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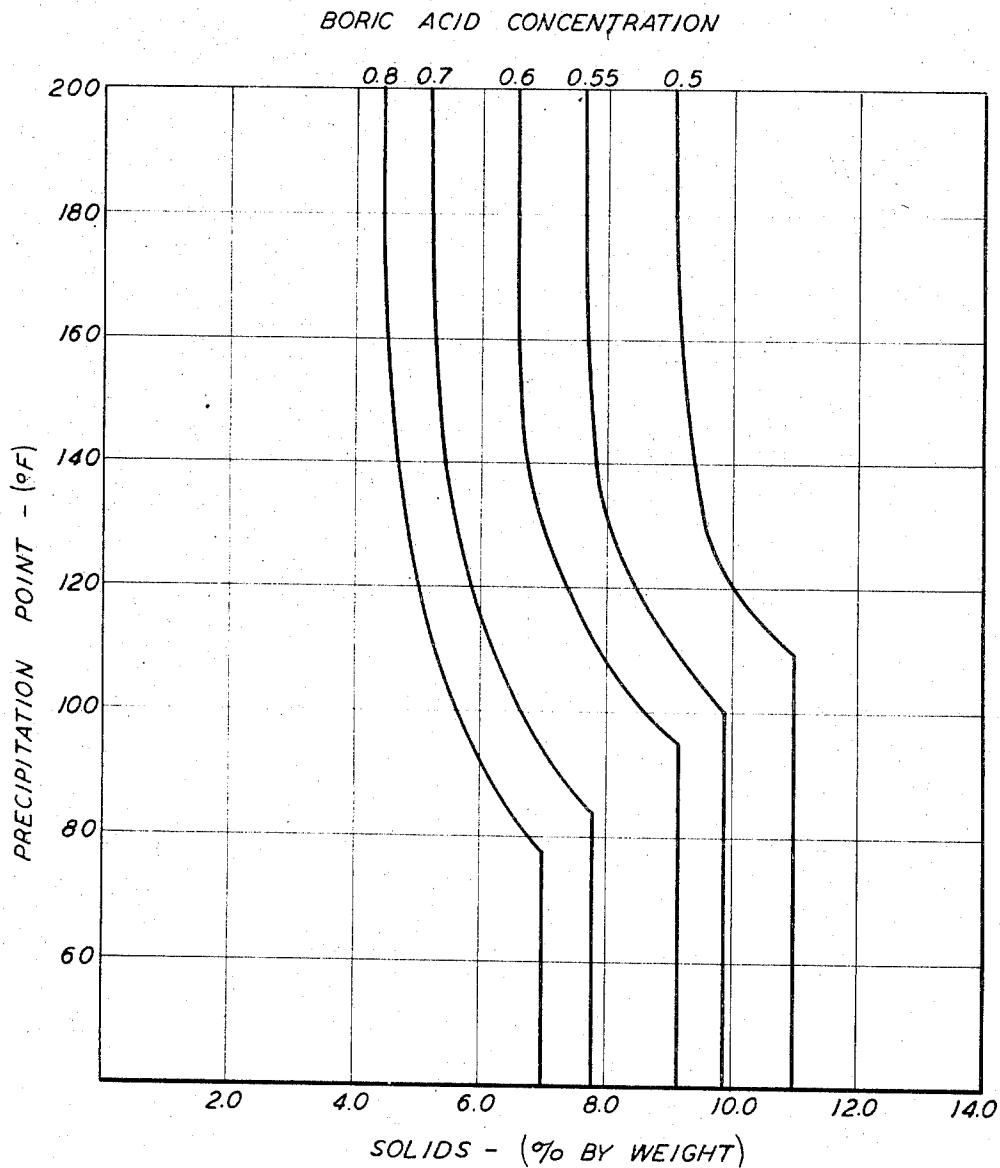
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POLYVINYL ALCOHOL-BORIC ACID-CONTAINING COMPOSITION, TREATMENT
OF PAPER WEB THEREWITH AND THE TREATED PAPER WEB

