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PROCESS FOR PRODUCING HIGH WET STRENGTH PAPER

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This invention relates to the treatment of papers and, more particularly, to the imparting of certain desired surface and body properties to said paper by said treatment.

Papers of high wet strength fall in the following categories as designated by their mode of preparation:

1. Parchments, fish papers, etc., are made by treating water leaf webs of cellulosic fibers with concentrated sulfuric acid, concentrated aqueous zinc chloride or concentrated aqueous calcium thiocyanate solutions under carefully controlled and specific conditions, washing out the treating agent and drying. The web during contact with the treating liquid and the removal of the treating material is so weak that high speed treatment is impracticable. This puts such paper in the high cost class.

2. Papers of this type may be formed by application of adhesives such as viscose, glue, urea-formaldehyde or phenol-formaldehyde to webs of paper-making fibers before or after web formation with specific after-treatment to convert these adhesive substances into the water-insoluble form. The viscose treatment requires considerable washing at time-consuming speeds. The glue treatment requires formaldehyde to insolubilize the glue, the product is odorless and it must contain large ratios of glycerol or other softeners. Urea-formaldehyde treated paper is very stiff. Phenol-formaldehyde treated paper is very stiff, odorless and colored.

3. Such papers may be formed by treatment of webs of paper-making fibers with formaldehyde and mineral acid catalysts and heating above 110° C. to absolute dryness. The product is degraded considerably by drying completely at such high temperatures in the presence of mineral acids and it gives off free formaldehyde whenever moistened, so it constitutes a health hazard.

4. These papers may be formed by flash heating a web of paper-making fibers with or without a glue size at 400° to 450° C. The paper is degraded somewhat by the high temperature of heating.

5. These papers may be prepared by impregnation of dry paper webs with solutions of resins or water-insoluble cellulose derivatives in organic solvents and drying. The raw materials are costly due in part to the use of organic solvents and in part to an extra processing.

6. These papers may be prepared by application of pigmented coating compositions to one or both sides of the paper web using adhesives,

such as casein, glue or vegetable protein with formaldehyde to produce a limited degree of water resistance. The proteins are unstable and they impart a yellow cast to the coating.

5 This invention has as its object the production of a high wet strength paper. Another object is to produce such paper by a method that will operate at speeds of at least 500 ft. per min. Another object is to produce a high wet strength paper free from odor and injurious substances. Still another object is to produce a paper having a high wet strength and which also has good printing properties, is resistant to finger-marking, and is capable of being washed with water. 15 Another object is to prepare a high wet strength paper which has a high color. Other objects will be apparent from the following description of the invention.

20 These objects are accomplished by applying to a web of paper-making fibers polyvinyl alcohol and a water soluble N-methylol aliphatic nitrogen-containing compound preferably in aqueous solution having a pH in excess of 5.5 and heating said treated paper to such a degree as to cause 25 an insolubilizing reaction between the polyvinyl alcohol and the N-methylol compound. This insolubilizing reaction is best carried out in the presence of a catalyst such as an acid, preferably, however, in the presence of an ammonium salt 30 of a mineral acid.

The aqueous solution of polyvinyl alcohol is mixed with the water-soluble N-methylol aliphatic nitrogen-containing compound, preferably a methylol-melamine and an ammonium salt of 35 a mineral acid in concentrations that give workable viscosities, is applied to one or both sides of the paper simultaneously, is passed through a drier system where both surfaces are in contact with metal surfaces that are at a temperature above 65° C. until dried to a moisture content of about 4 to 20% or until the wet strength 40 is at least 50% greater than that of the same sheet treated under the same conditions with the same amount of polyvinyl alcohol but without the addition of the N-methylol aliphatic nitrogen containing compound and ammonium salt.

The following examples set forth certain well defined instances of this invention. They are, however, not to be considered as limitations 45 thereof, since many modifications may be made without departing from the spirit and scope of this invention.

