

1

2

3,535,202

PROCESS OF INHIBITING DISCOLORATION OF PAPER AND PAPERBOARD BY CROSS-LINKING CARBOHYDRATES WITH MELAMINE OR UREA FORMALDEHYDE RESINS

Denis K. Huang, Laurel, Md., assignor to Westvaco Corporation, New York, N.Y., a corporation of Delaware
No Drawing. Filed Feb. 16, 1968, Ser. No. 705,899

Int. Cl. D21d 3/00

U.S. Cl. 162—160

8 Claims

ABSTRACT OF THE DISCLOSURE

Starch in sizings and coatings applied to paper or paperboard, used in packaging detergents containing a persalt, is treated with a cross-linking agent to prevent discoloration and mottling of the paper or paperboard due to oxidative degradation of carbohydrate materials to colored products. Protein materials applied to the paper or paperboard after the treatment are also protected from discoloration. The cross linking agent serves to tie up functional groups of the carbohydrate materials such as the cellulose in the paperboard and starch materials on and in the paperboard which would otherwise be oxidized to colored products by the release of hydrogen peroxide from the persalt.

BRIEF SUMMARY OF THE INVENTION

This invention relates to the treatment of paper or paperboard, comprising carbohydrate and protein materials, with a cross-linking agent such as a water-soluble modified formaldehyde resin, to prevent the paper and paperboard from becoming discolored and mottled in the presence of perborate-containing detergents.

It is known to employ starch in sizings and coatings for paper and paperboard. Starch has several advantages which make it a valuable component of surface sizings for paper and paperboard, among these being low cost, good pigment and surface binding power, ease of handling, and good coating holdout properties. Though starch performs well in sizings and coatings, there are some drawbacks to its use for specific applications. Under certain conditions, starch molecules may be degraded into colored products which render the surface of the paper or paperboard brown and unsightly. This situation is especially acute when the paper or paperboard is used to package materials which provide an oxidative environment for starch and other carbohydrates such as cellulose.

It is well known to employ persalts as bleaching agents in detergent formulations. The use of sodium perborate as an oxygen carrier or producer in a washing compound was suggested at least as early as 1914 in U.S. Pat. 1,144,186. Persalts, sometimes referred to as peroxyhydrates, such as alkali-metal perborates, percarbonates, perpyrophosphates, and persulfates, have been suggested for use in detergent compositions, as shown in U.S. Pat. 3,185,649. Because of the high bleaching efficiency of the persalts and the fact that they do not damage clothes to the extent of other known bleaching agents, the persalts, especially sodium perborate, are getting increased attention in detergent compositions.

The use of sodium perborate in detergents has had certain disadvantages. Because of its high oxidative efficiency, paper and paperboard containers for the detergents become discolored during storage and are no longer esthetically appealing. The discoloration occurs on both the inside and outside surfaces of the container or box. Generally, the inside surface has spots of brown color and in the severest cases, the surface assumes a substantially uniform brown color, whereas the outside of the box may have a mottled appearance, a non-uniform

browning consisting of dark brown areas adjacent to light yellow areas.

One known attempt to solve the detergent box discoloration problem has not been successful. This method involves a masking technique in which white ink is used to print over the board surface. This method has proven to be uneconomical as well as ineffective.

It is believed that the discoloration of the paperboard is a result of oxidative degradation of carbohydrate materials and protein materials which may be present. During storage, especially in hot and humid areas, the perborate material becomes active, releasing hydrogen peroxide which oxidatively reacts with carbohydrate material such as the cellulose in the paperboard and starch materials on and in the paperboard which are used to size the board during its manufacture. In similar manner, protein materials, such as soya protein and casein used as adhesives in coatings on the paperboard, become yellow to brown due to oxidative degradation. In terms of a detergent box, these reactions generally mean that the browning of the box on the inside surface involves the discoloration of the cellulose of the paperboard and the starch in the sizing, and the discoloration and mottling on the outside surface of the box is due to the oxidation products of cellulose, starch in the sizing and coating, and protein in the coating. The mottling on the outside surface is believed to be caused by borate materials which migrate through the paperboard. On the outside surface of the box, the mottled appearance generally consists of dark brown color in the valleys of the paperboard and brown to light yellow color on the high points of the paperboard.

While it has been established that a raw stock without sizing or coating will become discolored at a greater rate than a sized and/or coated paper or board, conventional sizings and coatings do not prevent the discoloration and, in fact, starch sizings and starch or protein coatings may also be attacked to produce colored products. I have found, however, that if the starch or protein materials are treated with a cross-linking agent, the discoloration of the paper or paperboard and the detergent box made therefrom is prevented or eliminated. The cross-linking agent serves to increase the molecular weight of the starch, and thereby increase the chemical resistance of the starch by tying up functional groups which are oxidizable to colored products. By treatment with a cross-linking agent, it is believed that not only is the starch stabilized but also some of the cellulose molecules in the substrate are cross-linked, and the color stability of the sized or coated substrate is further enhanced. While it is not definitely known why the protein, in a coating applied after application of the cross-linking agent, is protected against discoloration, it is believed that residual cross-linking agent migrates from the paperboard into the subsequently applied coating layer and cross-links the protein therein.