Filed April 22, 1965

Sheet 1 of 2

FIG. 1



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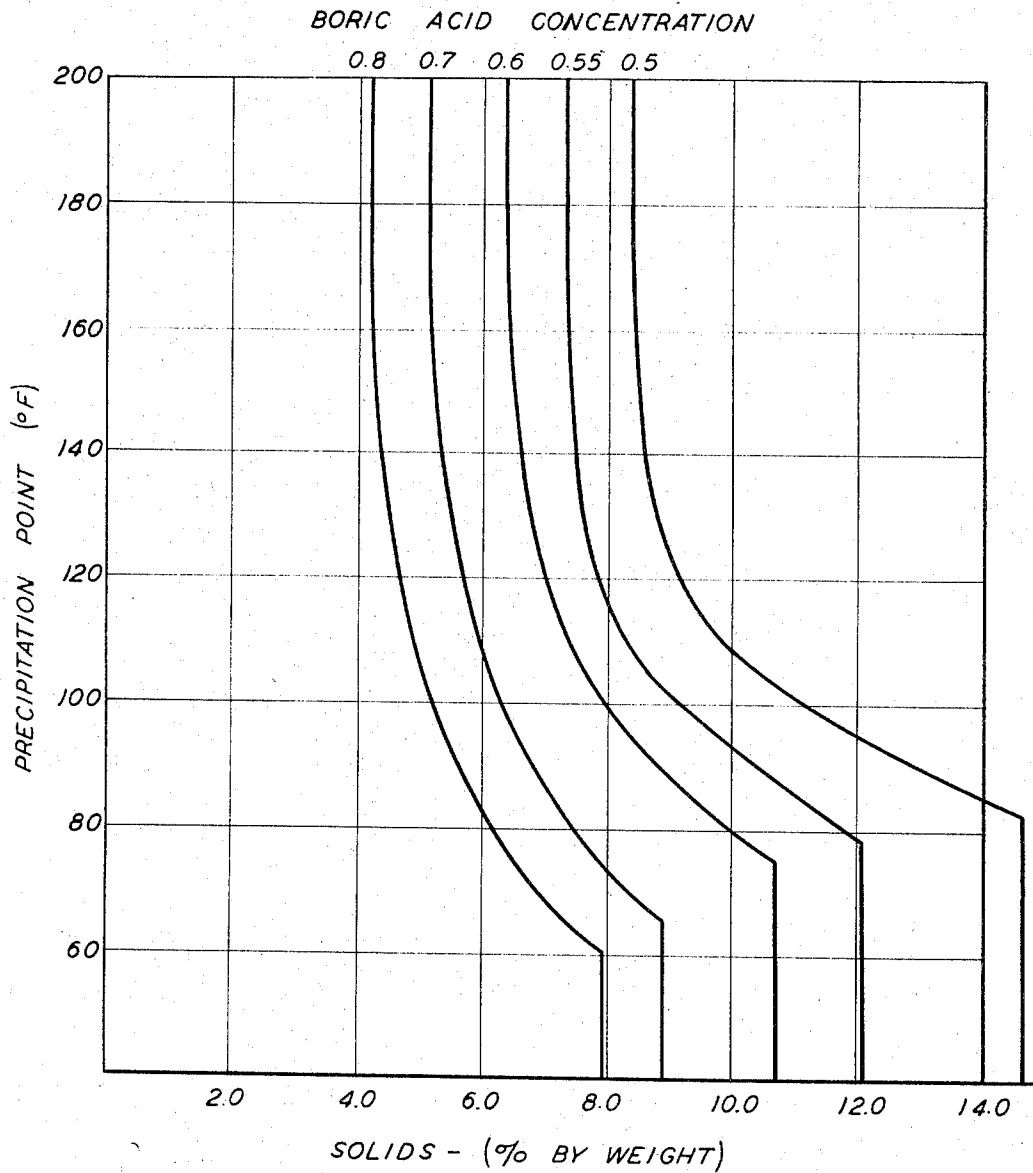
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Sheet 2 of 2

FIG. 2



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POLYVINYL ALCOHOL-BORIC ACID-CONTAINING COMPOSITION, TREATMENT OF PAPER WEB THEREWITH AND THE TREATED PAPER WEB

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12 Claims

ABSTRACT OF THE DISCLOSURE

Cellulosic fibrous webs are treated to apply polyvinyl alcohol to them with minimum penetration of the polyvinyl alcohol into the web by preparing an aqueous composition containing the polyvinyl alcohol in admixture with boric acid in the amount of more than 15% and at most 50% by weight of the polyvinyl alcohol, the composition having a pH of at most 6.0, applying the composition to the web at a temperature up to about 210° F., and drying the web with the polyvinyl alcohol thereon. Most suitably there is used an aqueous composition containing 0.5% to 35% of polyvinyl alcohol with the ratio of polyvinyl alcohol to boric acid being 0.5 to 1.3 parts by weight of boric acid per 3 parts of polyvinyl alcohol.

This invention relates to the treatment of fibrous webs and is more specifically concerned with the surface sizing of such webs with polyvinyl alcohol.

Surface sizing is primarily concerned with the creation of surface films, and consequently it is usually desirable to keep the size on the surface of the paper as much as possible, where it will do the most good. This is particularly true when using expensive sizing agents. On the other hand, it is desirable in the case of some grades of paper, to obtain some penetration of the sizing agent into the paper in order to build up the burst strength and other internal properties of the sheet.

Polyvinyl alcohol is an excellent sizing agent but has been restricted in its usage because migration into the paper substrate makes it necessary for an uneconomic amount to be used for full effectiveness. Thus, it is desirable to limit penetration of this polymer into the sheet when it is used for surface sizing, and this can be accomplished, for example, by first coating the web with an insolubilizing agent and then applying the polyvinyl alcohol to the thus-coated sheet. For example, a 2-step application sizing system utilizing polyvinyl alcohol and borax was developed to overcome the above-mentioned normal behavior of polyvinyl alcohol. Basically, this system consists of the steps of applying a borax solution to the sheet to be surface sized, followed by the application of polyvinyl alcohol to the borax-treated surface. The borax forms an instantaneous gel with the polyvinyl alcohol, hindering the migration of the polyvinyl alcohol into the sheet.

