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3,476,582

METHOD OF IMPROVING THE WATER
RESISTANCE OF PAPER

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4 Claims

ABSTRACT OF THE DISCLOSURE

A method for improving the water resistance of paper coated with polyvinyl alcohol and a pigment which comprises incorporating in the surface of the coated paper borax and a water-soluble alkali metal salt of an amphoteric compound of a metal selected from the group consisting of aluminum, zinc, tin, lead and titanium or a water-soluble alkali metal silicate. The coating composition desirably contains an amount of a hydroxide, oxide or carbonate of a metal from Groups II, III or IV of the Periodic Table, in an amount sufficient to provide a pH of at least 7 on the surface of the coated paper.

This invention relates to a method of improving the water resistance of paper coated with a polyvinyl alcohol-pigment composition. More specifically, the present invention relates to a method of rendering paper water resistant by coating the paper with a coating solution composed essentially of polyvinyl alcohol and pigment, and then surfacing the coated paper with an aqueous solution of borax. As a preferred embodiment of the present invention the polyvinyl alcohol-pigment coating solution is provided additionally with one or more of the group consisting of the oxides, hydroxides and carbonates of metals in Groups II, III, and IV of the Periodic Table and satin white. Another preferred embodiment of the present invention involves adding to the polyvinyl alcohol-containing coating solution one or more members of the group consisting of water-soluble alkali metal salts of the amphoteric compounds of metals such as aluminum, zinc, tin, lead, titanium, and the like, and the water-soluble alkali metal silicates, or in the alternative, an aqueous solution of such member or members can be applied to the polyvinyl alcohol coated paper before or after the treatment with the aqueous solution of borax.

Conventional polyvinyl alcohol-pigment-coated paper has poor resistance to water and presents many problems in use. For example, art paper and coated paper surfaced with polyvinyl alcohol-pigment compositions present problems in offset printing because of insufficient water resistance.

In order to improve the water resistance of such paper, extensive studies have been made and materials such as melamine resin, urea resin, and the like have been found useful for this purpose. These thermosetting resins, however, have a shortcoming in that they are not effective unless rather rigorous drying conditions and acidity are maintained.

Polyvinyl alcohol and its derivatives, hereinafter referred to as PVA, are known to gel on reaction with borax and boric acid and the resulting reaction product has been used in the sizing of paper. For example, in sizing paper with PVA, the paper is treated beforehand with an aqueous solution of borax to prevent permeation of PVA thereinto, and then an aqueous solution of PVA is

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applied to the paper. It is also known that, when PVA is used as a warp sizing agent, boric acid may be added to the preparation to improve the desizing effect. There is no precedent, however, for use of the reaction product of PVA and borax or boric acid to improve the water resistance of paper because such product lacks water resisting characteristics. For example, PVA film and filament swell and dissolve in borax solution, and PVA filament treated with borax, when exposed to running water, reverts to its original state as PVA. It is not surprising, therefore, that no proposal has ever been made for using borax as a means for improving the resistance of PVA to water.

We have found that when pigment is contained in a PVA coating solution, treatment with an aqueous solution of borax of paper coated with said PVA-pigment solution, is highly effective for giving water resistance to the PVA. Moreover, the treatment with borax in no way affects the stability of the PVA-pigment coating solution because the paper is treated with an aqueous solution of borax only after the coating with the PVA-pigment solution. Another advantage of the process of the invention is that there is no need of heat treatment because the reaction of borax and PVA takes place at normal or ambient temperature. Further, inasmuch as increasing the pH of the borax solution improves the gellability of the PVA, more desirable results can be obtained by adding alkali such as caustic soda, caustic potash, or ammonia to increase the pH of the borax solution.

