COATING OF PRINTED PAPER WITH POLYVINYL ALCOHOL COATING COMPOSITIONS

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6 Claims. (Cl. 117—15)

This invention relates generally to new and useful coating compositions, to methods of coating articles, and to coated articles having new and improved properties.

More particularly, this invention relates to compositions of matter comprising resinoxy polymers, and to coating, sizing, or similar film-forming compositions to be applied onto bases of fibrous material, especially cellulose webs, such as paper, textiles, and the like, or onto wood, glass, porcelain or the like. The compositions disclosed herein form tough and rugged, although elastic and flexible, water-resistant and tenaciously adherent films on the surfaces, and enhance the appearance of the base surfaces.

The compositions and methods described herein are especially suitable for coating cellulosic webs, and more particularly printed paper webs, such as, for example, magazine covers, and the like.

One object of the invention is to provide cellulosic webs with a coating of a polymeric material to improve the characteristics of the paper with respect to gloss, wear resistance, ink color tone and resistance to smudging.

Still another object of the invention is to provide methods of coating cellulosic webs and the like to impart thereto the above-described characteristics.

Other objects of the invention will be obvious and will appear hereinafter.

According to one embodiment of the present invention, paper having improved characteristics with respect to gloss, wear resistance, and so forth has been made by applying to the paper an aqueous solution of polyvinyl alcohol, and drying the aqueous solution to form a thin, water resistant film tenaciously adhered to the surface of the paper.

According to a preferred embodiment of the present invention, improved printed magazine covers have been prepared by applying thereto an aqueous composition comprising polyvinyl alcohol and a fluorescent brightening agent, and drying the aqueous solution to form a thin water resistant film tenaciously adhered to the surface of the paper.

In the art of coating paper sheet stock, and more particularly paper sheet stock containing printed matter, such as magazine covers and the like, which are subject to heavy handling, the problem of preventing smudging of the ink and preserving clear color tones arises. It has been suggested to coat such material with so-called overprint varnishes to alleviate this problem. Use of a wide variety of lacquers for this purpose has been suggested. The prior art lacquers, however, have a number of disadvantages. Many of these, for example, affect the inks or even the paper adversely, reduce brightness and obscure the color tones. Moreover, many of these prior art lacquers tend to discolor with age, thereby considerably reducing the overall appearance of the paper. Additionally, many, if not the vast majority, of these prior art lacquers require organic solvents which produce an undesirable fire hazard in printing plants attempting to employ them.

These and many other disadvantages of the prior art are overcome by the coatings described herein.

The polyvinyl alcohol suitable for use in the coatings described herein is prepared by saponification of polyvinyl acetate. The method of preparing polyvinyl alcohol from polyvinyl acetate is well understood in the art, and does not constitute part of the present invention.

The percent hydrolysis of the polyvinyl alcohol may vary from about 25% to 100%. Polyvinyl alcohol polymers of this type have a viscosity between about 2 to 150 centipoises in a 4% aqueous solution at 20° C.

Especially suitable for use in the coating solutions of the present invention is polyvinyl alcohol which has an extremely high degree of hydrolysis such as polyvinyl acetate which is hydrolyzed to a percent hydrolysis of from about 96 to about 100%.

The polyvinyl alcohol which is from about 96 to about 100% hydrolyzed is advantageous in that films produced therefrom are extremely resistant to attack by cold water. Also the resistance to cold water attack of films produced, apparently reaches a maximum when the degree of hydrolysis of the polyvinyl alcohol is at a maximum. This, of course, is an important property to consider in coating the webs described herein.