The cross-linking agent can be conveniently applied to the paper or paperboard during manufacture at the size press as a dispersion in water or as part of a sizing formulation which comprises conventional ingredients such as starch and clay. The cross-linking agent can also be applied at a water box on a calender stack which is normally located before, but may be after, the coating operation.

The preferred cross-linking agents for use in practicing the present invention are melamine formaldehyde and urea formaldehyde resins. The cross-linking agent is applied as an aqueous dispersion at concentrations varying from about .25% to 30%, the preferred range being from about .5% to 7.5% at the size press, and up to about 20% at the water box. Of course, concentrations higher than 30% may be employed if desired.

I have found that the paper or paperboard must pick up at least about .09 lb. of cross-linking agent per 3000 sq. ft. per side (.09 lb./ream/side) when applied at the size press to be effective in preventing discoloration of the paperboard in the presence of a persalt-containing detergent. The minimum effective pickup of cross-linking agent at the water box has been found to be about .5 lb./ream/side. It is believed that the reason for the increased amount of cross-linking agent needed at the water box is due to the fact that the agent must penetrate any starch already applied at the size press. The cross-linking agent can be applied, by itself or as part of a sizing, to only one surface of the paperboard to protect that side, or it can be applied in the preferred manner to both sides of the paperboard to protect both sides.

DETAILED DESCRIPTION

The invention will be described in greater detail with the aid of the following examples.

Examples 1-3

Paperboard, having a basis weight of about 190 pounds per 3000 square feet, was sized on both sides with about 2½ pounds of a conventional sizing having about 8% solids comprising 40% clay and 60% starch. After drying, the sized paperboard was coated on one side (wire side) with about 8 pounds of a conventional coating having about 55% solids comprising adhesive and pigment. In these runs, the adhesive comprised soya protein and resin, and the pigment was coating clay. After coating, the paperboard was dried in known manner. This paperboard is designated as "Control" in the table below. It had a brightness on the uncoated side of about 78.6 and a brightness of about 79.3 on the coated side before undergoing the aging test described below.

The compositions of the conventional sizing and coating disclosed above are purely illustrative. Any conventional sizing or coating adhesive or pigment can be used as they form no part of the present invention. The invention is not limited to the use of a particular starch as any of the usual papermaking starches, such as pearl, dextrins, oxidized, cationic, acid modified, and ethylated starches, can be used.

Some of the same paperboard from above was treatments on both its sides in accordance with the present invention. In some instances, melamine formaldehyde or urea formaldehyde resin was included in the sizing formulation in varying concentrations. In other instances, each resin was applied to the control paperboard at waterboxes on a calender located after the sizing and before the coating operations described above. The data on cross-linking agent concentration, application, and pickup were as follows:

Example	Cross-linking agent	Application and concentration at—		Agent pickup, lbs./ream/side
		Size press	Water box	
Control	0	0	0	0
1	Melamine formaldehyde	.5%	0	.09
2	Melamine formaldehyde	0	(1)	1.8
3	Urea formaldehyde	0	(2)	1.35

¹ 20% solution. ² 15% solution.

An accelerated aging test, which correlates well with actual field experience, has been used to test the effectiveness of the treatments of this invention. Detergent boxes were constructed from the treated and untreated paperboards, with the coated side forming the outside surface of each box, and the boxes were filled with detergent which contained sodium perborate as a bleaching agent. The detergent filled boxes were placed in a vacuum oven which was evacuated and maintained at 20 inches of mercury, and a temperature of 80° C. was maintained. After 72 hours in the oven, the boxes were removed

and examined for brightness loss and mottling. The following data was collected:

Example	LRL Brightness			
	Inside surface	Outside surface	Inside mottle	Outside mottle
Control	66.5	59.5	Yes	Yes
1	72.6	72.4	No	No
2	74.1	77.0	No	No
3	69.2	71.9	No	No

From the above data, it can be seen that very significant improvements in maintaining brightness and eliminating mottle by use of a cross-linking agent have been effected. It is important to note that mottling observations as well as brightness measurements are necessary to determine the effectiveness of any treatment since a surface may give a relatively good brightness measurement and yet be very much mottled in appearance, or it may exhibit a somewhat lower brightness and not be mottled.