Although PVA-pigment-coated paper subsequently treated with borax is provided with sufficient water resistance at or about normal temperature, there is a tendency for the paper to gradually lose its water resistance with increasing temperature. Borax treatment of PVA-pigment-coated paper in a calender stack at a high temperature, e.g., 60° to 70° C., may cause deposition of the coating material on the calender. We have found that this disadvantage can be overcome and sufficient water resistance can be provided the coated paper by adding to the PVA-pigment coating solution one or more of the water-soluble alkali metal salts of the amphoteric compounds of metals such as aluminum, zinc, tin, lead, titanium, and the like, and the water-soluble alkali metal silicates. The useful water-soluble alkali metal salts of amphoteric hydroxides include for example, sodium aluminate, sodium zincate, sodium plumbite, and sodium stannate. The water-soluble alkali metal silicates useful include, for example, water glass obtained by the reaction of Na₂O with 1 to 4 mols of SiO₂, and those obtained by the reaction of K₂O with 1 to 4 mols of SiO₂. The water-soluble alkali metal salts of amphoteric compounds and water-soluble alkali metal silicates are either added to the pigment-PVA coating solution undercoat of the invention or are applied in the form of an aqueous solution on the undercoat, before or after the treatment with borax. The amount of alkali metal salts of amphoteric compounds added to the PVA-containing coating solution is usually a minor amount and may vary, but ordinarily about 0.25 to 5 parts per 100 parts of pigment are generally used. The alkali metal silicate may also often be used in a minor amount of about 0.25 to 5 parts per 100 parts of pigment in the coating solution. When the alkali metal salts of the amphoteric compounds or the alkali metal silicates are applied as a solution in minor concentrations of each up to about 10%, often at least about 0.5% are usually employed.

It is also useful for the purpose of the invention to add to the pigment-PVA coating solution an aqueous solution of aluminum hydroxide in excess caustic soda or an aqueous solution of excess caustic soda and aluminum sulfate or other salt, or to apply such composi-

tions on the paper already coated with the pigment-PVA coating solution, before or after the treatment with borax.

The effectiveness of the addition of a water-soluble alkali metal salt of an amphoteric compound in enhancing the resistance of PVA to water is demonstrated by the following experiment.

Test specimens of PVA film, 0.05 mm. in thickness, were dipped in a borax solution and then in either an aqueous solution of borax, or an aqueous solution of sodium aluminate, all kept at 60° C. Specimens not pretreated in borax solution were tested by dipping in either water or an aqueous solution of borax. The degree of swelling which resulted is shown in Table 1.

TABLE 1

Pretreatment	Liquid for swelling test (at 60° C. dipped for 10 min.)	Degree of swelling in area, ¹ percent
Not pretreated.....	Water.....	309.
Do.....	2% aq. sol. of borax.....	Partially dissolved, and unmeasurable.
Dipped in 2% aq. sol. of borax at 20° C. for 5 min.....	2% aq. sol. of borax.....	Do.
Dipped in 2% aq. sol. of borax at 20° C. for 10 min.....	2% aq. sol. of sodium aluminate.....	160.
	2% aq. sol. of sodium aluminate.....	142.

$$^1 \text{ Degree of swelling in area} = \frac{\text{Area of film before swelling}}{\text{Area of film after swelling}} \times 100$$

The following example shows that the addition of water glass prepared by the reaction of one mol of Na₂O and two mols of SiO₂ is useful in waterproofing PVA.

Test specimens of PVA film, 0.05 mm. in thickness, were dipped in a borax solution and then in either an aqueous solution of borax, or an aqueous solution of water glass, all kept at 60° C. Specimens not pretreated in borax solution were also tested by dipping in either water or an aqueous solution of borax. The degree of swelling which resulted is shown in Table 2.