The concentration of polyvinyl alcohol in the aqueous coating solutions will vary with the degree of polymerization, i.e., molecular weight of the polyvinyl alcohol polymer employed and the degree of hydrolysis of the polymer. In general, aqueous solutions containing from about 5% to 30%, and preferably between about 10% to 20%, by weight of polyvinyl alcohol may be used. In general, the higher concentrations are preferred because they prevent less water to be removed in the drying steps and because they make possible the application of greater amounts of solids per unit area of the paper sheet stock. Coating solutions having a viscosity of up to 10,000 centipoises have been employed with success and it is apparent according to the present invention, that viscosity up to a paste, e.g., about 70,000 centipoises may be employed. The viscosity/concentration relation of the aqueous coating solution varies with the particular polymer employed, and also, of course, with the temperature at which coating occurs. For a given concentration of a given polymer, the viscosity of the coating solution will, of course, vary inversely with the temperature. This means that for a given polymer the concentration of polyvinyl alcohol at a higher temperature could be greater than the concentration of a similar solution employed at a lower temperature.

The amount of the coating composition applied to the webs should be such that when the coated paper is dried under the conditions disclosed herein, a thin continuous film having a high gloss is obtained. The amount of polymer applied per square foot may vary depending upon the type of paper coated, since a denser paper with a higher finish will give a better coating with less absorption and therefore less polyvinyl alcohol than a more porous paper with a not too highly polished surface. The amount of solids applied will also depend upon the concentration of polyvinyl alcohol in the coating composition and the gloss which the paper manufacturer or coater desires.

The thickness of the film applied to the paper in accordance with this invention may vary widely but preferably is between about 0.0001 and 0.001 inch. A film of such thickness gives the desired protection, gloss and other characteristics desired in the coating paper and yet may be applied at low cost and gives economy with cracking or lack of flexibility even though no plasticizer is present. Plasticizers may be employed, if desired, although generally they are not necessary.
The amount of polyvinyl alcohol applied to the paper is such that at least about 0.3 pound and preferably at least about 0.6 pound of polyvinyl alcohol per 1,000 square feet of paper stock are provided. At the upper limit, 4 pounds of polyvinyl alcohol per 1,000 square feet of stock appear to be about maximum. More than this amount may, of course, be used; however, increasing the polyvinyl alcohol content above the upper limit indicated produces little, if any, improvement in results.

Any suitable method of effecting coating of the paper with the aqueous solution of polyvinyl alcohol may be employed. The coating can be effected, for example, by transfer roll, doctoring, dipping, spreading or with any of the commercial coating methods now in use.

After the paper is coated, the aqueous solution thereon is dried to effect substantially complete removal of the water therefrom. Ordinarily it is dried to approximately 7% moisture content or less by passing the wet coated paper through a heated tunnel oven or other type of drying equipment, such as drying cylinders or drying cans of paper machines, and so forth. It has been determined that greater water resistance is obtained if it is dried to a moisture content of 4% or below.

In drying webs, it is preferable to apply a tension there to so that the sheet will not wrinkle. Although the sheet material may be calendared following drying, in general this is not necessary.

The temperature at which the coated material is dried is not critical. However, care must be exercised so that the liquid does not evaporate at a rate of sufficient magnitude to form steam bubbles, which would tend to make the surface of the film discontinuous. In general, drying temperatures of between about 160° to 500° F, may be employed; however, care should be exercised in order to insure that the sheet material does not reach a temperature above about 200° F. It is preferred to dry at a sheet temperature of from about 160° to 195° F.

In the accompanying drawing which shows one method for protecting the invention, paper 2 is withdrawn continuously from a supply roll 22 and passed through coating device 4 which may be of any suitable type and which may coat only one side or both sides of the paper 2 with the aqueous solution of the polyvinyl alcohol. As illustrated, a reverse roll coater may be employed consisting of an upper roll 6 and a lower roll 8 between which the web and suitable pressure. A reservoir 10 contains the coating bath. Roll 12 is an idling roll which aids in developing a uniform film of coating solution on roll 8 in turn deposits a uniform coating on paper 2 as it passes between rolls 6 and 8. The use of the system shown effects application of a thin even film of the coating mixture to one side of the paper web 2 and enables ready control of the amount applied in a manner well known to the art.

The coated paper then passes through drying oven or tunnel 24 which effects removal of substantially all of the water under conditions of temperature described hereinabove.

Following drying, the web may be wound up immediately after leaving the dryer on a product roll 26.

While a continuous process has been illustrated in the drawing, it will be understood that a batch or discontinuous process may also be employed.