EXAMPLES 4-7

In these runs, paperboard was again sized and coated in the manner described above in connection with Examples 1-3. Some of the control paperboard was treated with a cross-linking agent at the size press and some was treated at the waterbox, as shown below:

Example	Cross-linking agent	Application and concentration at—		Agent pickup, lbs./ream/side
		Size press	Water box	
Control	0	0	0	0
4	Melamine formaldehyde	(1)	0	.2
5	Urea formaldehyde	(2)	0	.15
6	Melamine formaldehyde	0	(3)	1.8
7	Urea formaldehyde	0	(4)	.9

¹ 20% on starch. ² 10% on starch. ³ 20% solution. ⁴ 10% solution.

After the 72 hour aging test described above, the following data was gathered:

Example	LRL brightness			
	Inside surface	Outside surface	Mottle inside	Mottle outside
Control	66.4	59.2	Yes	Yes
4	70.5	70.8	No	No
5	69.5	69.3	No	No
6	74.3	76.9	No	No
7	69.1	71.9	No	No

Again, it can be seen that color stability and elimination or prevention of mottling were effected by the use of a cross-linking agent at the size press or at the waterbox.

From the above and other tests, I have found that the minimum effective pickup of cross-linking agent at the size press is about .09 pound/ream/side to prevent discoloration of the paperboard in the presence of a persalt-containing detergent. At the waterbox, the pickup should be at least about .5 pound/ream/side to be effective against discoloration.

While the theory behind the effectiveness of the cross-linking agent treatment is not fully understood, it is believed that when the perborate material breaks down during storage and releases hydrogen peroxide, sites on carbohydrate or protein material which would normally support oxidation are not reactive due to having been tied up by the cross-linking agent. It is believed that not only are starches and proteins so protected, but cellulose near the surface of the paper or paperboard substrate is also protected.

Various changes may be made in the treatments set forth herein without departing from the spirit of this invention or the scope of the appended claims.

I claim:

1. In the process of manufacturing paper and paperboard which involves the steps of sizing the paperboard with a carbohydrate-containing sizing and then coating at least one surface of the paperboard with a coating composition that includes carbohydrate or protein ma-

5

terials, the improvement for the prevention of discoloration of carbohydrate and protein materials in and on the paperboard in the presence of perborate-containing materials which comprises, between the sizing and coating steps, applying to the paperboard an aqueous dispersion of a cross-linking agent for carbohydrate and protein substances selected from the group consisting of melamine formaldehyde and urea formaldehyde, the amount of cross-linking agent applied being at least about 0.5 pound per 3000 square feet of paperboard surface, and cross-linking said carbohydrate and protein substances with the cross-linking agent.

2. In the process of manufacturing paper and paperboard which involves the steps of sizing the paperboard with a carbohydrate-containing sizing and then coating at least one surface of the paperboard with a coating composition that includes carbohydrate or protein materials, the improvement for the prevention of discoloration of carbohydrate and protein materials in and on the paperboard in the presence of perborate-containing materials which comprises applying to the paperboard in the sizing step an aqueous dispersion of a cross-linking agent for carbohydrate and protein substances selected from the group consisting of melamine formaldehyde and urea formaldehyde, the amount of cross-linking agent applied being at least about 0.09 pound per 3000 square feet of paperboard surface, and cross-linking said carbohydrate and protein substances with the cross-linking agent.

3. The process of treating paperboard to decrease the oxidative degradation of carbohydrate constituents thereof to colored products in the presence of a persalt which comprises applying to one side of the paperboard an aqueous dispersion of a cross-linking agent for carbohydrate substances, selected from the group consisting of urea formaldehyde and melamine formaldehyde resin, the amount of cross-linking agent being at least about 0.09 pound per 3000 square feet of paperboard surface,

6

and cross-linking carbohydrate constituents of the paperboard with the cross-linking agent.

4. The process of claim 3 in which the cross-linking agent is applied to the paperboard as a sizing.

5. The process of claim 3 in which the resin is applied to the paperboard in an amount equal to at least about 0.5 pound per 3000 square feet of paperboard surface.

6. The process of claim 5 in which the cross-linking agent is applied to the paperboard at a waterbox on a calender stack.

7. The process of claim 3 which includes the step of applying to the other side of the paperboard an aqueous dispersion of a cross-linking agent for carbohydrate substances selected from the group consisting of urea formaldehyde and melamine formaldehyde resin, the amount of cross-linking agent being at least about 0.09 pound per 3000 square feet of paperboard surface, and cross-linking carbohydrate constituents of the paperboard with the cross-linking agent.

8. The process of claim 7 in which the cross-linking agent is applied to said other side of the paperboard at a waterbox on a calendar stack in an amount of at least about 0.5 pound per 3000 square feet of paperboard surface.

References Cited

UNITED STATES PATENTS

2,409,629	10/1946	Heritage	162—166
2,554,639	5/1951	Ryan	162—166

S. LEON BASHORE, Primary Examiner

R. H. ANDERSON, Assistant Examiner

U.S. Cl. X.R.

8—116.2; 117—155, 156; 162—166, 175, 184