TABLE 2

Pretreatment	Liquid for swelling test (at 60° C. dipped for 10 min.)	Degree of swelling in area, ¹ percent
Not pretreated.....	Water.....	309.
Do.....	2% aq. sol. of borax.....	Partially dissolved, and unmeasurable.
Dipped in 2% aq. sol. of borax at 20° C. for 5 min.....	2% aq. sol. of borax.....	Do.
Dipped in 2% aq. sol. of borax at 20° C. for 10 min.....	2% aq. sol. of water glass.....	150.
	2% aq. sol. of water glass.....	138.

$$^1 \text{ Degree of swelling in area} = \frac{\text{Area of film after swelling}}{\text{Area of film before swelling}} \times 100.$$

The treatment of paper with an aqueous solution of borax after coating with an acidic clay-PVA solution is desirable as a method for improving the water resistance of the pigment-PVA coat because the treatment causes gelling of the PVA-pigment system at normal temperature. However, although as aforementioned, the resistance to water provided through borax treatment can be further enhanced by increasing the pH of the coating solution through addition of water-soluble alkali, this method of increasing the pH is disadvantageous in that the pH tends to change while the coating solution stands and is difficult to adjust. We have found that this difficulty can be overcome and a PVA-pigment coated paper having a water resistance that remains unaffected by the lapse of time can be obtained after the borax treatment if the acidic PVA-pigment coating solution contains one or more of the oxides, hydroxides, and carbonates of the metals in Groups II, III, and IV of the Periodic Table, and satin white. Illustrative of such suitable compounds are, for instance, one or more of the class consisting, for example, of calcium carbonate, calcium hydroxide, basic magnesium carbonates (3MgCO₃·Mg(OH)₂·3H₂O), zinc oxide, and satin white. Use of these compounds is most beneficial when they are added to provide a pH on the surface of the coated paper of at least 7. Since the coating solution and coated paper prepared on this manner give a stable and readily adjustable pH value, the surfaced paper can acquire varying degrees of desired water resistance. Ordinarily, minor amounts of about 1 to 30%

or more of these Groups II, III and IV compounds, based on the pigment, are employed.

In the present invention, further satisfactory results can be obtained by adding to the coating solution of PVA-pigment a latex such as styrene-butadiene or acrylate, melamine resin, urea resin, glyoxal resin or the like. These resinous additives not only render the paper more water resistant, but also promote the flexibility of the coated film.

The water-soluble PVAs useful in the invention include completely saponified PVA, partially saponified PVA or copolymers of PVA with other unsaturated, polymerizable monomers, for instance, vinyl ether, allyl

alcohol, isopropenyl alcohol, etc. The degree of polymerization of the polyvinyl alcohol, upon which viscosity is dependent, may vary widely but the polymerization degree is often at least about 1000. The amount of the polyvinyl alcohol employed and thus the concentration of the resulting solution may vary depending upon the degree of polymerization of the polyvinyl alcohol but minor concentrations of about 1 to 25%, preferably about 5 to 15%, are generally preferred.

The pigment of the coating composition is that or-

dinarly employed in paper coating and is of commercial grade. Illustrative of suitable pigment-fillers are various siliceous materials such as clay, kaolinite



silica (SiO₂) and the like. The amount of pigment can vary but is most advantageously at least about twice the amount of polyvinyl alcohol and may be up to about fifteen or twenty times or more by weight the amount of polyvinyl alcohol.

The concentration of the aqueous solution of borax for use in the invention is often a minor amount, e.g., in the range of about 1 to 5%, though the percentage may be suitably chosen according to the amount of PVA to be applied on paper.

The method of the invention is very effective in that it is merely necessary to use an aqueous solution of borax instead of water on calender stacks after the drying of paper coated with a pigment-PVA coating solution. Since the step of sizing the coated paper with an aqueous solution of borax on calender stacks can be added without difficulty to the waterproofing process, it is applicable not only to cardboard manufacture, but also to the manufacture of other coated paper, art paper and the like.

The present invention is illustrated by the following examples which should not be construed to be restrictive.