Although polyvinyl alcohol is a highly effective sizing agent, it must, of course, compete economically with other sizing agents. Accordingly, there has been a continuing search for a means of effectively sizing with polyvinyl alcohol, but with reduced quantities of this polymer than those conventionally used, and without the 2-step application procedure referred to above.

There are well-known disadvantages to the 2-step system. First of all, two application stations on the machine are required. Many paper mills do not normally have to have application stations to utilize this system. In addition, if the mill does have the necessary number of application stations, there are added expenses and operating compli-

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cations because of the need for separate pumping and holding systems to maintain the borax carefully out of contact with the polyvinyl alcohol solution. If premature gelatin did occur, it would cause havoc with the mechanical system and stop the production of paper.

Secondly, since two water applications are involved, there is an increase in the drying load placed on the machine. Many paper mills do not have the extra drying capacity for properly drying the sheet. In addition, there is the ever-occurring problem of leaching of the borax from the paper substrate into the polyvinyl alcohol solution. Upon continued running, the borax contamination can create a viscosity buildup in the polyvinyl alcohol solution which can and in many cases does cause operational difficulties, i.e. a nonuniform quality board is produced, picking or drying of the polyvinyl alcohol on the calendar stack occurs, and the like. The application of an excess of the borax solution, like other alkalies, will react with the internal aluminum resinate size, causing a loss of the water resistance properties of the sheet being treated. Furthermore, there may be a brightness drop of 1 to 2 points when borax (pH 9.3) is applied to bleached ground wood pulp.

In addition to its use for surface sizing, polyvinyl alcohol is also applied to paper for other purposes, e.g. as a coating wherein the polyvinyl alcohol may be mixed with pigments, and as an agent to lay fibers. However, in all of these applications, there is still the desire for obtaining maximum efficiency, i.e. a maximum improvement in properties with a minimum quantity of material.

It is, accordingly, an object of this invention to provide a method of treating a fibrous web with polyvinyl alcohol to provide the web with a polyvinyl alcohol deposit which, even in relatively small quantities, produces a significant improvement in desired properties.

It is another object of this invention to provide a method of surface sizing a fibrous web with polyvinyl alcohol, to provide the web with a polyvinyl alcohol coat while avoiding the drawbacks referred to above.

It is a further object of the invention to provide a method of surface sizing a fibrous web which involves a 1-step application, to form a polyvinyl alcohol coat on the web, and to make possible effective sizing with reduced quantities of polyvinyl alcohol.

It is a still further object of the invention to provide a process of the character indicated, which can be carried out on a conventional machine for forming fibrous webs without requiring special coating apparatus.

In accordance with the invention, treatment, e.g. surface sizing, of a fibrous web is effected by a process which comprises applying to the web an aqueous solution of polyvinyl alcohol containing a limiting quantity of boric acid, and the solution having a limiting pH and a limiting concentration of polyvinyl alcohol. It has been discovered that when a fibrous web is treated with such a polyvinyl alcohol solution, there is directly deposited upon the web a polyvinyl alcohol coat or deposit which dries in a form which does not appreciably migrate into the paper substrate, so that effective sizing, coating, or other treatment is achieved without excess quantities of polyvinyl alcohol. The critical relationships of the polyvinyl alcohol-boric acid solution can be defined as follows.

The pH of the solution must be at most 6, and the ratio of the boric acid to the polyvinyl alcohol must be more than 15% by weight of boric acid based on the polyvinyl alcohol and at most 50%, and most suitably the ratio is 0.5 to 1.3 parts of boric acid per three parts of polyvinyl alcohol. The maximum concentration of polyvinyl alcohol in the solution will tend to vary with the boric acid-polyvinyl alcohol ratio in the solution and the use to which the solution is to be put, e.g. the amount of polyvinyl alcohol which it is desired to deposit per