It has been discovered that the coatings described herein are greatly enhanced if a small amount of a watersoluble fluorescent agent is added to the coating composition.

Water-soluble fluorescent agents or dyes are known by a variety of names, such as brighteners, whitening agents, fluorescent bleaches, etc. Among those materials which are especially suitable in the present invention may be mentioned the class of compounds referred to as stilbenes. An especially preferred class of compounds are the stilbene triazine derivatives.

The stilbene triazine derivatives which are suitable for the present invention possess the following general formula

\[
\begin{align*}
N-\text{A}-N \quad & \quad \text{A} \quad \text{A} \quad \text{A} \quad \text{A} \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\end{align*}
\]

wherein A is selected from the group consisting of hydrogen, hydrogen sulfite and an alkali metal sulfite; X and Y are selected from the group consisting of lower alkoxy; aryl amine; hydrogen sulfite, alkali metal sulfite and chloro substituted aryl amine; and hydroxy lower alkyl amino. Specific examples of some of these stilbene triazine derivatives are 1-(4'- monoethanolaminophenyl) -2, 4- bis-(p-sulfamolino-s-triazorylaminio)-6-4' (4'-sulfamolino-4'-m-sulfamolino-s-triazorylaminio) stilbene-2, 2', 4'- disulfonic acid; 4', 4'- bis-(4'-amino-6-dichalcogenamino-s-triazoryl-2'-yaminio)-2', 2'-stilbenedisulfonic acid, disodium salt; and bis-(2'-4'-amino-4'-methylene-6-triazinyloxy)-4', 4'- dimalistallonene-2', 2'-dihydridisulfonate.


Good results are achieved by employing trace amounts of the above-described brightening agents. In general, the amount of brightening agent may vary from about 0.001% to 4% by weight of the aqueous composition. Preferably small amounts of the brightening agents, usually below about 1% or between about 0.01% to 1% by weight of the solution, are employed. In terms of polyvinyl alcohol, the brightening agent may vary from about 0.02% to 13% by weight of the polyvinyl alcohol. Usually, the brightening agent in the polyvinyl alcohol film coating amounts to less than about 5% by weight.

The nature of the present invention will be clear from the following examples, which, although specific, are merely illustrative and are not intended to limit the scope of the invention, except as such limitation may appear in the claims.

**Example 1**

Representative sample sheets of printed magazine cover stock were conditioned to constant weight at 73° F, and 50% relative humidity, which is a standard set forth by the Technical Association of the Pulp and Paper Industry, hereinafter referred to as TAPPI. The stock was die-cut into sixty-square-inch sheets. Each sheet was individually weighed to the nearest 0.001 gram.

Polyvinyl alcohol of 99.85 percent hydrolysis having a viscosity in a 4% aqueous solution at 20° C. of 30 centipoises was dissolved in water to give a solution containing 15% by weight of polyvinyl alcohol.

The inside covers of representative sample sheets of printed magazine stock were coated with the polyvinyl alcohol solution. Multiple passes through the coater were required to obtain higher coat levels. The coated sheets were air dried at 194° F. and subsequently reconditioned at the TAPPI standards described hereinabove before determining coating weight. The coating weights were calculated from the knowledge of the dimensions of the sheet and the coated and uncoated weight in an obvious manner.

The 75° specular gloss properties of the white areas of the coated sheets were determined on a Photovolt Reflectometer fitted with a 75° reflectance head. The procedure employed in measuring the gloss properties conformed to TAPPI Standard T-480m–51, tentative standard, dated February 1, 1951.
The specular gloss at 75°, it should be noted, is widely used as a partial measure of the surface quality and shiny appearance of paper. The higher the 75° gloss figure, the more shiny or lustrous is the appearance of the paper. The results of the 75° gloss tests appear in Table I.