EXAMPLE 1

One hundred parts of clay and an aqueous solution in which 0.4 part of sodium hexametaphosphate was dis-

solved were mixed with agitation to prepare a 65% slurry. Next, 8 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 98.5 mol. percent) and then 8 parts, on the basis of solids content, of styrene-butadiene latex were added to the slurry with stirring, to prepare a coating solution having a concentration of 40%.

The coating solution was applied on paper at a rate of 15 g./m.², and dried at 100° C. for 2 minutes. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper. After air drying, the surfaced paper was super calendered at 60° C.

When the test specimen treated with borax and an untreated control were dipped in water for swelling and then rubbed, the former showed good rubbing resistance while the latter whitened with the pigment.

EXAMPLE 2

One hundred parts of clay and an aqueous solution containing 0.4 part of sodium hexametaphosphate, were mixed with agitation to prepare a 65% slurry. An aqueous solution of caustic soda was dripped into the slurry to raise the pH to 10. Next, 8 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 88 mol. percent) and then 8 parts on the basis of solids content of styrene-butadiene latex were added to the slurry with stirring, to prepare a coating solution having a concentration of 40%.

The coating solution then was applied on paper at a rate of 15 g./m.² and dried. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper, and air dried.

Subsequently the surfaced paper was super calendered at 60° C. The pH of paper thus obtained was high, and the test specimen treated with borax showed better water resistance than a control of a low pH which was likewise treated with borax.

EXAMPLE 3

One hundred parts of clay was mixed with an aqueous solution in which 0.4 part of sodium hexametaphosphate was dissolved. With the addition of one part of sodium aluminate, the whole mixture was thoroughly agitated. To a 65% slurry thus prepared, 8 parts, on the basis of compound, of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 98.5 mol. percent) and then 8 parts on the basis of solids content of styrene-butadiene latex were added with stirring, to prepare a coating solution having a concentration of 40%. The coating solution was applied on paper at a rate of 15 g./m.², and dried at 100° C. for 2 minutes. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper. After air drying, the surfaced paper was super calendered at 60° C.

While the borax treatment was effective itself for enhancing the water resistance of coated paper, the property was all the more improved by the addition of sodium aluminate to the coating solution at a rate of one percent of the total amount of clay therein contained. Coated paper treated with borax without the addition of sodium aluminate lost its water resistance completely in a week, but a test specimen processed in accordance with the method of the invention showed no decline in water resistance. The results are shown in Table 3.

TABLE 3

Coating solution	pH of paper surface	Water resisting property immediately after coating	Water resisting property a week after coating
Not containing sodium aluminate..	6.4	Good.....	Fair.
Containing sodium aluminate.....	6.6	Excellent...	Excellent.

EXAMPLE 4

One hundred parts of clay and an aqueous solution containing 0.4 part of sodium hexametaphosphate, were mixed with agitation to prepare a 65% slurry. An aqueous solution of caustic soda was dripped into the slurry to raise the pH to 9. Next, 6 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 88 mol. percent) and then 12 parts, on the basis of solids content, of styrene-butadiene latex were added to the slurry with stirring, to prepare a coating solution having a concentration of 40%. The coating solution was applied on paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper, and air dried. Next, an aqueous solution containing 3% sodium zincate was applied and air dried, and the coated paper was super calendered.

Again the control subjected to the borax treatment alone exhibited less water resistance than the paper treated additionally with sodium zincate. As in Example 1, the test specimen showed no loss of water resistance after the lapse of one week.

EXAMPLE 5

One hundred parts of clay and an aqueous solution in which 0.4 part of sodium hexametaphosphate was dissolved, were mixed with agitation to prepare a 65% slurry. To the slurry thus obtained, 6 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1300, saponification degree 95 mol. percent) and then 10 parts, on the basis of solids content of styrene-butadiene latex were added with stirring to prepare two portions of coating solutions A and B, both at a concentration of 40%. Another coating solution C at a concentration of 40% was also prepared by adding melamine resin in an amount of 10% of the total amount of PVA in the above preparation. The coating solutions A, B and C were applied to paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. The test specimens coated with the coating solutions A, B and C are herein referred to as coated specimens A, B and C. The coated specimens A and C were directly coated with a 2% borax solution in such a manner that borax accounted for 2% of the total amount of the coat and was air dried. The coated specimen B was coated with a 2% sodium aluminate solution to render the coated surface alkaline, and then was coated with a 2% borax solution at such a rate that the borax content of the coat could be adjusted to 2%, and the surface coat air dried.