Example I

55 A web of paper is formed from a mixture of

70 parts of ground wood and 30 parts of unbleached sulfite fibers into a sheet of 34 lbs. for a 24 x 36 x 500 ream. The dry sheet is sprayed on one side with a solution comprising 5.0 parts polyvinyl alcohol, 1.0 part trimethylol melamine and 94 parts water in sufficient amount to add 1.0 part polyvinyl alcohol to 100 parts dry fiber weight. An aqueous solution of ammonium chloride is then sprayed on the sheet in sufficient amount to add 10.7 parts ammonium chloride. The sheet is then pressed against a heated, smooth, metal cylinder by means of a canvas belt for 30 seconds. The tensile strength of a strip 0.5 by 5.0" in wet state is 3.51 lbs. compared to 0.42 lb. for a strip of the same paper that is treated with water only before drying. The polyvinyl alcohol is of the hot water-soluble type with an intrinsic viscosity of 23 centipoises in 4% aqueous solution at 25° C. and with a saponification value of 6. The methylol melamine is prepared by adding 1 mol anhydrous melamine to 3 mols formaldehyde as a neutral 37% solution in water and methanol, heating at 80° C. for 30 minutes, pouring into enough hot water to make a 5% solution and cooling.

Example II

A 50-lb. sheet (ream=24 x 36 x 500) of white, sized, clay-filled paper is coated on the wire side with a clay slurry to the extent of 4 lbs. solids per ream. It is dried by passing the coated side over the smooth surface of heated metal cylinders for 30 seconds using a regular drying canvas to press the sheet against the cylinders which are heated by 20 lbs. gage steam pressure. The product is super-calendered to a high gloss. It gives a minimum coating pick of 6 and a minimum fiber pick of 9 and it withstands more than 4000 wet rubs without losing pigment from the surface. The coating composition consists of 100 parts high grade coating clay, 5.0 parts polyvinyl alcohol, 1.5 parts dimethylol biuret, 4.0 parts ammonium chloride and 196 parts water. The same sheet coated in the same manner with a slurry consisting of 100 parts of clay, 5.0 parts polyvinyl alcohol, and 202 parts water loses pigment on one wet rub. The polyvinyl alcohol has an intrinsic viscosity of 22 centipoises in 4% aqueous solution at 25° C. and has a saponification value of 11. The wet rub test is made by applying 10 drops of distilled water to the coated surface and rubbing with the forefinger in one inch strokes. Water is added dropwise as needed to keep the area wet. The white pigment is readily recognized when loosened from the paper. The same sheet coated in the same manner with a slurry consisting of 100 parts of clay, 15 parts casein, 37% solution of formaldehyde 0.6 part, and water 214 parts; and dried under the same conditions gives a minimum coating pick of 6, a maximum fiber pick of 8, and 3400 wet rubs.

Example III

A water leaf web of 30 lbs. weight for 24 x 36 x 500 ream if formed from a Mitscherlich grade of bleached sulfite fiber that is beaten to the condition to form a greaseproof paper with density of 17 lbs. per mil per ream. After passing over enough drying cylinders to reduce moisture content to 45%, the sheet is passed between tub-size rolls where both sides are treated with a solution of polyvinyl alcohol 3.0 parts, dimethylol ammonium sulfamate 0.5 part, ammonium nitrate 4.0 parts, and water 92.5 parts; and squeezed sufficiently to leave 2% polyvinyl alcohol based on

the dry fiber weight. The polyvinyl alcohol has an intrinsic viscosity of 17 centipoises in a 4% aqueous solution at 25° C. and has a saponification value of 7.2. The sheet then passes over more drying cylinders that are heated with 10 lbs. gage steam pressure. The time of passage over these cylinders is 30 seconds and the moisture content of the sheet on emerging is 7%. The sheet is then moistened further by passing through a solution containing glycerol 3.0 parts, invert sugar 9.0 parts, and water 88 parts with enough solution absorbed to add 4.0 parts total softener based on dry sheet weight, is allowed to stand in loose roll form 24 hrs. and is supercalendered with alternate rolls heated by 80 lbs. gage steam pressure. The product is a smooth, dense highly polished sheet of glassine paper with a resistance to turpentine greater than 8 hrs. and a wet tensile strength of 6.8 lbs. The turpentine resistance and wet strength of same sheet to which the glycerol-invert sugar mixture is applied to the extent of 8.0 parts instead of the polyvinyl alcohol composition is 3 hrs. and 0.6 lb., respectively. The turpentine resistance test is made as follows: Cut 16 samples 2" sq. each, from representative areas of each sample of paper; these are given a sharp bend a quarter inch from each end to facilitate handling. They are then arranged, on a large sheet of smooth white paper which serves as a tell-tale. One-inch squares of blotting paper (kerosene absorption 350%) 0.050" thick are placed on each test piece. Then 0.4 cc. of anhydrous turpentine, colored with a red dye (2.0 parts oil soluble red to 98 parts turpentine), is applied to the blotting paper square and a 1" cube of brass is placed promptly onto this square of blotting paper. Test sheets with blotting paper and brass cubes in position are pulled along the surface of the tell-tale paper to new positions at intervals in order to determine time in which the tell-tale sheet is marked by the colored turpentine. The turpentine resistance is expressed in minutes as a mean for all 16 samples. Samples that show no penetration at 480 minutes are treated with an additional 0.2 cc. colored turpentine and this is repeated until completion of test. Eight strips of 0.5 x 5.1" are cut across the grain and the other set with the grain. They are submerged in distilled water 15 minutes at 25° C., excess water is removed from the surface of each strip just before testing by means of blotting paper. The tensile strength is determined on an inclined plane type of Scott tensile tester which records strength and stretch automatically at intervals of approximately 0.01 lb.

Example IV

A 40-lb. sheet of white, sized, clay-filled paper is coated on both sides at once with 4 lbs. solids per side per ream by passing the dry sheet between rubber covered rolls and drying by passing over steam heated cylinders that are treated with 20 lbs. gage steam pressure. The time of heating is 30 seconds. The coating composition consists of 100 parts of chalk, 7 parts polyvinyl alcohol, 1.2 parts dimethylol thiourea, 5.0 parts ammonium chloride, and 138 parts of water. After calendering it has a minimum coating pick on the wire side of 6, a minimum fiber pick of 8 and wet rub resistance of 2176. This is in contrast to a coating pick of 5, fiber pick of 7, and wet rub resistance of 0 for the same coating in which the dimethylol thiourea and ammonium chloride are omitted. The polyvinyl alcohol has an intrinsic viscosity of 18 centipoises in a 4%

aqueous solution at 25° C. and a saponification value of 7.0. The dimethylol thiourea is prepared by adding 1.0 mol dry thiourea to 2.2 mols of a neutral formaldehyde solution of 37% strength, maintaining the reaction mixture at 40° to 50° C. for 1 hr. and then at room temperature for 12 hrs., and then adding to this solution gradually a sufficient amount of boiling water to make a 5% solution and cooling to room temperature.

Example V

A sheet of cardboard, weighing 240 lbs. per ream, is coated on one side with 12 lbs. solid per ream by passing the dry sheet through a brush coater system and drying by passing over a system of cylindrical driers heated to 5 lbs. gage steam pressure with total heating time of 45 seconds. It is then calendered to develop gloss and smoothness. The coating composition consists of calcium sulfite 100 parts, polyvinyl alcohol 8 parts, monomethylol adipamide 0.6 part, ammonium bromide 2.0 parts, and water 110 parts. The polyvinyl alcohol has an intrinsic viscosity of 65 in a 4% aqueous solution at 25° C. and has a saponification value of 245. The coating after calendering has a coating pick of 6, a fiber pick of 9 and wet rub resistance of 1570 in comparison to a coating pick of 6, a fiber pick of 8 and wet rub resistance of 0 for the same coating from which the monomethylol adipamide and ammonium bromide are omitted.

Example VI

A web of paper is formed from a mixture of ground wood 70 parts and unbleached sulfite 30 parts into a sheet of 34 lbs. for 24" x 36" x 500 ream. The dry sheet is sprayed on one side with an aqueous solution comprising polyvinyl alcohol 1.0 part, trimethylol melamine 0.2 part and water 98.8 parts in sufficient amount to add 1 part polyvinyl alcohol to 100 parts bone dry weight fiber. The sheet is then pressed against a heated, smooth, metal cylinder by means of a canvas felt for 60 seconds. The tensile strength of a strip 0.5" by 5.0" in the wet state is 165 grams. (For this test strips are submerged in distilled water at 25° C. for 15 minutes, excess water is removed by blotting and tensile strength is determined.) The polyvinyl alcohol is of the hot water soluble type with a specific viscosity of 23 centipoises and a saponification value of 6. The trimethylol melamine is prepared by adding 1 mol dry melamine to 3 mols formaldehyde as a neutral 37% solution in water and methanol, heating at 80° C. for 15 minutes, letting stand for 8 hours at room temperature, adding water enough to make a 10% solution, heating to 80° C. just long enough to effect solution and pouring enough cold water into this hot solution to make a 5% solution. For comparison with the same paper treated with equal amounts of other aqueous solutions and dried under the same conditions the following table is given:

	Test #1	Test #2	Test #3	Test #4	Test #5
Polyvinyl alcohol	0.00	1.00	1.00	1.00	1.00
Trimethylol melamine	0.00	0.00	0.20	0.20	0.20
0.1% hydrochloric acid solution	0.00	0.00	0.00	1.5	0.00
Ammonium chloride	0.00	0.00	0.00	0.00	0.60
pH	7.0	7.1	7.3	5.9	6.3
Pounds wet tensile strength	0.24	0.33	0.36	0.39	0.62
Percent increase in tensile strength over test #1		37.5	50.0	62.5	158

The figures given for the first four items repre-

sent percent of the ingredients absorbed in the paper on the basis of bone dry weight of fibers.

Example VII

A 50 lb. sheet (ream=24 x 36 x 500) of white, sized clay-filled paper is coated on the wire side with a clay slurry coating composition to the extent of 4 lbs. solids per ream. It is dried by pressing the coated side against the smooth surface of a heated metal cylinder for 30 seconds using a regular drying canvas to press the sheet against the cylinder which is heated by 20 lbs. gage steam pressure. The product is supercalendered to a high gloss. It gives a minimum coating pick of 5 and a minimum fiber pick of 8 and it withstands more than 4,000 wet rubs by hand without losing pigment from the surface. The coating composition consists of 100 parts of a high grade coating clay, 5.0 parts polyvinyl alcohol, 2.1 parts trimethylol melamine, 1.0 part ammonium nitrate, and 200 parts water. The pH of this coating slurry is 6.4. The same sheet coated in the same manner with a slurry consisting of 100 parts of clay, 5.0 parts polyvinyl alcohol, and 202 parts water loses pigment on one wet rub. The polyvinyl alcohol has a specific viscosity of 31 centipoises and a saponification value of 15.

The same sheet coated in the same manner with a slurry consisting of 100 parts clay, 15 parts casein, 0.6 part formaldehyde, and 214 parts water and dried under the same conditions gives a minimum coating pick of 6, and a minimum fiber pick of 8, and 3,400 wet rubs.

Example VIII

A water leaf web of 30 lbs. weight for 24 x 36 x 500 ream is formed from a Mitscherlich grade of bleached sulfite fibers that are beaten to the condition to form a grease-proof paper with density of 17 lbs. per mil per ream. After passing over enough drying cylinders to reduce moisture content to 45% the sheet is passed between tub-size rolls where both sides are treated with a solution of 3 parts polyvinyl alcohol, 0.6 part trimethylol melamine, 0.4 part ammonium sulfate and 96 parts water and squeezed sufficiently to leave 2% polyvinyl alcohol based on the dry fiber weight. The polyvinyl alcohol has an intrinsic viscosity of 12 centipoises in 4% aqueous solution at 25° C. and a saponification value of 5.0. The sheet then passes over more drying cylinders that are heated with 10 lbs. gage steam pressure. Time of passage over these cylinders is 30 seconds and the moisture content of the sheet on emerging is 6%. The sheet is then moistened by passing through a solution containing 1.0 part glycerol, 3.0 parts invert sugar, and 96 parts water with enough solution absorbed to add 4.0 parts total softener based on dry sheet weight, is allowed to stand in loose roll form for 24 hours, and is supercalendered. The product is a smooth, dense, highly polished sheet of glassine paper with a turpentine resistance greater than 8 hours and a wet tensile strength of 7.2 lbs. The turpentine resistance and wet strength of same sheet to which the glycerol-invert sugar mixture is applied to the extent of 8.0 parts instead of the polyvinyl alcohol composition is 3 hours and 0.6 lb., respectively.

Example IX

A 40 lb. sheet of white, sized, unfilled paper is coated on both sides at once with 4 lbs. solids per side per ream by passing the dry sheet be-

tween rubber covered rolls and drying by passing over steam heated cylinders that are heated with 20 lbs. gage steam pressure. The time of heating is 30 seconds. The coating composition consists of 100 parts of chalk, 7.0 parts polyvinyl alcohol, 3.0 parts methylol melamine, 4.0 parts ammonium chloride, and 137 parts water. It has a pH of 9.8. After calendering it has a minimum coating pick on the wire side of 5, a minimum fiber pick of 8, and wet rub resistance of 3,050. This is in contrast to a coating pick of 5, fiber pick of 7, and wet rub resistance of 0 for the same coating in which the methylol-melamine and ammonium chloride are omitted. The polyvinyl alcohol has an intrinsic viscosity of 18 centipoises in 4% aqueous solution at 25° C. and has a saponification value of 7.0. The methylolmelamine is prepared by adding 1.0 mol dry melamine to 4.5 mols of a neutral formaldehyde solution of 35% strength, heating in a water bath under reflux 30 minutes, cooling rapidly and then adding this solution gradually to sufficient boiling water to make a 3% solution, and cooling this solution as soon as transparency of solution is effected.

Example X

A sheet of cardboard weighing 240 lbs. per ream is coated on one side with 12 lbs. solids per ream by passing the dry sheet through a brush coater system and drying by passing over a system of cylindrical driers heated to 5 lbs. steam pressure with total heating time of 45 seconds. It is then calendered to develop gloss and smoothness. The coating composition consists of 100 parts of calcium sulfite, 8.0 parts polyvinyl alcohol, 0.3 part trimethylol-melamine, 2.0 parts ammonium bromide, and 112 parts water, and has a pH of 8.1. The polyvinyl alcohol has an intrinsic viscosity of 65 in a 4% aqueous solution at 25° C. and has a saponification value of 245. The coating after calendering has a coating pick of 7, a fiber pick of 10, and wet rub resistance of 1920 in comparison to a coating pick of 6, a fiber pick of 8, and wet rub resistance of 0 for the same coating from which the trimethylol melamine and ammonium chloride are omitted. The trimethylol melamine is prepared by the method described in Example I.

Although the preferred ratio of polyvinyl alcohol to fibrous ingredients for towel or tissue paper is 1.0 part to 99 parts fiber on bone dry weight basis, smaller and larger ratios of polyvinyl alcohol are useful for certain special requirements. Ratios of polyvinyl alcohol as low as 0.3 part impart appreciable wet strengths to such papers. Where very high resistance to grease is required or where extremely high wet strength is required ratios of polyvinyl alcohol up to 12.0 parts are useful. The ratio of trimethylol melamine to polyvinyl alcohol may vary from a minimum of 0.1 part for 5.0 parts polyvinyl alcohol to maximum of 2.0 parts when an acid catalyst is used. When no catalyst, acid or neutral, is used the ratio of trimethylol melamine to polyvinyl alcohol may vary from a minimum of 0.5 part for 5.0 parts of polyvinyl alcohol to a maximum of 5.0 parts. The acid may be used in quantities to produce a pH as low as 5.5. Use of more acid will cause undue degradation of the paper.

Any paper web may be used which is made in single or multiple layers and the fiber composition may be the same for all layers, or the surface layers may be different, such as a cardboard with body of unbleached and surface of

bleached fibers, or variations in compositions, such as different pigments and different pigment content in body and surface layers; or the surfaces of the web may be presized with various materials such as starches or glues. The web might also be sized with rosin or other emulsion sizes or it might be in the water leaf condition.

The webs of paper are prepared by any of the well known methods of preparing webs from fibers of paper-making length, such as on a cylinder mold, a Fourdrinier, or a Harper Fourdrinier; and they may be prepared in any thickness of single or multiple layers and at densities from about 20 lbs. per mil to 4 lbs. per mil for a 24 x 36 x 500 ream. They may be made from fibers alone in highly beaten or slightly beaten form or they may contain mineral fillers, sizes, waxes, etc.

The fibers may be made from wood by the sulfate, sulfite, soda or ground wood method in bleached or unbleached form. They may also be made from cotton rag, linen rag, flax, ramie, jute, straw, pineapple, *Musa textilis*, or banana in bleached or unbleached form.

The sheets may vary in density from that of glassine to the most bulky book paper or from 20 lbs. to 5 lbs. per mil for a 24 x 36 x 500 ream.