unit area of the fibrous web being treated, the nature of the polyvinyl alcohol and the temperature of the solution at the time of application. However, the aqueous solution containing boric acid and polyvinyl alcohol at a predetermined pH in accordance with the invention has a maximum polyvinyl alcohol content such that the polyvinyl alcohol does not materially precipitate from the solution until after it has been applied to the web to be treated. Ordinarily the solution thus has a polyvinyl alcohol concentration at 70° F. of at most 7% by weight using a solution containing high-viscosity polyvinyl alcohol (45-70 centipoises) and 0.8 part of boric acid per three parts of polyvinyl alcohol, as a standard. When lesser amounts of boric acid are used, or when the viscosity of the polyvinyl alcohol is less, i.e. when it has a medium viscosity (20-40 centipoises), or a low viscosity (4-6 centipoises) greater amounts of polyvinyl alcohol can be tolerated. For example, with 0.5 part of boric acid per three parts of polyvinyl alcohol and a low-viscosity polyvinyl alcohol, concentrations up to 35% can be used. In like manner, it has been found that when the pH is established by a mineral acid, such as phosphoric acid, higher concentrations of polyvinyl alcohol in the solution can be employed than when an organic acid, such as citric acid, is used to establish the desired pH. However, the particular maximum polyvinyl alcohol concentration for any specific combination of polyvinyl alcohol-boric acid-acid combination for a particular use can be readily determined by routine test. Typical maxima are illustrated in the accompanying drawings wherein FIG. 1 shows the precipitation points of solutions containing various percentages of high-viscosity polyvinyl alcohol with various concentrations of boric acid, expressed as parts by weight of boric acid per 3 parts of polyvinyl alcohol, using 0.04 part of an organic acid such as citric acid or sulfamic acid for each 3 parts of polyvinyl alcohol in the solution, and FIG. 2 shows similar precipitation points in the case of various percentages of high-viscosity polyvinyl alcohol with various amounts of boric acid, using phosphoric acid to establish a pH of 4.8. Thus, the maximum concentrations at various boric acid to polyvinyl alcohol ratios, and at various temperatures within the range at which the solutions may be applied, are readily determined by reference to the charts illustrated in the accompanying drawings, supplemented, when the specific combination desired is not specifically included in the charts by routine tests to establish the precipitation curve. The practical minimum concentration of polyvinyl alcohol for efficient operation is about 0.5%. In the drawings, the generally vertically extending lines designate the maximum concentrations in relationship to the specified boric acid-polyvinyl alcohol ratios at the temperatures indicated. It will be noted that the maximum concentrations decrease as the boric acid to polyvinyl alcohol ratio increases. Consequently, in those cases where it is desired to deposit a higher concentration of polyvinyl alcohol per unit area of web, a higher solids content with a lower boric acid to polyvinyl alcohol ratio is employed, the appropriate ratio being readily determinable by reference to the drawings, with or without routine tests. It has also been observed that when the polyvinyl alcohol has a low viscosity, greater amounts of boric acid (within the range specified above) are suitably used to achieve maximum results.

In carrying out the invention, a boric acid-polyvinyl alcohol solution corresponding to the criteria set forth above is directly applied to the web to be treated. It is a feature of the invention that a single application at a single point in the line of travel of the web is sufficient, and multiple applications, as in the 2-stage borax and polyvinyl alcohol treatment procedure previously mentioned, can be eliminated. Yet, there is obtained an effective application of polyvinyl alcohol with a very low penetration into the web. When the aqueous solution containing polyvinyl alcohol and the specified quantities of

boric acid is applied to the sheet, some of the water rapidly penetrates into the web and some is lost by evaporation, and the critical "precipitation" solids concentration is reached, the polyvinyl alcohol becoming immobile and remaining at the surface, thus providing the greatest size efficiency for the amount applied.

The effectiveness of the sizing agent, i.e. polyvinyl alcohol, is conventionally measured by a Vanceometer which measures the penetration of oil into the web through the applied polyvinyl alcohol film or coat, and the ability of the polyvinyl alcohol film or coat to impede the penetration of the oil is referred to in the art as "hold-out." The standard Vanceometer test procedure is that provided by Tappi Standard T454M-44. The Vanceometer Absorption Tester consists of a projection lamp and condenser lenses, mounted in such a way as to cast a beam of light on a sheet surface at an angle of twenty degrees. The light is then reflected in a straight beam, through an iris diaphragm, into a photo-electric cell connected to a microammeter. A thin film of oil is cast onto the surface of the sheet and placed in the path of the beam of light, so that the light from the projector is reflected off the oil film into the photo-electric cell. By this means, it is possible to determine the gloss of the oil surface. As the oil film gradually disappears below the surface of the sheet, the light reflected into the photo-cell is lowered in proportion to the loss of oil into the sheet surface.

Paper is most commonly surface-sized on the paper machine by the use of a size press by means of which the sizing agent is applied to both sides of the paper and the paper is then passed through press rolls to remove the excess size from the surface of the paper. In many cases, the size is sprayed onto the top side of the sheet so that the paper runs through a puddle just before entering the nip of the rolls. The paper is in contact with the size for only a short period of time, and the pick-up of size is relatively low.

The size press consists of two rolls either vertically or horizontally arranged. One size-press roll is usually a hard roll, whereas the other roll of the size press is generally a softer rubber-covered roll.

After the sheet leaves the press, it is often passed over a spread roll to remove wrinkles. The angle at which the sheet passes over this roll and the distances between this roll and the press are important factors in the operation of a size press.

Another method of surface-sizing utilizes a tub for holding the size into which the sheet is dipped. The time of contact of the paper with the size depends upon the speed of the machine, the dimensions of the tub, and the area of the sheet submerged in the size at one time. Usually, the size tub is located within the drier section so that the sheet is partially dried before reaching the tub. Drying of the sized paper is completed by passing the paper over six to eight driers. The size tub results in longer contact of the paper with the size, and results in about 25% more size being picked up by the paper.

Calender sizing is another method of applying size to the surface of paper on the paper machine. This method of sizing is used only with heavy papers such as paper-board, since lightweight papers are best sized with a size press where the treatment can be followed by drying. The reason that it is possible to size heavy papers at the calenders without supplementary drying is that the board, when it reaches the stack, carries a considerable amount of latent heat which permits some evaporation of water before winding. The water which remains can be absorbed throughout the entire mass of the board with any appreciable increase in the overall moisture content.