The coated specimens A, B and C thus obtained were all super calendered at 60° C. The coated specimens invariably exhibited good water resistance immediately after the coating, but in a week the specimen A lost most of its water resistance, while the specimens B and C both retained their property.

EXAMPLE 6

One hundred parts of clay and an aqueous solution containing 0.4 part of sodium hexametaphosphate, were mixed with agitation to prepare a 65% slurry. An aqueous solution of caustic soda was dripped into the slurry to raise the pH to 9. Next, 5 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and a saponification degree 98 mol. percent)

and then 10 parts, on the basis of solids content, of styrene-butadiene latex were added to the slurry with stirring, to prepare a coating solution having a concentration of 40%. The coating solution was applied on paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper, and air dried. Next, a 2% aqueous solution of water glass (composed of Na₂O and SiO₂ at a molar ratio of 1:3) was applied to the coated surface and the paper was super calendered at 60° C. The combined treatment of coated paper with borax and water glass proved more effective than the treatment with borax alone. When allowed to stand indefinitely, the water resisting property of the coated paper was stable.

EXAMPLE 7

One hundred parts of clay was mixed with an aqueous solution in which 0.4 part of sodium hexametaphosphate was dissolved. With the addition of one part of water glass (composed of Na₂O and SiO₂ at a molar ratio of 1:2), the whole mixture was thoroughly agitated. To a 65% slurry thus prepared, 8 parts on the basis of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 98.5 mol. percent) and then 8 parts, on the basis of solids content of styrene-butadiene latex were added with stirring, to prepare a coating solution having a concentration of 40%. The coating solution was applied on paper at a rate of 15 g./m.², and dried at 100° C. for 2 minutes. On the thus coated surface, a 2% aqueous solution of borax was applied at such a rate that the solid borax content accounted for 2% of the total coating material contained in the paper. After air drying, the surfaced paper was super calendered at 60° C.

While the borax treatment was effective itself for enhancing the water resistance of coated paper, the property was all the more improved by the condition of water glass to the coating solution. Coated paper treated with borax without the addition of water glass lost its water resistance completely in a week, but a test specimen processed in accordance with the method of the invention showed no decline in water resistance.

EXAMPLE 8

One hundred parts of clay was mixed with an aqueous solution containing 0.4 part of sodium hexametaphosphate. With the addition of one part of K₂O·SiO₂, the whole mixture was thoroughly agitated. To a 65% slurry thus prepared, 7 parts in terms of compound of a 10% aqueous solution of a PVA (polymerization degree 1750, and saponification degree 98.5 mol. percent) and then 8 parts, on the basis of solids content of styrene-butadiene latex were added with stirring, to prepare a coating solution having a concentration of 40%.

The coating solution was applied on paper at a rate of 15 g./m.², and dried at 100° C. for 2 minutes. On the coated surface, a 2% aqueous solution of borax was applied at such a rate that the solid borax content accounted for 2% of the total coating material paper deposited on the paper. After air drying, the surfaced paper was super calendered at 70° C. While the borax treatment was effective for enhancing the water resistance of the coated paper, the property was all the more improved by the addition of K₂O·SiO₂ to the coating solution. Coated paper treated with borax without the addition of K₂O·SiO₂ lost its water resistance completely in a week, but a test specimen processed in accordance with the method of the invention showed no decline in water resistance.

