United States Patent Office 3,125,455 Patented Mar. 17, 1964

3,125,455

COATING COMPOSITIONS

Glenn H. Perkins, West Peru, Maine, assignor to Oxford Paper Company, Rumford, Maine, a corporation of Maine

No Drawing. Filed Sept. 12, 1960, Ser. No. 55,145
11 Claims. (Cl. 106—154)

This invention relates to coating compositions and to articles of manufacture coated therewith. More particularly, the invention relates to an improved water-resistant coating composition containing a protein and 4,4-bis(4'-hydroxyphenyl)pentanoic acid.

Coating compositions are frequently applied to paper in order to form a water-resistant coating thereon. Many of the coating compositions commonly employed are composed of a pigment and a binder which may be any one or more of several suitable adhesive materials. Such coated paper or paper products have been employed in the production of printing and label paper, wallpaper, washable window shades, offset printing, box board and container board, etc.

It has been found that when a coating composition, containing a protein and 4,4-bis(4'-hydroxyphenyl)pentanoic acid and preferably also a pigment, is applied to a paper base and dried, the coated paper possesses excellent water-resistant and wet-rub properties. These papers or other paper products which are coated with the compositions of this invention are useful wherever water-resistant and wet-rub properties are desired. In particular, these coated papers are useful in the production of planographic printing plates where a suitable planographic surface is applied to these coated papers.

It has furthermore been found that in preparing the coated papers of this invention, the viscosity of the coating composition is not appreciably increased by the addition of the 4,4-bis(4'-hydroxyphenyl)pentanoic acid and therefore the necessity of using liquefying agents to decrease the viscosity of the coating composition is substantially avoided. This is of considerable commercial significance since these coating compositions can be prepared easily and inexpensively.

Another advantage of the coating compositions of this invention resides in the fact that there is an early development of wet-rub resistance. Heretofore in the manufacture of water-resistant coated paper, it was necessary to permit the coated paper to age for considerable periods of time before it was even possible to determine by the wet-rub test whether or not the resulting coated paper possessed the necessary water-resistant properties or the particular water-resistant properties desired. The compositions of the present invention, after being applied to the paper and dried, may be immediately tested for wet-rub resistance, and it is not necessary to age the coated paper of the present invention in order to determine the wet-rub resistance.

Moreover, it has been found that the use of the 4,4-bis-(4'-hydroxyphenyl)pentanoic acid in these coating compositions does not adversely effect the pick resistance of the resultant coated paper as is the case with many protein insolubilizing agents.

4,4-bis(4'-hydroxyphenyl)pentanoic acid is not soluble in water and therefore it should be solubilized so that it may readily react with the protein in the coating composition, as will be apparent to those skilled in the art. Advantageously, 4,4-bis(4'-hydroxyphenyl)pentanoic acid may be dissolved readily in ammonium hydroxide solution to form the ammonium salt. 4,4-bis(4'-hydroxyphenyl)pentanoic acid is marketed by S. C. Johnson & Son, Inc., under the trade name Diphenolic Acid.

Various proteins can be used and reacted or cross-linked with the 4,4-bis(4'-hydroxyphenyl)pentanoic acid according to this invention including casein, soya proteins, such as Alpha Protein and Delta Protein marketed by Central Soya Company, gelatin, and the like. Mixtures of these proteins may be used, and, if desired, a synthetic rubber latex (50–50 butadiene-styrene copolymer) can be included in the protein component of the coating compositions. This latex has an adhesive power equivalent to that of casein, and may advantageously be substituted for about 25–50% of the protein in the color formulation. Depending upon the particular protein employed, cutting agents such as ammonium hydroxide or mixtures of ammonium hydroxide and sodium carbonate may advantageously be employed in order to get the protein into solution, as will be apparent to those skilled in the art. For example, it has been found that when using soya protein the combined use of ammonia hydroxide and sodium hydroxide in the coating composition is advantageous. When utilizing the above combination, it is necessary to maintain a proper proportion of the sodium hydroxide to the ammonia hydroxide. When using 15% by weight of ammonia hydroxide, 26° Bé., based on the weight of soya protein, for example, the sodium hydroxide should not be used much in excess of 3% by weight based on the soya protein, and it is advantageous to employ 1–2% by weight of sodium hydroxide with 15% by weight of ammonia hydroxide.

Various pigments, both organic and inorganic, can be advantageously incorporated into the aqueous coating compositions according to this invention including clay, silica, titanium dioxide, barium sulfate, diatomaceous earth, fuller's earth, calcium silicate, zinc oxide and carbon black as well as other colored organic and inorganic pigments as will be apparent to those skilled in the art.

The amount of pigment, when used, can vary quite widely and will depend upon the particular protein or pigment employed and upon the final properties desired in the coated paper. Generally, as the proportion of the pigment in the color is decreased, the pick resistance of the resultant coated paper will go up, but the gloss, ink receptivity, and brightness will increase. It has been found that a pigment/protein ratio of between about 3:1 to 8:1 is generally suitable although both higher and lower ratios can be used. A ratio of 6:1 is preferred.

Dispersing agents may be employed in these coating compositions along with the pigments, and include agents such as sodium hexametaphosphate, disodium dihydrogen pyrophosphate, tetrapotassium pyrophosphate, sodium silicate, etc. Likewise, emulsion plasticizers such as calcium stearate can advantageously be included in these compositions.

The ratio of 4,4-bis(4'-hydroxyphenyl)pentanoic acid to the protein can also vary widely depending upon the final properties desired in the coated paper. It has been found that from about 5 to 20%, and preferably about 6 to 10%, based on the protein is generally suitable although both higher and lower ratios can be used.