In addition to the compounds containing methylol groups given in examples, other substances containing methylol groups may be used, such as those made by reacting formaldehyde, paraformaldehyde or trioxane, or other compounds yielding formaldehyde, with amines or amides or derivatives of amines or amides, all of which should be at least slightly soluble in water. Typical examples of aliphatic amines, amides, etc., that will form useful insolubilizers for polyvinyl alcohol are melamine, urea, thiourea, biuret, formamide, acetamide, guanyl urea sulfate, monobutyl urea, hexamethylenediamine, hexamethylenetriamine sulfamate, ethanolamine, diethanolamine, monomethylamine, monoethylamine, ethyl formamide, ethyl acetamide, and derivatives of these. Ammonium, sodium or calcium sulfamate may also be used. The preferred method of preparation consists in neutralizing the acidity of the formaldehyde solution, neutralizing the reactive nitrogen-containing compound if it is strongly alkaline, and then mixing the formaldehyde with the other reactants as concentrated aqueous solution in proper molar ratios at a slightly elevated temperature. In some cases the concentrated forms of formaldehyde, such as paraformaldehyde or trioxane, are preferred in order to obtain a high yield.

The preferred methylol melamine is prepared by adding 1 mol of 2,4,6-triamino-1,3,5-triazine (melamine) to 3 mols formaldehyde as a 35% solution of formaldehyde in water and methanol which has been adjusted to a pH of 3.5 to 6.2, heating at 80° C. for 15 minutes and cooling rapidly to stop the reaction by diluting with cold water until a clear solution is obtained of a concentration below 6% methylol-melamine. The product may be used directly or before the dilution stage it may be dried at low temperature to a white powder. The white powder is non-hygroscopic and dissolves in water at 80° C. to make a clear solution that remains clear when cooled at concentrations below 6%. Slight alterations in this method may be used to obtain more complete reaction without rendering the product insoluble at concentrations below 6%, such as by cooling rapidly without dilution after

the 15 minute heating period, letting stand at room temperature 12 hours, diluting with hot water and cooling.

If the pH of the formaldehyde solution is below 3.5 the reaction is not so readily controlled and products may be obtained that are insoluble in water. If the pH of the formaldehyde solution is above 7.0 the product tends to be insoluble at concentrations below 6% unless acid is added to a pH of not greater than 3.0. Or if the temperature of heating is increased much beyond 80° C. or if the time of heating is extended much beyond 15 minutes, such as 30 to 40 minutes, the product is hygroscopic, forms clear solutions at 25 to 50% concentrations and precipitates on further dilution in cold or hot water. The preferred product is soluble in water at concentrations below 6%, is readily blended with other ingredients in the paper-treating compositions, is more efficient than the type which precipitates on dilution in water, and can be handled with greater ease.

Methylol-melamine compounds are also useful that contain lower or higher ratios of methylol groups, such as monomethylol melamine and up to as many methylol groups as can be added without making a water-insoluble product. At least a slight degree of water solubility is essential to insure the reaction between the methylol melamine and the polyvinyl alcohol.

The dimethylolurea is prepared by treating 2 moles formaldehyde as a neutral 37% solution in water with 1 mol urea to form a water white product that is freely soluble and stable as a 10% solution for several weeks at room temperature.

The polyvinyl alcohol should be of the water-soluble type with a specific viscosity as a 4% solution at 25° C. of 1 to 100 centipoises and a saponification value low enough to insure solubility in water, e. g., below 350. They are tough, water-white, resin-like materials which are usually obtained by the hydrolysis of polyvinyl esters such as polyvinyl acetate. They are soluble to insoluble in cold water, but all of them are soluble in hot water and remain dissolved when the solution is cooled. The term "polyvinyl alcohol" is used herein and in appended claims to designate generically pure polyvinyl alcohol and also such partial derivatives thereof that contain a sufficient number of free hydroxyl groups to render the composition soluble in water.