EXAMPLE 9

Clay was dispersed in an aqueous solution of sodium hexametaphosphate in an amount of 0.4% of the total amount of the clay, to prepare a 65% slurry. A mixed

solution consisting of satin white in a concentration of 20% and a 10% aqueous solution of a PVA (polymerization degree 1750 and saponification degree 88 mol. percent) was added to the slurry with stirring. In this way, 6 portions of coating solution were prepared, all with a concentration of 40% but having different mixing ratios of clay and satin white. The different portions of coating solution were applied on paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. Further, a 2% aqueous solution of borax was applied on the coated paper in such a manner that the solid borax content could account for 2% of the total amount of coating material contained in the coat, and the paper specimens were air dried and super calendered at 60° C. The effects of the amount of satin white and of the borax treatment upon the water resistance of the coated paper are shown in Table 4. Specimens treated with borax showed good water resistance as compared with the untreated specimens.

TABLE 4.—PERCENTAGE OF SATIN WHITE IN PIGMENT AND WATER RESISTING PROPERTY OF COATED PAPER.

Satin white content, percent	Treatment with borax	pH of coated surface	Water resisting property	
			Immediately after coating	7 days after coating
0	No	5.0	Poor	Poor
2	No	6.8	do	Do.
5	No	Over 8.8	do	Do.
10	No	do	do	Do.
15	No	do	do	Do.
20	No	do	do	Do.
0	Yes	6.4	Good	Do.
2	Yes	7.2	do	Good.
5	Yes	7.4	Excellent	Excellent.
10	Yes	8.4	do	Do.
15	Yes	Over 8.8	do	Do.
20	Yes	do	do	Do.

NOTE.—The amount of PVA contained in the coating solution was 7% of the total amount of pigment in the solution.

EXAMPLE 10

Clay was dispersed in an aqueous solution of sodium hexametaphosphate in an amount of 0.4% of the total amount of the clay, to prepare a 65% slurry. A 50% paste of calcium carbonate was added to the slurry in different mixing ratios with the clay to obtain different pigment slurries. To 100 parts of each pigment slurry, 8 parts, on the basis of solids content, of a 10% aqueous solution of a PVA (polymerization degree 1750 and saponification degree 98.8 percent) and 8 parts, on the basis of solids content, of styrene-butadiene latex were added with stirring, to prepare a coating solution with a concentration of 40%.

This coating solution was applied on paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. Then, a 2% aqueous solution of borax was applied on the coated surface at such a rate that the solid borax content of the coating material contained in the paper could account for 2% of the total amount of the material, and the paper was super calendered at 60° C. The paper exhibited good water resistance on the alkaline side.

EXAMPLE 11

One hundred parts of clay and an aqueous solution containing 0.4 part of sodium hexametaphosphate were mixed with agitation to prepare a 65% slurry. An aqueous solution of caustic soda was dripped into the slurry to raise the pH to 9. Next, 5 parts in terms of compound of a 10% aqueous solution of a PVA derivative (vinyl alcohol-vinyl ether copolymer) and then 10 parts, on the basis of solids content, of styrene-butadiene latex were added to the slurry with stirring, to prepare a coating solution having a concentration of 40%. The coating

solution was applied on paper at a rate of 15 g./m.² and dried at 100° C. for 2 minutes. On the coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper, and air dried. Next, a 2% aqueous solution of water glass (composed of Na₂O and SiO₂ at a molar ratio of 1:3) was applied to the coated surface and the paper was super calendered at 60° C.

The combined treatment of coated paper with borax and water glass proved more effective than the treatment with borax alone. When allowed to stand indefinitely, the water resisting property of the coated paper was stable.