The coating compositions according to this invention can generally be prepared by simply blending the protein into the pigment, when a pigment is used, and then adding the 4,4-bis(4'-hydroxyphenyl)pentanoic acid. The amount of water can readily be adjusted to obtain a suitable flowing composition which can be readily coated upon a base paper. If desired, a small amount of formaldehyde may be added to the color in order to shorten the time in which the coated paper develops wet-rub resistance. For example, a 4,4-bis(4'-hydroxyphenyl)pentanoic acid/formaldehyde ratio of from about 4:1 to 1:1 may advantageously be used in preparing coated papers which develop wet-rub properties very rapidly.

The particular solids content of the composition will depend primarily upon the coating method used, and the

weight of coat desired. Advantageously, the solids content may vary from 25% to about 65%, although both higher and lower percentages may be used. Depending on the particular coating composition employed, the pH may advantageously be in the range of from about 7.0 to about 9.5.

The coating composition may be applied to a base web or sheet by conventional apparatus (such as air knives or roll coaters). The amount of coating may vary from about 2 to 10 pounds per ream of 3300 square feet, with 6 to 8 pounds being most satisfactory. After coating, the stock is dried at room temperature to effect the insolubilization reaction of the protein and the 4,4-bis(4'-hydroxyphenyl) pentanoic acid. If desired, heat may be employed in the drying operation to speed up the coating procedure. The coating composition is self-insolubilizing and the components react during the drying stage to produce a coated paper having excellent wet-rub properties.

The following examples illustrate the manner of producing the coating compositions and coated paper according to this invention in more detail. Parts are by weight.

Example 1

20 parts of 4,4-bis(4'-hydroxyphenyl)pentanoic acid (10% solution of the ammonium salt) were mixed together with 50 parts of a 60% suspension of clay, 100 parts of a 5% solution of soya bean protein, and 2 parts of a 40% formaldehyde solution. The composition was then coated on a suitable coating raw stock and dried at room temperature. The resulting coating was hard and possessed good wet-rub properties after approximately 2 hours.

Example 2

A composition was prepared according to Example 1 except that 100 parts of a 5% solution of gelatin was used instead of the soya bean protein. The resulting coating was hard and possessed good wet-rub properties after approximately 2 hours.

Example 3

3.5 parts of 4,4-bis(4'-hydroxyphenyl)pentanoic acid (10% solution of the ammonium salt) were mixed together with 50 parts of a 60% suspension of clay and 100 parts of a 5% solution of casein. The composition was then coated on a suitable coating raw stock and dried at room temperature. The coated paper developed good resistance to wet-rub in approximately 12 hours.

Example 4

A composition was prepared according to Example 3 except that 7.0 parts of 4,4-bis(4'-hydroxyphenyl)pentanoic acid were used instead of 3.5 parts. The coated paper developed good resistance to wet-rub in approximately 2 hours.

Example 5

24.5 parts of 4,4-bis(4'-hydroxyphenyl)pentanoic acid (10% solution of the ammonium salt) were mixed with 153 parts of a 60% suspension of clay, 7.7 parts of titanium dioxide, 81.5 parts of a 15% solution of soya bean protein, 9.6 parts of a 47% emulsion of a synthetic rubber latex (50–50 butadiene-styrene copolymer), and 1.3 parts of a 50% solution of calcium stearate. The composition was coated on a suitable coating raw stock and dried at room temperature. The coated paper developed good resistance to wet-rub in approximately 2 hours.

Example 6

4.5 parts of a 40% solution of formaldehyde were added to a coating composition prepared according to Example 5. The composition was coated on a suitable coating raw stock and dried at room temperature. This composition developed resistance to wet-rub more rapidly than in Example 5. After one hour, the resistance to wet-rub in Example 5 was less than in Example 6 after one hour. After the 2-hour period, however, the compositions of both Examples 5 and 6 had developed equally good wet-rub resistance.

I claim:

1. An aqueous coating composition comprising a protein and solubilized 4,4-bis(4'-hydroxyphenyl)pentanoic acid.

2. An aqueous coating composition comprising a pigment, a protein, and solubilized 4,4-bis(4'-hydroxyphenyl)pentanoic acid.

3. An aqueous coating composition comprising a pigment, a protein, solubilized 4,4-bis(4'-hydroxyphenyl)-pentanoic acid, and formaldehyde.

4. The composition of claim 2 in which the protein is soya protein.

5. An aqueous coating composition comprising a protein and an ammonium salt of 4,4-bis(4'-hydroxyphenyl) pentanoic acid.

6. The coating composition of claim 1 in which the solubilized 4,4-bis(4'-hydroxylphenyl) pentanoic acid is present in an amount equivalent to from about 5% to about 20% by weight based on the protein.

7. An article of manufacture comprising a paper having a coating thereon, said coating comprising the reaction product of a protein and solubilized 4,4-bis(4'-hydroxyphenyl) pentanoic acid.

8. An article of manufacture comprising a paper having a coating thereon, said coating comprising a pigment and the reaction product of a protein and solubilized 4,4-bis(4'-hydroxyphenyl) pentanoic acid.

9. An article of manufacture comprising a paper having a coating thereon, said coating comprising a pigment, the reaction product of a protein and solubilized 4,4-bis-(4'-hydroxyphenyl) pentanoic acid, and formaldehyde.

10. The article of claim 7 in which the protein is soya protein.

11. An article of manufacture comprising a paper having a coating thereon, said coating comprising the reaction product of a protein and the ammonium salt of 4,4-bis(4'-hydroxyphenyl) pentanoic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,380,043	Hochwalt	July 10, 1945
2,786,786	Novak et al.	Mar. 26, 1957
2,844,482	Maskey	July 22, 1958
2,894,847	Wright	July 14, 1959
2,933,520	Bader	Apr. 19, 1960
2,933,523	Greenlee	Apr. 19, 1960