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TREATMENT OF PAPER AND PAPERBOARD TO PREVENT DISCOLORATION

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ABSTRACT OF THE DISCLOSURE

Paper and paperboard, for use in packaging detergents containing a persalt, are treated with an inorganic alkali salt selected from the group consisting of water-soluble inorganic carbonates, bicarbonates, hydroxides, phosphates, and nitrites to provide the paper or paperboard with a surface pH within a particular alkaline range, to prevent the paper and paperboard from becoming discolored and mottled in the presence of such detergents due to oxidative degradation of carbohydrate and protein materials in and on the paper or paperboard.

BRIEF SUMMARY OF THE INVENTION

This invention relates to the treatment of paperboard with materials which provide the paperboard with a surface pH in the range of about 8.0 to 10.5, to inhibit the discoloration of the paperboard when used in containers to package detergents containing persalts.

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 persilicates, 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 or 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 most severe 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 materials such as the cellulose in the paperboard and starch materials in an on 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,

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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 board, conventional sizings and coatings do not prevent the discoloration. We have found, however, that the mottle or discoloration problem can be eliminated by manipulating the surface pH of the paperboard. This can be done by treating the paperboard with chemical materials which provide the board with a surface pH within a particular alkaline range. For this purpose, inorganic salts have been used, and we refer to these materials as inorganic alkali salts. The effective surface pH range has been found to be between about 8.0 and 10.5, with a preferred range between about 9.0 to 10.0. Within these ranges, carbohydrates and proteins have been found to have the best color stability in the presence of detergents containing persalts. Above about pH 10.5 and below about pH 8.0, the color stability of the paperboard deteriorates rapidly.

Many inorganic alkali salts have been found to be effective in modifying the surface pH of the paperboard to the desirable range. Among these are carbonates, bicarbonates, hydroxides, phosphates, and nitrites. Of course, as those skilled in the art will recognize, there are other alkali salts similar to those mentioned which could be used to provide the desired surface pH.

Among the alkali salts set forth above, in general there is no preference in regard to chemical species, as long as colored and catalytic ions are not present, such as copper and iron, and there is not preference as to the amount of salt required so long as the surface pH of the paperboard is brought to the desired range. Tests have shown that surface pH is the controlling factor and not the pH of the substrates beneath the surface layers which in most cases continues to have an acid pH after application of the alkali salts to the paperboard surface.

The alkali salts can conveniently be applied to paper or paperboard during manufacture, at the size press as a dispersion in water or as part of a sizing composition comprising conventional ingredients such as starch and clay. The alkali salts can be applied at a waterbox on a calender stack or during a post application to the paperboard or to the already constructed detergent container.

While it has been stated that there is no preference among the inorganic alkali salts used, for practical purposes a salt which has low equivalent weight and a water solution pH close to the desired range is obviously preferred. Because of their relatively high water solubility, alkali metal salts are used in the preferred embodiments of this invention to provide a surface pH within the range of 8.0 to 10.5 and preferably 9.0 to 10.0.

DETAILED DESCRIPTION

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

EXAMPLES 1–17

Paperboard, having a basis weight of about 190 pounds per 3000 square feet, was sized on both sides with about 2½ pounds per side 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.

Some of the same paperboard from above was given treatments on both its sides in accordance with the present invention. The alkali salts were applied as water solutions to the paperboard at waterboxes on a calender located after the sizing and before the coating operations described above. The salt solutions used were as follows:

Example	Waterbox finishing reagent	Reagent conc., percent	pH of finishing solution
Control	None		
1	KH_2PO_4, 52.5% Na_3PO_4, 47.5%	7.5	5.3
2	KH_2PO_4, 25% Na_3PO_4, 75%	7.5	9.6
3	KH_2PO_4, 22% Na_3PO_4, 78%	7.5	10.7
4	KH_2PO_4, 11% Na_3PO_4, 89%	7.5	11.7
5	Na_3PO_4	7.5	12.1
6	$NaHCO_3$, 33% Na_2CO_3, 67%	7.5	9.6
7	$NaHCO_3$		7.9
8	Na_2CO_3	7.5	11.3
9	K_2CO_3		11.8
10	$KHCO_3$		8.0
11	$CaCO_3$	(1)	10.0
12	$BaCO_3$	(1)	11.3
13	$Ba(OH)_2$	(1)	13.2
14	$Mg(OH)_2$	(1)	10.4
15	$NaOH$	3	14
16	$NaOH$	1.5	13.8
17	$NaNO_2$	2.5	10.2