EXAMPLE 12

One hundred parts of clay was mixed with an aqueous solution in which 0.4 part of sodium hexametaphosphate was dissolved. With the addition of one part of sodium aluminate, the whole mixture was thoroughly agitated. To a 65% slurry thus prepared, 8 parts in terms of compound of a 10% aqueous solution of a PVA derivative (vinyl alcohol-vinyl ether copolymer) and then 8 parts on the basis of solids content of styrene-butadiene latex were added with stirring, to prepare a coating solution having a concentration of 40%. The coating solution was applied on paper at a rate of 15 g./m.², and dried at 100° C. for 2 minutes. On the coated surface, a 2% aqueous solution of borax was applied at such a rate that the borax accounted for 2% of the total coating material contained in the paper. After air drying, the surfaced paper was super calendered at 60° C.

While the borax treatment was effective itself for enhancing the water resistance of coated paper, the property was all the more improved by the addition of sodium aluminate to the coating solution. Coated paper treated with borax without the addition of sodium aluminate lost its water resistance completely in a week, but a test specimen processed in accordance with the method of the invention showed no decline in the water resisting property. The results are shown in Table 5.

TABLE 5

Coating solution	pH of paper surface	Water resisting property	
		Immediately after coating	Week after coating
Not containing sodium aluminate.....	6.4	Good.....	Fair.
Containing sodium aluminate.....	6.6	Excellent.....	Excellent.

sive property or privilege is claimed are defined as follows:

1. A method of improving the water resistance of paper which comprises the steps of coating paper with an aqueous coating solution containing about 1 to 25 percent polyvinyl alcohol and a siliceous pigment in an amount by weight of about 2 to 20 times the polyvinyl alcohol, applying to the coated paper an aqueous solution containing about 0.5 to 10 percent of a member selected from the group consisting of water-soluble alkali metal salts of an amphoteric compound of a metal selected from the group consisting of aluminum, zinc, tin, lead and titanium and water-soluble alkali metal silicates then surfacing the coated paper with an aqueous solution containing about 1 to 5 percent borax and drying the coated paper.

2. The method of claim 1 wherein the coating solution contains in addition a member selected from the group consisting of the oxides, hydroxides, and carbonates of metals in Groups II, III, and IV of the Periodic Table, and satin white in an amount sufficient to provide a pH of at least 7 on the surface of the paper.

3. A method of improving the water resistance of paper which comprises the steps of coating paper with an aqueous coating solution containing about 1 to 25 percent polyvinyl alcohol and a siliceous pigment in an amount by weight of about 2 to 20 times the polyvinyl alcohol, applying an aqueous solution containing about 1 to 5 percent borax to the coated paper, then surfacing the coated paper with an aqueous solution containing about 0.5 to 10 percent of a water-soluble alkali metal salt of an amphoteric compound of a metal selected from the group consisting of aluminum, zinc, tin, lead and titanium and water-soluble alkali metal silicates and drying the coated paper.

4. The method of claim 3 wherein the coating solution contains in addition a member selected from the group consisting of the oxides, hydroxides, and carbonates of metals in Groups II, III, and IV of the Periodic Table, and satin white in an amount sufficient to provide a pH of at least 7 on the surface of the paper.

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WILLIAM D. MARTIN, Primary Examiner

M. LUSIGNAN, Assistant Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,476,582 Dated November 4, 1969

Inventor(s) Saburo Imoto and Tatsuaki Hattori

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Table 1, second column, add --) -- after "10 min.";
second column, last line "alumiuate" should read
-- aluminate --.

Table 1, reference 1, "Area of film before swelling
Area of film after swelling"
should read

-- Area of film after swelling
Area of film before swelling --;

Col. 3, line 71, "on" should read -- in --.

Col. 7, line 39, "condition" should read -- addition --;
line 61, "th" should read -- the --;
line 61, delete the word "paper" after "material".

Table 4, first line of the "Note", the word "coatlng" should
read -- coating --.

Col. 10, add the following before line 1, -- The embodiments
of the invention in which an exclu- -

SIGNED AND
SEALED

AUG 25 1970

(SEAL)

Attest:

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Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents