated through the bottom of the paper to the visible top, the test was terminated and time measured at this point. Of course, the longer the time it takes for the ink to penetrate the sheet the greater the ink hold-out of the treated sheet.
In this test a permanent blue-black water-based ink fluid was utilized having a pH of about 2.5. In addition to the just discussed test the paper was also tested for dry strength by means of the conventional Mullen test (TAPPI Standard Test No. T403).

As is clearly evident the combination use of starch phosphate and rosin was even superior to use of rosin alone in rendering the thus-treated paper ink repellent. Yet, on the other hand, sole use of starch phosphate at varying levels, even as high as 1.0 percent, failed completely as an additive here in terms of attempting to impart repellency properties to paper. Also, it should be noted that the starch phosphate-rosin combination actually increased the paper dry strength as measured by the Mullen test. This should be contrasted to rosin size itself which oftentimes detrimentally affects paper dry strength though increasing water repellency.

As can be seen from Table II below, rosin combinations of anionic starch derivatives, other than starch phosphates, are surprisingly ineffective in rendering a treated paper article impermeable to water. While the rosin-starch monophosphate combination was just as effective as rosin alone in this test on a total dosage basis, combinations of other anionic starches and rosin were decidedly inferior to use of rosin alone at the same overall treatment levels.

In order to test water repellency of the thus treated paper hand sheets, a water penetration test was employed. Essentially, this test involved placing the treated paper on a plate acting as an electrode. A drop of water was then placed on the paper and then a second metal weight placed on top of the drop of water. The second metal acted as a second electrode. As soon as the water penetrated the paper, current begins to flow and at the time when a current of 5 milliamperes is reached the test is terminated. The time it takes to reach this current level from the startup of the test is measured. Again, the longer the above takes to occur the greater the water repellency of the treated hand sheet.

<table>
<thead>
<tr>
<th>Water Repellency Agents, Percent Added Based on Fiber Weight</th>
<th>Water Penetration Test, Seconds</th>
<th>Mullen Test, Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3% Rosin</td>
<td>64</td>
<td>11.6</td>
</tr>
<tr>
<td>1.0% Rosin-0.3% Red Milo Starch Monophosphate (0.21% Bound Phosphorus)</td>
<td>64</td>
<td>14.5</td>
</tr>
<tr>
<td>1.0% Rosin-0.3% Carboxymethyl Corn Starch</td>
<td>47</td>
<td>—</td>
</tr>
<tr>
<td>1.0% Rosin-0.3% Oxidized Corn Starch</td>
<td>39</td>
<td>—</td>
</tr>
<tr>
<td>1.3% Red Milo Starch Monophosphate (0.21% Bound Phosphorus)</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table II**

**EXAMPLE II**

Here, paper hand sheets were made from the pulp described in Example I which was slurried at 0.625 percent consistency and adjusted to 5.0 pH with sulfuric acid. In addition to starch phosphate other starch derivatives were also tested in order to determine their effectiveness in increasing paper water repellency. In each case, the tested anionic starches after gelatinization were diluted to 0.125 percent solids and added to the pulp after addition to the pulp slurry of a 1.25 percent solution of fortified rosin. After addition of rosin and anionic starches, alum was added at a level of 2.0 percent based on fiber weight as a 2.50 percent solution.

Further paper hand sheets were prepared according to the directions outlined in Example II by pulp treatment with rosin, rosin-starch monophosphate compositions and other anionic starch derivatives. Again, compositions comprising rosin and anionic derivatives (other than the anionic starch phosphates) were decidedly inferior to rosin alone, in terms of imparting water repellency to paper articles. Also, it can be seen that unmodified starch utilized in combination with rosin
was markedly less effective compared to like use of starch phosphate and rosin.

### TABLE III

<table>
<thead>
<tr>
<th>Water Repellency Agents, Fiber Weight</th>
<th>Water Penetration Test, Seconds</th>
<th>Mullen Test, Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0% Rosin</td>
<td>49</td>
<td>14.6</td>
</tr>
<tr>
<td>0.7% Rosin-0.3% Red Milo Starch</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Monophosphate (0.21% Bound Phosphorus)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7% Rosin-0.3% Oxidized Corn Starch</td>
<td>38</td>
<td>17.1</td>
</tr>
<tr>
<td>0.7% Rosin-0.3% Corn Starch</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Sulfate Ester</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>0.7% Rosin-0.3% Sulfopropyl Ester of Corn Starch</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>0.7% Rosin-0.3% Unmodified Corn Starch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0% Red Milo Starch Phosphate (0.21% Bound Phosphorus)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

### EXAMPLE IV

The superiority of simultaneous addition of the rosin and starch phosphate with respect to the addition separately of these two materials is shown by the following test results, obtained from the Cobb Size Test, the Ink Flotation Test and the Thiocyanate Flotation Test. In each case the test results were obtained from paper prepared on a pilot paper machine.

Table IV

<table>
<thead>
<tr>
<th>Additives (% on Pulp)</th>
<th>Stock Chest</th>
<th>Cobb Size Test (g/m²)</th>
<th>Ink Flotation (sec.)</th>
<th>Thiocyanate Flotation (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Point of Addition</td>
<td>Mixing Chest</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7% Rosin Size—</td>
<td></td>
<td>2.0% Alum</td>
<td>13.8</td>
<td>16</td>
</tr>
<tr>
<td>Added First</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3% Starch Phosphate (0.2% P)</td>
<td>Added Second</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7% Rosin Size</td>
<td></td>
<td>2.0% Alum</td>
<td>12.6</td>
<td>26</td>
</tr>
<tr>
<td>0.3% Starch Phosphate (0.2% P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0% Rosin Size</td>
<td></td>
<td>2.0% Alum</td>
<td>12.0</td>
<td>12</td>
</tr>
</tbody>
</table>

a) Pelg dry fortified rosin size ("Pexoff", Hercules, Inc.)
b) Measure of weight of H₂O absorbed, therefore, the lower the value the higher the repellency.
c) Penetration time in seconds, therefore, the higher the value, the higher the repellency.

The Cobb Test, identified more formally as TAPPI Test No. 441 OS-69, measures the water absorptiveness of sized (non-bibulous) paper and paperboard. A metal ring (11.28 cm. inside diameter and 2.5 cm. high) is placed on a specimen of sized paper resting on a dry rubber mat, and water is poured into the ring so as to form a pool of water about 1 cm. deep. After 120 seconds, the water is poured out, the specimen removed and blotting paper placed upon it, and a roller passed over the blotting paper twice. The weight of the specimen then is determined and the difference between that weight and the weight of the dry specimen is taken as a measure of the absorptiveness of the specimen.

The Ink Flotation Test has already been described.

The Thiocyanate Flotation Test, identified formally as TAPPI RC-213, involves placing 2-inch squares of sized paper specimens in a porcelain dish half full of a 6 percent solution of ammonium thiocyanate ferric chloride (FeCl₃) and noting the time required for the development of a red coloration.

It will be noted that, in each case, the combination of rosin and starch phosphate was superior to the use separately of these two materials.

### EXAMPLE V

The superiority of the combination of rosin and a starch phosphate, with respect to the use separately of these two materials, is shown further by the results of the following Water Penetration Test results:

<table>
<thead>
<tr>
<th>Order of Addition</th>
<th>Additives</th>
<th>% on Pulp</th>
<th>Water Penetration (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>1.00% Rosin Size</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>2nd</td>
<td>0.20% Starch Phosphate (0.2% P)</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>3rd</td>
<td>2.00% Alum</td>
<td></td>
<td>65</td>
</tr>
</tbody>
</table>

It will be noted that the use of the above materials in combination resulted in a test result of 62 seconds.
whereas the use of the additives separately resulted in a test result of 53 seconds. It is evident that the combination of additives is superior to use of these additives separately.

As is clearly evident from the results shown in the examples above, the compositions of the invention are extremely effective in rendering thus treated paper articles resistant to adsorption by water. It has been noted that they are particularly efficient in resisting adsorption of water-based inks of a relatively low pH level, say in the range of pH 2.4 and more specifically around pH 2.5.

The desired result of water repellency is achieved without sacrifice of other desired paper properties. In point of fact, the combination use of rosin and starch phosphate materially increases the strength of thus treated papers. In addition, the chemicals used in the present invention are not affected by other additives normally used in the paper processing operation. Also, they demonstrate their effectiveness in treating pulps having somewhat varied pH ranges.

In addition to the above advantages, the compositions described herein are relatively safe to handle, are effective at relatively low treatment ranges, do not render the treated paper unduly stiff or hard, and do not create other subsidiary problems with their use.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinafter set forth, and as fall within the scope of the invention.

What is claimed is:
1. A method of producing a paper article having improved water repellency without adversely affecting other desired properties such as dry strength which comprises the steps of treating an aqueous suspension of cellulosic paper fibers comprising a paper pulp with a unitary composition comprising rosin and a starch phosphate whereby said additives are adsorbed upon said fibers, draining the suspended water therefrom to produce a matted product, and drying said matted product to yield said improved paper article being relatively impermeable to water and ink.

2. The method of claim 1 wherein said pulp prior to treatment has a pH ranging from about 4.0 to about 6.0.

3. The method of claim 2 whereby an aluminum salt is also added to said pulp to aid in affixing said additives to said fibers.

4. A method of producing a paper article having improved water repellency without adversely affecting other desired properties such as dry strength which comprises the steps of treating an aqueous suspension of cellulosic paper fibers comprising a paper pulp with a unitary composition comprising rosin and a starch phosphate product prepared by reacting starch with an inorganic phosphate salt, whereby said additives are adsorbed upon said fibers, draining the suspended water therefrom to produce a matted product, and drying said matted product to yield said improved paper article being relatively impermeable to water and ink.

5. The method of claim 4 wherein said inorganic phosphate salt is an alkali metal phosphate salt.

6. The method of claim 1 wherein said starch phosphate is a corn starch phosphate.

7. The method of claim 1 wherein said starch phosphate is a red milo phosphate.

8. The method of claim 4 wherein said phosphate product is a corn starch phosphate product.

9. The method of claim 4 wherein said starch phosphate product is a red milo starch phosphate product.

10. A paper article characterized as having improved impermeability to water as derived from the process of claim 1.

11. A paper article characterized as having improved impermeability to water as derived from the process of claim 4.

* * * * *