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AQUEOUS PAPER SIZING COMPOSITION CONTAINING STYRENE-MALEIC ANHYDRIDE COPOLYMER SALT AND POLYVINYL ALCOHOL

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This invention relates to a novel sizing composition and to cellulosic paper products sized therewith.

Wax compositions of various types have long been used as a protective coating on paper substrates, particularly those items employed in containing or wrapping food and dairy products such as milk, cheese, butter, meats, etc. The wax coating serves the purpose of protecting the paper substrate from direct contact with the particular food product contained therein. Paperboard milk cartons, for example, are coated with a wax composition in order to protect the paperboard from attack by the lactic acid contained in the milk and thereby preserving the rigidity of the container. This in turn maintains the usefulness and sales appeal of the milk carton.

However, in the application of such wax coatings, there are several drawbacks and shortcomings. For example, when applying a hot fluid wax coating to cellulosic paper, the wax composition penetrates the interstices of the paper. This results in a poor surface wax coating which seriously defeats the protective purpose intended by employing the wax coating. Alternatively, to obtain a sufficient protective coating, excessive quantities of wax are required. This results in bulkiness, ease of flaking and increased cost due to increased wax consumption through an increase of dwell time in the fluid wax bath. Although this provides a better surface coating, it still does not overcome the deficiency of protecting the paper substrate from attack by lactic acid.

To overcome these problems, certain modifications were employed wherein the paper substrate was first treated with a sizing solution. One of the sizing solutions so employed was a polyvinyl alcohol. Although paper sized with this solution allowed a better wax coating to be applied with a decrease in wax consumption, the wax coated paper was still deficient in sufficiently protecting the paper substrate from attack by lactic acid.

Therefore, it is an object of this invention to provide a sizing composition which, when employed to size cellulosic paper that is subsequently coated with wax, improves the lactic acid resistance while minimizing the penetration of the wax into the cellulosic paper substrate.

Another object of this invention is to provide a sized cellulosic paper sheet having a wax coating thereon.

Still another object of this invention is to provide a sized cellulosic paper milk carton having a wax coating deposited on at least the interior surfaces thereof, which milk carton has improved lactic acid resistance.

The above and other objects of this invention are attained with a sizing composition consisting of 95–40 parts by weight of a styrene maleic anhydride copolymer and, correspondingly, 5–60 parts by weight of a polyvinyl alcohol. When sizing cellulosic paper with this composition and subsequently coating the sized cellulosic paper with a wax composition, the item is found to have increased resistance to lactic acid attack while minimizing the penetration of the wax into the paper substrate. This resistance to wax penetration is commonly known in the trade as "wax holdout." The overall effect obtained with the sizing solution of this invention is considerably greater than if either of the component parts were employed separately in a sizing solution. This effect is subsequently shown in the examples described hereafter.

As used herein, all parts or percentages are parts or percentages by weight unless otherwise indicated.

EXAMPLE I

This example illustrates one embodiment of the invention employed in the preparation of the polyvinyl alcohol-styrene maleic anhydride copolymer sizing solution. First, blend by hand-mixing dry polyvinyl alcohol and a dry styrene maleic anhydride copolymer in the proportion of 30 parts and 70 parts respectively. The polyvinyl alcohol employed in this example has a viscosity of about 45–55 centipoises as determined by the viscosity of a 4% water solution at 20° C. by means of the Hoeppler falling ball method. The styrene maleic anhydride copolymer employed herein has a specific viscosity of about 3 as determined by a 1% solution of the copolymer in cyclohexanone measured at 25° C. Both of these methods are a means of determining the molecular weight of the respective ingredients in terms of viscosity and specific viscosity respectively, and are the methods employed in the other examples.

To 75 parts of water, slowly add 5 parts of the above dry blend while agitating so as to disperse the blend in water. Add ammonium hydroxide until the pH of 6.5–7.5 is obtained. Heat the mixture to 90–95° C., add 20 parts of water and hold at this temperature for approximately 30 minutes while agitating. A clear aqueous solution will result. Adjust the pH to 6.5–7.5 with ammonium hydroxide if necessary and cool the solution to room temperature.

The resulting sizing solution contains 5% solids and is subsequently identified as A.

EXAMPLE II

Prepare an aqueous ammonium hydroxide sizing solution containing 5% of a styrene maleic anhydride copolymer by adding 5 parts of the copolymer, having a specific viscosity of about 3, to approximately 95 parts of water. Add ammonium hydroxide and adjust the pH to 6.5 to 7.5. Heat the mixture to about 90–95° C. and hold the mixture at this temperature, while agitating, for about 30 minutes. A clear solution will result. Adjust the pH to 6.5–7.5 with ammonium hydroxide if necessary, and cool to room temperature.

This resulting sizing solution is subsequently identified as B.

EXAMPLE III

Prepare an aqueous sizing composition containing 5% of a polyvinyl alcohol, having a viscosity of about 45–55 centipoises, by adding 5 parts of the polyvinyl alcohol to about 95 parts of water. Heat the mixture to about 75–85° C. and hold at this temperature, while agitating, until a clear solution is obtained. Cool the solution to room temperature.

This resulting sizing solution is subsequently identified as C.