1 Saturated 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, and the boxes were filled with detergent which contained sodium perborate as a bleaching agent. The coated side of the paperboard was the outside surface of each box. The detergent filled boxes were placed in a vacuum oven which was evacuated and maintained at 20 inches of mercury, and at a temperature of 80° C. After 48 hours in the oven, the boxes were removed and examined for brightness loss and mottle. The following data was collected:

Example	Treated board surface, pH		LRL Brightness		Mottle outside	Mottle inside
	Wire	Felt	Outside surface	Inside surface		
Control	6.0 or less	6.0 or less	59.0	59.3	Yes	Yes.
1	do	do	62.6	51.0	Yes	Yes.
2	8.4	8.4	63.9	75.8	Yes	No.
3	9.2–9.6	9.6	71.5	76.6	No	No.
4	9.2–9.6	9.6	74.1	76.6	No	No.
5	Above 10	Above 10	65.9	59.3	Yes	Yes.
6	9.6–10	9.6–10	73.8	68.3	No	No.
7	9.6	9.6	74.0	74.9	No	No.
8	9.2–9.6	9.6	75.6	76.8	No	No.
9	9.6–10	9.6–10	76.5	76.5	No	No.
10	9.6–10	9.6	74.9	73.9	No	No.
11	6.8 or less	6.8 or less	58.5	73.4	Yes	No.
12	6.8–7.6	6.8–7.6	61.1	66.5	Yes	Yes.
13	9.2	9.6	76.2	75.0	No	No.
14	6.8–7.6	6.8–7.6	60.5	67.7	Yes	No.
15	9.6–10	9.6–10	75.1	74.7	No	No.
16	9.2–9.6	9.6	74.7	74.6	No	No.
17	8.4	8.4	67.9	68.1	No	No.

From the above data, it can be seen that brightness stability and elimination of mottle can be achieved by manipulating the surface pH of the paperboard. It is important to note that mottle observations as well as brightness measurements are necessary to determine the effectiveness of any treatment since a surface may exhibit a relatively high brightness and yet be very mottled in

appearance, or it may exhibit a somewhat lower brightness and not be mottled.

From the above and other tests, the effective surface pH range has been found to be from about 8.0 to 10.5, with a preferred range from about 9.0 to 10.0. It can be seen from Examples 1 and 5 that a surface pH which is too high or too low will not protect the paperboard from either discoloration or mottling. Obviously, salts other than those shown above can be used to provide the paperboard with the desired surface pH.

While the theory behind the effectiveness of providing the surfaces of the paperboard with a particular pH is not fully understood, it is believed that either the carbohydrate and protein materials are not oxidized by the hydrogen peroxide released from the perborate in the detergent, or the oxidized materials produced are not colored in the pH range provided at the paperboard surfaces.

The surface pH of the various paperboard surfaces has been established in known manner by using commercially available indicator solutions. The indicators used have been: bromothymol blue, which is yellow at pH 6.0 and is blue at pH 7.6; phenol red, which is yellow at pH 6.8 and is red at pH 8.4; cresol red, which is yellow at pH 7.2 and is yellow-red-blue at pH 8.8; metacresol purple, which is yellow at pH 7.6 and is yellow-purple at pH 9.2; thymol blue, which is yellow at pH 8.0 and is blue at pH 9.6; and phenolphthalein, which is colorless at pH 8.2 and is red at pH 10.0.

In practice, each of the above indicator solutions was applied to the surface of the paperboard to determine the surface pH of the board. The indicator solutions were read after being in contact with a surface for one to two minutes on the coated side of the paperboard (wire side), and after 30 seconds on the felt side. For example, if on a paperboard surface, the metacresol purple changed from yellow to purple while the thymol blue remained yellow, the surface pH was taken to be about 9.2. However, if the thymol blue remained substantially yellow but had a tint of blue, the surface pH was rated to be in the range of 9.2 to 9.6.