Heating to effect insolubilization is best accomplished during the drying step. The freshly treated web is dried at elevated temperature to a moisture content in the sheet of 4 to 20% or until the wet strength is at least 50% greater than that of the same sheet material treated under the same conditions with the same amount of polyvinyl alcohol but without the addition of the N-methylol aliphatic nitrogen containing compound and the ammonium salt. In this drying step any temperature above 65° C. has been found to be operative for producing the insolubilizing reaction. The upper temperature limits from the point of view of operativeness depends upon the degradation temperature of the compounds in the treating composition. Temperatures between 100° and 125° C. are, however, preferred as steam at temperatures in excess of 125° C. is relatively expensive. It is essential that the heating step be carried out in the presence of moisture and that the moisture content of the paper at the termination of the heating be not less than 4%. Heating to a moisture content of

less in amount than 4% produces a brittle product and destroys the qualities desired and obtained by the use of this invention. The time of heating should be such that there is an insolubilizing reaction between the starch and the water-soluble N-methylol aliphatic nitrogen-containing compound. For successful operation at the drying step there should be present in the paper at the start of the heating period an amount of water equivalent to at least 30% of the total solids. Where it is inconvenient to heat the paper to a temperature of 65° C. or above for a sufficient time to dry the sheet, the sheet may be dried at a lower temperature, then remoistened with enough water to make at least 30% moisture (based on sheet weight) and then heated at 65° C. or above until the moisture content is about 5%.

Although the preferred ratio of polyvinyl alcohol to fibrous ingredients for towel or tissue paper is 1.0 part to 99 parts fiber on a dry weight basis, smaller ratios and larger ratios of polyvinyl alcohol are useful for certain special requirements. Ratios of polyvinyl alcohol as low as 0.1 part impart appreciable wet strength to such papers. Where a very high resistance to grease is required or where extremely high wet strength is required, ratios of polyvinyl alcohol up to 12 parts per 100 parts of fibers are useful. The preferred ratio for grease-proof papers is polyvinyl alcohol 2.0 parts per 100.

The range of ratios for polyvinyl alcohol to pigment in coating compositions may vary from 3.0 parts to 15.0 parts polyvinyl alcohol for 100 parts pigment. The preferred ratio of polyvinyl alcohol to pigment in coating compositions varies with the pigment and paper base, but falls between polyvinyl alcohol 3 to 8 parts to 100 parts pigment.

The ratio of N-methylol compound to polyvinyl alcohol may vary from a minimum of 2 parts to 100 parts of polyvinyl alcohol to a maximum of 40 parts to 100 parts of polyvinyl alcohol. It is preferred, however, to operate within the ratio of 5:100 to 15:100.

The ratio of ammonium salt of a mineral acid to N-methylol compound may vary from a minimum of 0.3 part of ammonium salt to a maximum of 12 parts of ammonium salt for 1 part of N-methylol compounds. The preferred ratio of ammonium salt to N-methylol compound is in the range of 1 to 5 parts of salt per 1 part of N-methylol compound.

The ammonium salts of mineral acids, such as hydrochloric, hydrobromic, nitric, sulfurous, sulfuric, persulfuric and phosphoric acids are operative in this process; e. g., ammonium chloride, ammonium bromide, ammonium nitrate, ammonium sulfate, ammonium sulfite, ammonium persulfate; ammonium phosphate. The ammonium salts of a few strong organic acids can also be used. The 2% aqueous solution of the above ammonium salts should have a pH not lower than 6.1.

While it is preferred to use an ammonium salt of a mineral acid, the mineral acid itself may be used, although with less efficient results. This is evidenced by the following tests which show by comparison the effect of a mineral acid such as hydrochloric acid. In these tests sheets of paper base 5' wide by 10' long were coated on the felt side with 1.7 grams (+ or -0.1 gram) of the coating compositions indicated, using a Martinson laboratory coater. The amount applied was equivalent to 12.5 lbs. of solids per ream

(3,300 sq. ft. of paper). The coated sheets were air dried for from 35 to 60 minutes, then calendered and heated with the coated side in contact with the metal surface at a temperature of 100° C. for 30 seconds. The water resistance of the coating was then determined by the usual wet rub method. In all of the tests the polyvinyl alcohol employed was one having an intrinsic viscosity of 25 centipoises in 4% aqueous solution at 20° C.