The process of this invention is no way limited to the apparatus used for applying the polyvinyl alcohol-boric acid solution to the web and any convenient apparatus can be used. For example, the solution can be applied by means of a Champion coater and in general the solu-

tion performs well on roll coaters, air knife coaters and on blade coaters, and in the latter cases speeds in excess of 2000 f.p.m. may be involved. In general, the solution can be applied to the web, in accordance with the process of the invention, at any point after formation of the web.

Polyvinyl alcohol is a water-soluble member of the class of vinyl resins which are generally made from vinyl acetate by hydrolysis. The hydrolysis can be carried to any degree of completion, resulting in polyvinyl alcohol of several different degrees of hydrolysis or grades. The percentage hydrolysis indicates the percentage of the original acetate groups that have been replaced by —OH groups. Arbitrarily, any polyvinyl acetate which is more than 50% hydrolyzed is termed polyvinyl alcohol.

Starting from pure polyvinyl acetate, as the number of —OH groups increases, marked property changes occur. For example, the water solubility characteristics are greatly affected. The —OH groups have the initial effect of making the product more water sensitive, but then as they increase in number, and can, therefore, readily form intermolecular hydrogen bonds, the polymer becomes insoluble in cold water and can be dissolved only in hot water. At the same time, the increased ability to form hydrogen bonds produces greater cohesive as well as adhesive strength. In addition, as the number of —OH groups increases, resistance to organic solvents steadily increases. Whereas polyvinyl acetate is readily dissolved by organic solvents, fully-hydrolyzed polyvinyl alcohol is totally unaffected by all but a few particular solvents. Hence, in general, the higher hydrolyzed grades will have the greatest water and organic solvent resistance and the best strength characteristics.

The number of acetate groups which are converted to hydroxyl groups is referred to as the degree of hydrolysis. This is frequently expressed as percent hydrolysis, that is, a polyvinyl alcohol which is 85% hydrolyzed is one in which 85% of the acetate groups have been converted to hydroxyl groups. Polyvinyl alcohol having a degree of hydrolysis of from about 80–89% is generally referred to as partially-hydrolyzed polyvinyl alcohol. Polyvinyl alcohol having a minimum degree of hydrolysis of about 96% is generally referred to as fully-hydrolyzed polyvinyl alcohol, and polyvinyl alcohol having a minimum degree of hydrolysis of 99.7+ % is commonly referred to as super-fully-hydrolyzed polyvinyl alcohol.

The molecular chain length of the polyvinyl alcohol also affects properties. The most outstanding effect is that as molecular weight increases the viscosity of solutions of polyvinyl alcohol increases. Water resistance also is notably greater in the higher viscosity types. The degree of polymerization of the higher viscosity types is in the range 1500–3000, and of the lower viscosity types, 200–1000.

Somewhat like starch, concentrated solutions of the highly-hydrolyzed grades of polyvinyl alcohol tend to thicken and gel on standing. All molecular weight grades display this property. The gels are readily broken by heating but reform again on cooling. Polyvinyl alcohol this is less than 99% hydrolyzed is essentially free of this gelling tendency, but one of the features of the composition of this invention is that the boric acid significantly reduces the gelling tendency even of the most highly hydrolyzed grades.

The percent hydrolysis of the polyvinyl alcohol suitable for use in accordance with this invention can vary from about 55 percent to 100 percent. Naturally, for a specific application it may be desirable to employ a polyvinyl alcohol having a particular percent hydrolysis. Polyvinyl alcohol having a particular percent hydrolysis also varies in viscosity. Thus, it is possible to obtain a low, medium or high viscosity partially-hydrolyzed polyvinyl alcohol. The viscosity of the polyvinyl alcohol is determined by the degree of polymerization of the polyvinyl acetate, i.e., if the degree of polymerization of the polyvinyl acetate is high, a high viscosity polyvinyl alcohol will generally result. Thus, here again it is possible to

select a desired viscosity polyvinyl alcohol for a specific application; however, any polyvinyl alcohol having a viscosity of 2 to 150 centipoises in a 4% aqueous solution at 20° C. is generally acceptable. However, studies have shown that for the best results the polyvinyl alcohol should be highly hydrolyzed and should be of the medium or high viscosity type, viz having a viscosity of 20–40 centipoises (medium viscosity) or a viscosity of 45 to 70 centipoises (high viscosity). The higher the degree of hydrolysis, the greater is the pick strength and the water resistance of the finished coating. The medium viscosity type of polyvinyl alcohol provides pick strength that is greater than that achievable with the low-viscosity types but essentially equivalent to that of the high-viscosity types. When the polyvinyl alcohol-boric acid solution is combined with pigments for the preparation of colors with high solids, the medium viscosity type is preferred.

Especially suitable for use in the coating compositions of the present invention is polyvinyl alcohol which has an extremely high degree of hydrolysis. Such materials are known in the art as "super-hydrolyzed" polyvinyl alcohol resin or fully-hydrolyzed polyvinyl alcohol resin. The super-hydrolyzed grade may, as mentioned, have a degree of hydrolysis of 99.7+ % and the fully-hydrolyzed grade may, as mentioned, have a percent hydrolysis of 96% or higher. Such material is sold under a variety of trade names. Among the commercially available super-hydrolyzed grades may be mentioned Vinol 125 and Vinol 165 produced by Air Reduction Company, Incorporated. Among examples of fully-hydrolyzed polyvinyl alcohol having a percent hydrolysis of 99% may be mentioned Vinol 260, Vinol 230 and Vinol 205. Other polyvinyl alcohols having a percent hydrolysis between about 98% and 99% and sold under the trade names Vinol 325 and Vinol 350 by the same company are also especially suitable.