### TABLE I

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cost wt. #/320 sq. ft.</th>
<th>75° gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated stock</td>
<td>1.4</td>
<td>55</td>
</tr>
<tr>
<td>2.</td>
<td>2.0</td>
<td>58</td>
</tr>
<tr>
<td>3.</td>
<td>2.7</td>
<td>55</td>
</tr>
<tr>
<td>4.</td>
<td>8.8</td>
<td>72</td>
</tr>
<tr>
<td>5.</td>
<td>10.0</td>
<td>75</td>
</tr>
<tr>
<td>6.</td>
<td>11.5</td>
<td>77</td>
</tr>
</tbody>
</table>

* Average of 5 determinations.

As can be seen from Table I, an increase in gloss results from the polystyrene alcohol coating at all cost weight levels, and the 75° gloss increases greatly at coating weights of polystyrene alcohol greater than 2.0 pounds/3300 square feet, or 0.66 pound/1000 square feet.

Visual comparison of the coated sheets showed that at all cost weight levels the sheets coated with the polystyrene alcohol displayed superior finish characteristics with respect to ink, color tone and brilliance to ink smudging. Ink color tones on all sheets coated with the polystyrene alcohol appeared deeper with a higher contrast when compared to uncoated stock.

Ink smudging resistance was observed by rubbing the palm of the hand over a coated and uncoated sheet with approximately equal pressure. Subsequently the degree of smudging on each sheet was visually observed. All of the sheets that had been coated displayed improved resistance to smudging, with the high cost weights showing the best resistance.

### Example 2

Example 1 was repeated, with the exception that the coated sheets were cut in half and one-half of each sheet was super-calendered by passing it through a calender roll at a pressure of 10 lbs./sq. in. and a temperature of 23° C. It was discovered that the gloss characteristics of the sheets were not improved with super-calendering.

### Example 3

This example was run to show the effects of adding an optical brightener of the type described hereinabove to the polystyrene alcohol coating solution. A solution containing 14% polystyrene alcohol of the type described in Example 1 and 0.2% by weight based on the weight of polystyrene alcohol of a brightener of the stilbene class was prepared. Three different brighteners of the stilbene class were employed. In Table II stilbene A is (4,2-monoethanolamino - 4 - p - sulfoanilino - s - triazollyaminino - 4' - (2 - monoethanol - 4 - m - sulfoanilino - s - triazollyaminino)) stilbene-2,2'-dialcrylic acid; stilbene B is 4,4' - bis(4 - anilino - 6 - diethanolamine - s - triazinyl-2-ylamino)-2,2'-stilbenedicarboxylic acid, disodium salt and stilbene C is bis-(2-anilino-4-methoxy-6-triazinyl)-4,4'-diaminostilbene-2,2'-disodium disulfonate.

The viscosity of the polystyrene alcohol solution was measured before and after the addition of the brightening agent, and it was determined that no viscosity change resulted from addition of the brightening agent.

Representative magazine cover sheets conditioned to the TAPPI standards described in Example 1 and die-cut into sixty-square-inch sheets were individually weighed to the nearest 0.01 gram. The sample sheets were coated with the coating composition. As a standard was employed a 14% polystyrene alcohol solution of the type described in Example 1, to which no brightener had been added. All coatings were dried in a forced air oven at 194° F. for three minutes. Coat weight determinations were made and the coating weights were found to vary from about 3.5 to 8 pounds per 3300 square feet.

The 75° gloss, 45° brightness ("whiteness"), and 90° opacity properties of the non-printed sheets were measured with a Photovolt Reflectometer. The procedure in measuring gloss was the same as that described in Example 1. The procedure in measuring opacity conformed to TAPPI Standard T-425m-44, corrected August 1944. The procedure for measuring brightness conformed to TAPPI Standard 452m-58, revised July 1958. Optical measurements were made only on those coated specimens which had a variation in coat weight of less than 1.0 pound/3300 square feet.

### TABLE II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cost wt. #/320 sq. ft.</th>
<th>75° gloss</th>
<th>45° bright</th>
<th>90° opacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH...</td>
<td>8</td>
<td>78-84</td>
<td>72</td>
<td>90</td>
</tr>
<tr>
<td>PVOH-stilbene A</td>
<td>7</td>
<td>78-84</td>
<td>72</td>
<td>80</td>
</tr>
<tr>
<td>PVOH-stilbene B</td>
<td>5</td>
<td>78-84</td>
<td>72</td>
<td>70</td>
</tr>
<tr>
<td>PVOH-stilbene C</td>
<td>8</td>
<td>78-84</td>
<td>72</td>
<td>60</td>
</tr>
<tr>
<td>Uncoated stock</td>
<td>0</td>
<td>55</td>
<td>72</td>
<td>60</td>
</tr>
</tbody>
</table>

As indicated in Table II, the sheets coated with polyvinyl alcohol and polystyrene alcohol plus the brightening agent showed a 20-point increase in 75° gloss over the noncoated stock.

The sheets coated with the polyvinyl alcohol-brightening agent compositions showed an increase of 6 points in 45° brightness when compared to straight polystyrene alcohol overcoated stock, and a 3-point increase over the nonovercoated stock.

The 90° opacity of all the coated sheets was 2 points lower than the uncoated stock.

When printed paper sheets are coated with an aqueous solution of polystyrene alcohol containing the fluorescein brightening agents described herein, a greatly improved appearance results. A greater whiteness over the white areas of the printed sheet is clearly noticeable. Additionally, higher contrasts and sharper color tones result when the brightening agents are employed.

The invention in its broader aspects is not limited to the specific compositions, steps, and methods described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

We claim:

1. A method of coating a printed paper sheet having a dry printed surface which comprises applying an aqueous solution consisting essentially of water and from about 5 percent to 30 percent by weight of polyvinyl alcohol having a degree of hydrolysis ranging from 98 percent to 100 percent and a viscosity in 4 percent aqueous solution at 20° C. ranging from about 2 to 150 centipoises to said dry printed surface of said paper sheet, said solution being applied in a quantity to provide about 0.6 pound to about 4 pounds of polyvinyl alcohol per 1,000 square feet of said paper sheet, and drying the paper sheet at a sheet temperature of about 105° to 195° F. to a moisture content of at most 4 percent, to produce a thin, water-resistant, transparent film of polyvinyl alcohol superimposed on said printed surface of said sheet.

2. A method according to claim 1, wherein said polyvinyl alcohol solution also contains a fluorescent brightening agent in the amount of 0.02 percent to 13 percent by weight of the polyvinyl alcohol.
3. A method according to claim 1, wherein said polyvinyl alcohol solution contains from 10 percent to 20 percent by weight of polyvinyl alcohol.

4. A method of coating a dry printed paper sheet which comprises applying a solution consisting essentially of water and from about 5 percent to 30 percent by weight of polyvinyl alcohol having a degree of hydrolysis ranging from 96 to 100 percent and a viscosity in 4 percent aqueous solution at 20° C. ranging from about 2 to 150 centipoises to a dry printed surface of a paper sheet, and 

5. A method of coating a printed paper sheet having a dry printed surface which comprises applying an aqueous solution consisting essentially of water and from about 5 percent to 30 percent by weight of polyvinyl alcohol having a degree of hydrolysis ranging from 96 percent to 100 percent and a viscosity in 4 percent aqueous solution at 20° C. ranging from about 2 to 150 centipoises to said dry printed surface of said paper sheet, said solution being applied in a quantity to provide about 0.6 pound to about 4 pounds of polyvinyl alcohol per 1,000 square feet of said paper sheet, and drying the paper sheet at a sheet temperature of about 160° to 195° F. to a moisture content of at most 4 percent, to produce a thin, water-resistant, transparent film of polyvinyl alcohol superimposed on the printed surface of said sheet, said polyvinyl alcohol film having a thickness of 0.0001 to 0.01 inch, a coating weight of 0.6 to 4 pounds per 1,000 square feet of said paper sheet, and said polyvinyl alcohol having a degree of hydrolysis of at least 96 percent.

6. A method as defined in claim 5 wherein said polyvinyl alcohol solution also contains a fluorescent brightening agent in the amount of 0.02 percent to 13 percent by weight of the polyvinyl alcohol.

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