EXAMPLE 18

As was previously stated, an alkali salt can be applied to the paperboard at various locations during the latter's manufacture. For example, aqueous dispersions of sodium nitrite, ranging in concentration upwardly from about 0.5%, have been used at the size press to provide paperboard with a surface pH within the effective range. In some instances, the sodium nitrite was used as a part of a sizing which contained conventional components such as starch and clay. In these runs, brightness stability was greatly improved over the untreated controls, and mottle was significantly decreased or eliminated. For example, in one run, sodium nitrite was applied to paperboard at the size press at a concentration of about 2.5%. The sized paperboard was subsequently coated on the wire side with about 8 pounds of a coating composition having about 55% solids comprising coating clay, soya protein, and resin. After drying, the surface pH of this paperboard was about 9.2. Other paperboard, prepared in identical manner except that the sodium nitrite was omitted, had a brightness on the wire side of about 78 and a brightness on the felt side of about 79. The surface pH of this board was less than 6.0. After the aging test decribed above, the untreated paperboard had a brightness of 61.5 on the wire side and 67.5 on the felt side and was badly mottled on both sides, while the sodium nitrite treated paperboard exhibited a brightness of 72.9 on the wire side and 75.2 on the felt side and was not mottled on either side.

EXAMPLE 19

Some of the paperboard designated as "Control" in Examples 1–17 was treated with sodium nitrite after the paperboard had been coated and dried. A 15% solution of sodium nitrite in water was applied to both sides of the coated and dried paperboard by an off-machine coater. After the aging test, the sodium nitrite paperboard had a brightness of 75.3 on the wire side and 73.6 on the felt side and was not mottled on either side. The untreated "Control" was badly mottled and discolored as indicated above in Examples 1–17.

From the above examples, it is apparent that the treatment of paperboard to provide a surface pH within the herein defined range is an effective deterrent to the discoloration and mottle problems frequently attendant with the use of paperboard in containers for persalt-containing detergents.

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

We 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 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 solution of an inorganic alkali salt in sufficient amount to provide the paperboard with a surface pH of about 8.0 to 10.5.

2. Paperboard, suitable for use in containers to package detergents containing a persalt as bleaching agent, bearing on at least one side thereof a coating of a water-soluble inorganic alkali salt in sufficient amount to provide the so-coated side of the paperboard with a surface pH of about 8.0 to 10.5.

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 at least a first side of the paperboard an aqueous solution of an inorganic alkali salt in sufficient quantity to provide said first side of the paperboard with a surface pH of about 8.0 to 10.5.

4. The process of claim **3** which includes the step of applying to a second side of the paperboard an aqueous solution of an inorganic alkali salt in sufficient quantity to provide said second side of the paperboard with a surface pH of about 8.0 to 10.5.

5. The process of claim **3** in which the inorganic alkali salt is applied to the paperboard as a sizing.

6. The process of claim **3** in which the inorganic alkali salt is applied to the paperboard at a waterbox on a calender stack.

7. The process of claim **3** in which the inorganic alkali salt is applied in sufficient quantity to provide said first side of the paperboard with a surface pH of about 9.0 to 10.0.

8. The process of claim **3** in which the inorganic alkali salt is selected from the group consisting of water-soluble inorganic carbonates, bicarbonates, hydroxides, phosphates, and nitrites.

9. The process of claim **3** in which the inorganic alkali salt is sodium nitrite.

10. The process of claim **1** in which the inorganic alkali salt is sodium nitrite.

11. 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, between the sizing and coating steps, the step of applying to the paperboard an aqueous solution of an inorganic alkali salt in sufficient amount to provide the paperboard with a surface pH of about 8.0 to 10.5.

12. The process of claim **11** in which the inorganic alkali salt is sodium nitrite.

13. 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, after the coating step, the additional step of applying to the paperboard an aqueous solution of an inorganic alkali salt in sufficient amount to provide the paperboard with a surface pH of about 8.0 to 10.5.

14. The process of claim **13** in which the inorganic alkali salt is sodium nitrite.

15. Paperboard containing sodium nitrite in sufficient quantity to provide the surfaces of the paperboard with a pH of about 8.0–10.5.

16. Paperboard bearing a coating of sodium nitrite in sufficient amount to provide the coated surface of the paperboard with a surface pH of about 8.0 to 10.5.

17. Paperboard containing sodium nitrite in sufficient quantity to provide the surfaces of the paperboard with a pH of about 9.0 to 10.0.

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