EXAMPLE IV

Part A

With the sizing solutions prepared in Examples I–III, separately treat strips (4" x 4") of 16 point cellulosic paperboard on each side thereof with each of the sizing solutions (2 strips per solution). Dry the strips in an air circulating oven for 5 minutes at 105° C. Weigh all strips separately and immerse them in a petroleum wax at 120° C. for 30 seconds, including two blank strips of the 16 point cellulosic paperboard which have not been treated with any of the sizing solutions. Drain off the excess wax and cool to room temperature. Reweigh to determine total wax pickup which is subsequently recorded in Table I.

Part B

With one sample of each of the specimens prepared in Part A, determine the amount of wax that has penetrated into the interstices of the treated cellulosic paperboard by scraping off the surface wax and reweighing the samples, which values are recorded in Table I.

Part C

With the remaining samples as prepared in Part A, soak them in a 1% aqueous lactic acid solution for 48 hours at room temperature. Dry the samples between blotters to remove excess surface solution and reweigh to determine lactic acid pickup. Test the samples for wet stiffness on a Gurley R. D. Stiffness tester to determine the effect that lactic acid has on the rigidity of the samples.

Part D

The results of Parts A, B and C are as follows with the blank untreated specimens being employed as a control.

TABLE I

[Percent wax pickup]

Sizing Solution	Total	Internal	Surface	Percent Lactic Acid Pickup	Wet Stiffness, gms.
A	16.8	8.5	8.3	38.7	7.9
B	22.4	15.6	6.8	46.0	5.4
C	15.3	7.1	8.2	42.5	4.8
Control	43.2	37.8	5.4	40.0	3.2

The results as described in Table I show that the sizing solution of this invention, Solution A, has increased the lactic acid resistance of the cellulosic paperboard substrate over that of the other sizing solutions as employed herein while still maintaining good "wax holdout." The increase in resistance to lactic acid is particularly significant in the rigidity retention of the samples as determined by wet stiffness on a Gurley R. D. Stiffness tester. This measures the force in grams required to bend the sample, the greater the force required, the greater the rigidity. As noted in the table, a sample sized with sizing Solution A and then coated with wax has a rigidity of about 46% greater than a similar sample sized with Solution B, which solution contains only the styrene maleic anhydride copolymer. In comparison to the sample sized with Solution C, which contains only polyvinyl alcohol, an increase of about 63% is obtained. Also with a similar comparison of the untreated sample, an increase of about 150% is noted. Therefore, there is a substantial improvement in the lactic acid resistance in a sized cellulosic paper substrate having a wax coating thereon when employing the sizing solution of this invention.

This invention is directed to a cellulosic paper sizing composition selected from the group consisting of (a) 95–40 parts by weight of a styrene maleic anhydride copolymer and, correspondingly, 5–60 parts by weight of a polyvinyl alcohol and (b) the ammonium, amine and alkali metal salts of (a). The styrene maleic anhydride copolymer employed in the practice of this invention has a specific viscosity of 2–5 and the polyvinyl alcohol has a viscosity of 40–60 centipoises at 20° C. These methods are used as a means of determining the molecular weight of the specific compounds employed herein in terms of specific viscosity and viscosity respectively, which methods are fully described in Example I.

By converting the composition to the ammonium, amine or alkali metal salt, the composition is rendered soluble in water to form an aqueous solution thereof. The solids content should be in the range of 1–20 weight percent and

preferably 2–10 weight percent. This allows for ease of application of the sizing composition and insures uniform sizing of the cellulosic paper employed therewith. For best results, the pH of the sizing solution should be in the range of 5–9 and preferably 6–8.

Typical examples of the amines which may be employed in converting the sizing composition to the amine salt thereof are ethylamine, butylamine, propylamine, diethylamine, dipropylamine, dibutylamine, triethylamine, tripropylamine, tributylamine and mixtures thereof.

Typical examples of the alkali metal hydroxides which may be employed in converting the sizing composition to the alkali metal salt thereof are sodium, magnesium, potassium, calcium and mixtures thereof.

In the practice of this invention, the preferred embodiment is to employ an aqueous solution of the ammonium salt of the composition in sizing cellulosic paper.

The advantage of this invention is found in the ability of the sizing composition to render cellulosic paper, when sized and subsequently coated with a wax, highly resistant to lactic acid attack as compared to unsized cellulosic paper coated with a wax. Also the sized cellulosic paper has better "wax holdout" than unsized cellulosic paper thereby minimizing excessive consumption of wax. Cellulosic paperboard sized with the composition of this invention for example and coated with a wax is extremely useful in fabricating milk cartons since the milk cartons retain good rigidity for sales appeal and handling when in contact with milk.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained. Since certain changes may be made in the above-described processes and compositions without departing from the spirit and scope of the invention, it is intended that all matters contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An aqueous solution having in admixture 1–20 weight percent of a cellulosic paper sizing composition selected from the group consisting of the ammonium, amine and alkali metal salts of 95–40 parts by weight of a styrene-maleic anhydride copolymer having a specific viscosity of 2–5 and correspondingly 5–60 parts by weight of a polyvinyl alcohol having a viscosity of 40–60 centipoises at 20° C.; said solution having a pH of 5–9.

2. A sizing composition as described in claim **1** wherein the composition consists of 80–50 parts by weight of a styrene-maleic anhydride copolymer and, correspondingly, 20–50 parts by weight of a polyvinyl alcohol.

3. An aqueous solution as described in claim **1** containing therein **2–10** weight percent of the cellulosic paper sizing composition.

4. An aqueous solution as described in claim **1** containing therein the ammonium salt of the cellulosic paper sizing composition.

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