The super-hydrolyzed and fully-hydrolyzed grades of polyvinyl alcohol have the advantage that films produced therefrom are extremely resistant to attack by cold water. The resistance of films produced from polyvinyl alcohol to cold water attack apparently reaches a maximum when the degree of hydrolysis of the polyvinyl alcohol is at a maximum.

Various methods may be employed in preparing the polyvinyl alcohol solutions used in the present invention. In one method, a premix is formed by dissolving the boric acid in acidified water and heating the solution to a temperature of from 160 to 210° F. The premix is then added with agitation to a solution of polyvinyl alcohol in acidified water which has also been heated to from about 160 to 210° F. After combining the premix with the polyvinyl alcohol solution, the mass is cooked with agitation for a short period of time such as about 30 minutes. The mass is then cooled to room temperature and the pH of the mass is determined. If the pH is above 6.0, it is adjusted to 6.0 or below, preferably 5.0 or below. It is advantageous to employ sufficient acid in the premix in order that the final product will have a pH of below 6.0 rather than having to adjust the final product by the addition of more acid, since it has been found that where the pH of the solution at the time of cooking is low, the viscosity of the resulting product is lower than when the pH of the mass at the time of cooking is about 6.0.

In a second method, all of the ingredients are added to cold water, that is, the polyvinyl alcohol, the boric acid and a pH-adjusting acid are added to cold water, and the mass is then heated with agitation to a temperature sufficient to dissolve the polyvinyl alcohol, and the mass is cooked at a temperature of from about 160 to 210° F. for a short period of time, such as about 30 minutes.

A further method for the preparation of polyvinyl alcohol solutions for use in the method of the present invention consists of forming a dry blend which is comprised of polyvinyl alcohol, boric acid, and a dry acid. The dry blend may also contain a biocide such as DOWICIDE A,

and an antifoam agent. This dry blend may be stored for extended periods and shipped to the user. When it is desired to prepare the solution for use, the dry blend is added to the appropriate quantity of water with agitation to form a uniform mixture, the mixture is heated to a temperature of from about 160° to about 210° F. and cooked for about 30 minutes, the amount of pH-adjusting acid being sufficient to provide a pH of at most 6.0.

As has been indicated above, it is imperative that the solution as applied possess a pH of at most 6.0. As the pH decreases from 6.0, the viscosity decreases slightly. Thus, a particularly suitable solution for use according to the present invention can be made if the pH is maintained within the range of 6.0 to 2.0, preferably 5.0 to 2.0. As has been indicated above, as the pH decreases the viscosity also decreases slightly; however, even at a pH of 2.0 the solution possesses an acceptable viscosity.

The pH of the solutions of the present invention may be controlled by the use of any water-soluble acid or acid salt, such as alum. Examples of suitable water-soluble acids are hydrochloric acid, acetic acid, formic acid and phosphoric acid, although other acids, either organic or inorganic, may be employed. If a dry blend is to be formed, it is desirable to employ a dry acid such as citric acid, oxalic acid or sulfamic acid. It has also been found that an acid anhydride such as maleic anhydride may be employed for controlling the pH. The term acid as employed herein refers to any acidic material which is capable as controlling the pH of the solutions within the limits set forth.

When the boric acid-polyvinyl alcohol solution described above is to be used for coating, the pigments and other additives normally used in polyvinyl alcohol coating compositions can be employed as long as they are acid stable, i.e. capable of being made acidic without decomposition or deterioration. Thus, in making coating compositions in which polyvinyl alcohol is employed as the pigment binder, it is conventional practice to form a mixture of water and a pigment, such as clay or the light, sometimes with other materials such as, for example, a soluble pyrophosphate which may act as a dispersing and stabilizing agent, e.g. tetrasodium pyrophosphate. This mixture, commonly termed a pigment "slip" or, since it usually contains clay, a clay "slip," is then compounded with the binder material to produce a composition known in the art as a coating "color," which is useful for coating a cellulose web, e.g. a paper or paperboard web.

The clay employed can be conventional coating clay and is used in conventional manner in the form of a "slip," i.e. dispersed in water to a solids content, for example, of 66%. The present invention permits the use of any of the clays customarily used for coating paper, including the hydrous aluminum silicates or kaolin group clays, hydrated silica clays, and the specific types of clays recommended in "Kaolin Clays and Their Industrial Uses," copyright 1949 by J. M. Huber Corp., New York, N.Y., particularly in chapters 10-16.

In addition to clay itself, there may be utilized other paper-filling compositions and materials such as, for example, titanium dioxide, zinc oxide, or other coating pigments in various ratios, e.g. up to 70% by weight of the clay. As previously indicated, the slip may also contain a small amount, e.g. 0.1 to 0.50, of a dispersing or stabilizing agent such as tetrasodium pyrophosphate. The modification of the coating color using these materials or other conventional additives, will be within the knowledge of those skilled in the art.