	Parts by weight	Wet rubs
Test #1:		
Polyvinyl alcohol.....	8	1 to 2.
Clay (kaolin).....	100	
Water.....	201	
Sodium silicate—42° Be. aqueous solution.....	0.5	
Test #2:		
Polyvinyl alcohol.....	8	4 to 5.
Clay (kaolin).....	100	
Trimethylol melamine.....	0.8	
Sodium silicate—42° Be. solution.....	0.5	
Water.....	202.2	
Test #3:		
Composition the same as in test #2, but made acid to methyl red indicator by the addition of 1-N HCl solution.....		More than 300
Test #4:		
Polyvinyl alcohol.....	8	4 to 5.
Clay (kaolin).....	100	
Trimethylol melamine.....	1.6	
Sodium silicate—42° Be. solution.....	0.5	
Water.....	203.4	
Test #5:		
Same as #4 but the mixture made acid to methyl red with 1-N HCl.....		More than 300.

For promoting the insolubilizing reaction of a methylol melamine on polyvinyl alcohol, an ammonium salt of a mineral acid has advantage over a mineral acid in respect to scope of use and degree of insolubility that can be obtained within limits of acidity which can be tolerated in commercial practice.

In order to develop a high degree of insolubility a pH as low as 3.0 must be obtained. This degree of acidity has a very deleterious effect on cellulose, such as paper or cloth. About the highest degree of acidity that can be tolerated on cloth or paper during manufacturing processing is a pH of 5.5.

Where alkaline pigments are used in polyvinyl alcohol compositions, acids are not very effective in promoting insolubilization of polyvinyl alcohol. Under such conditions the ammonium salts of mineral acids have distinct advantages because they do not react with the alkaline pigments on storage of the treating compositions before use, and they function in the presence of alkaline pigments such as satin white and commercial silk.

The pH range of the clear coatings is preferably maintained between 6.1 and 7.0 to obtain maximum insolubility and to prevent subsequent degradation of the paper due to acidity.

The pH range of the pigmented compositions is determined in some cases (with chalk, satin white, etc.) by the nature of the pigment. It can be as high as 12.5 with ammonium chloride as catalyst. The preferred pH range of pigmented compositions is 6.1 to 11.5.

Softeners may be used in the treating compositions or may be applied to the paper after application of the treating compositions. These softeners make the product more pliable. Examples of such softeners include formamide, ethanol formamide, ethanol acetamide, glycerol, glycols, invert sugars, certain hygroscopic salts, such as sodium lactate, and higher fat alcohol sulfates. Other ingredients such as anti-foams can also be used.

The products are useful as printing papers, food wraps, bags, liners for boxes, cartons, and uses for packaging materials that require resistance to greases, fats or oils.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. The process which comprises treating a web of paper-making fibers with an aqueous solution of polyvinyl alcohol and a water-soluble N-methylol aliphatic compound said solution having a pH within the range of 6.1 to 12.5, and then heating said treated paper web between 30 and 60 seconds to such a degree as to cause an insolubilizing reaction between the polyvinyl alcohol and the N-methylol compound.

2. A process in accordance with claim 1 characterized in that the polyvinyl alcohol has an intrinsic viscosity as a 4% solution in water at 25° C. of from 1 to 100 centipoises and has a saponification number below 350.

3. The process which comprises treating a web of paper-making fibers with an aqueous solution of polyvinyl alcohol and an ammonium salt of a mineral acid and a water-soluble N-methylol aliphatic compound said solution having a pH within the range of 6.1 to 12.5 under conditions that will leave at least 30% moisture in said web, then drying said paper web by heating same for from 30 to 60 seconds at a temperature in excess of 65° C. so as to cause an insolubilizing reaction between the polyvinyl alcohol and the N-methylol compound said temperature being insufficient to cause the drying of the paper web to a degree that said paper web will contain less than 4% moisture.

4. The process in accordance with claim 1 characterized in that the water-soluble N-methylol aliphatic compound is a methylol melamine.

5. The process in accordance with claim 3 characterized in that the water-soluble N-methylol aliphatic compound is a methylol-melamine.

6. The process in accordance with claim 1 characterized in that the water-soluble N-methylol aliphatic compound is trimethylol-melamine.

7. The process in accordance with claim 1 characterized in that the water-soluble N-methylol aliphatic compound is dimethylol biuret.

8. The process in accordance with claim 1 characterized in that the water-soluble N-methylol aliphatic compound is dimethylol ammonium sulfamate.

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Patent No. 2,322,888.

CERTIFICATE OF CORRECTION.

June 29, 1943.

GEORGE L. SCHWARTZ, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 65, for "if formed" read --is formed--; page 6, first column, line 57, for "silk" read --chalk--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of August, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.