Surfactants that also perform as defoamers can be employed. Typical defoaming agents include tributyl phosphate, pine oil, and symmetrical ditertiary acetylenic glycols sold under the trade name "Surfynol 104A" and "Surfynol PC."

The aqueous polyvinyl alcohol-boric acid solutions of this invention can be applied to the fibrous sheet or web at temperatures up to about 210° F. although about 205°

F. is usually a practical maximum. Ordinarily the temperature of application is not below room temperature (ambient temperature) e.g. 70° F., but lower temperatures, e.g. 35° F. can be employed if desired by preliminary refrigeration. The amount of the solution applied per unit area of the web can vary, but ordinarily it is applied at a rate to provide a polyvinyl alcohol deposition of 0.05 to 2 pounds per 1000 square feet, preferably 0.1 to 0.5 pound per 1000 square feet.

While, as previously mentioned, it is a significant feature of the invention that the above-described solutions can be applied in a single-stage application with fully effective results, it will, of course, be apparent that the solutions can be applied at a plurality of stations or points if desired, e.g. half of the desired amount being applied at one station or point, and the remainder being applied at a second station or point.

It is thus a characteristic feature that the method of the present invention, the use of a boric acid-polyvinyl alcohol aqueous solution having specific characteristics, with or without other conventional additives used in the paper and paperboard art, makes possible the fully economic use of polyvinyl alcohol to take maximum advantage of its highly desirable properties without requiring the use of excessive amounts of this polymer. The invention will now be further described by reference to specific examples of practical application. The following examples, however, are intended to be illustrative only, and not limitative, of the invention. In the following examples all parts are by weight, unless otherwise indicated.

While boric acid is specifically referred to above and is used in the numbered examples of actual operation which follow, it will be understood that the term "boric acid" includes other water-soluble boron compounds, e.g. boron compounds such as sodium borate which form boric acid in aqueous solutions at pH values of 6 or less.

EXAMPLE I

This example illustrates the preparation of a sizing composition and the treatment of a web of paper in accordance with the process of this invention.

0.7 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 58 parts of water at a temperature of 75° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation for 25 minutes at 200° F. Water was then added to the solution thus produced to adjust its polyvinyl alcohol concentration to 3.0%, and 85% phosphoric acid was added to give the solution a final pH of about 4.8.

This solution was then applied to a web of paper having a moisture content of 5% by means of a size press to provide 0.04 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 75° F. when applied and the web was later dried to a final moisture content of about 5%. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer value, percent gloss (NCS-12 oil)			
	5 secs.	20 secs.	30 secs.	60 secs.
Example 1.....	98	91	85	62
3.0% polyvinyl alcohol control..	84	57	43	25

EXAMPLE II

In this example, the procedure of Example I was repeated, except that the ratio of boric acid to polyvinyl alcohol was 0.5:3.0 and the solution was equivalent to a polyvinyl alcohol concentration of 3.0%. The final solution pH was 4.8. The solution was applied to the web at a deposit rate of 0.05 lb. of polyvinyl alcohol per

1000 square feet. When the surface of the dried web was tested with the Vanceometer Absorption Tester, the following results were observed:

	Avg. Vanceometer value, percent gloss (NCS-12 oil)			
	5 secs.	20 secs.	30 secs.	60 secs.
Example II.....	92	86	78	58
0.05 lb. per 1,000 square feet polyvinyl alcohol control.....	84	57	43	25

EXAMPLE III

This example also illustrates the preparation of a sizing composition and the treatment of a web of paperboard in accordance with the process of this invention.

0.9 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 61.1 parts of water at a temperature of 75° and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation of 25 min. at 200° F. Water was then added to the solution thus produced to adjust its polyvinyl alcohol concentration to 3.0% and additional 85% phosphoric acid was added to give the solution a final pH of about 4.8.

This solution was then applied to a web of paperboard having a moisture content of 5% by means of a size press to provide 0.04 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 75° F. when applied. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer value, gloss (NCS-12 oil)		
	5 secs.	30 secs.	60 secs.
Example III.....	87	84	75
0.04 lb. per 1,000 square feet polyvinyl alcohol control.....	84	43	25
0.06 lb. per 1,000 square feet starch (oxidized).....	39	23	22
0.12 lb. per 1,000 square feet starch (oxidized).....	65	28	24
0.26 lb. per 1,000 square feet starch (oxidized).....	81	55	38

EXAMPLE IV

This example further illustrates the preparation of a sizing composition and the treatment of a web of paperboard in accordance with the process of this invention.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 50.4 parts of water at a temperature of 90° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 2.8 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation of 25 min. at 200° F. Water was then added to the solution thus produced to adjust the solids concentration to 4.2%. No additional phosphoric acid was required as the final solution pH was 3.0.

This solution was then applied to a web of paperboard having a moisture content of 3-6% by means of a calender water box to provide 0.11 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 140-160° F. when applied. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer value, percent gloss		
	5 secs.	20 secs.	60 secs.
NCS-12 oil.....	81	70	46
Nujol.....	94	89	71

EXAMPLE V

This example also illustrates the preparation of a sizing composition and the treatment of a web of paper-

board in accordance with the process of this invention.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 50.4 parts of water at a temperature of 90° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 2.8 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation of 25 min. at 200° F. Water was then added to the solution thus produced to adjust the solids concentration to 4.2% and no additional phosphoric acid was required as the final solution pH was 3.0. An acid stable wax emulsion (about 50% solids) was added to the solution to give water holdout properties in addition to the oil holdout properties exhibited by the invention.

This solution was then applied to a web of paperboard having a moisture content of 3-6% by means of a calender box to provide 0.11 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 140-160° F. when applied. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer value, percent gloss			Water drop test, secs.
	5 secs.	20 secs.	60 secs.	
Solution wax emul. NCS-12 oil.....	79	55	25	110
Nujol.....	94	89	73	-----
Solution only, NCS-12 oil.....	81	70	46	34
Nujol.....	94	89	71	-----
Base stock, no treatment NCS-12 oil.....	26	22	21	29
Nujol.....	35	25	23	-----

EXAMPLE VI

Following the procedures of the foregoing examples, 0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 50.4 parts of water at a temperature of 105° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 3.0 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation for 25 min. at 200° F. Water was then added to the solution thus produced to adjust the solids concentration to 4.5% and additional 85% phosphoric acid was added to give the solution a final pH of about 3.8.

This solution was then applied to a web of paperboard having a moisture content of 2-4% by means of calender water boxes to provide from 0.08 to 0.17 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 140-160° F. when applied. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer value, percent gloss		
	5 secs.	30 secs.	60 secs.
1 box (0.08 lb. per 1,000 square feet) NCS-12 oil.....	77	53	34
Nujol.....	90	81	69
2 boxes (0.17 lb. per 1,000 square feet) NCS-12 oil.....	93	93	92
Nujol.....	95	95	94
Starch sized board NCS-12 oil.....	66	30	24
Nujol.....	84	53	33

EXAMPLE VII

Again following the procedures of the preceding examples, 0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 54.9 parts of water at a temperature of 75° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 2.2, 3.8 and 5.7 by the addition of 85% phosphoric acid to three separate portions of the slurry. The slurry portions were

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then cooked with agitation for 25 min. at 200° F. Water was then added to the solutions thus produced to adjust their polyvinyl alcohol concentration to 3.0% and addition 85% phosphoric acid was added to the three portions of the solution to give three solutions of a final pH of about 2.2, 3.9 and 5.7.

Each solution was then applied to a web of paperboard having a moisture content of 5.0% by means of a size press to provide 0.04 lb. of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 75° F. when applied. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	pH	Avg. Vanceometer value, percent gloss (NCS-12 oil)		
		5 secs.	30 secs.	60 secs.
Example VII, 0.04 lb. per 1,000 square feet.	2.2	90	80	61
	3.9	91	80	65
	5.7	86	79	66

EXAMPLE VIII

This example illustrates the application of the invention to the coating of a web of paper by means of a coating "color." The invention is used as the binder in the formulation. The color employed was prepared in the following manner.

A pigment slip was made by adding to water 0.10 part dispersant (TSPP), 10 parts TiO₂, and 90 parts clay to a 66% solids content, and dispersed in a colloid mill.

A second mixture was made consisting of 90 parts water, 10 parts of a mixture of 0.5 part boric acid, and 3.0 parts polyvinyl alcohol, 0.10 part defoamer and sufficient phosphoric acid to give a pH less than 5.8. The mixture had a 10% solids content.

The two mixtures were combined and pH maintained below 5.8.

The combined mixture was applied to the paper web in the manner described in the foregoing examples using a Champion coater, with fully satisfactory coating properties being obtained.

EXAMPLE IX

This example illustrates the application of the invention to the coating or upgrading of a web of paper by means of a coating color while still maintaining holdout properties.

A coating color was made by mixing 91 parts water, 0.1 part dispersant and 5.0 parts TiO₂. This mixture was dispersed and there were added to it 4.0 parts of a mixture of boric acid and polyvinyl alcohol in the ratio of 0.5 boric acid and 3.0 polyvinyl alcohol.

This color was applied to a web of paperboard by means of a size press to form a coating wherein the polyvinyl alcohol was in a concentration of 0.09 pound per 1000 square feet. There was a definite brightness improvement of the treated board along with no loss in holdout properties. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester and the following results were obtained:

Size solution	Polyvinyl alcohol coat wt., lb./1,000 square feet	Avg. Vanceometer value, percent gloss (NCS-12 oil)		
		5 secs.	30 secs.	60 secs.
0.6 part boric acid and 3.4 parts VINOL 165.	0.07	93	93	92
0.6 part boric acid, 3.4 parts VINOL 165 and 5.0 parts TiO ₂ (RA46)	0.08	95	95	94
	0.09	92	92	90

¹ + 0.13 lb. per 1,000 sq. ft. of TiO₂.

EXAMPLE X

This example illustrates the preparation of a sizing composition and the treatment of a web of 42 lb. un-

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bleached kraft (beer liner stock) in accordance with the process of this invention.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 96.5 parts of water at a temperature of 75° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of one part 85% phosphoric acid. The slurry was then cooked with agitation for 25 min. at 200° F. Water was then added to the solution thus produced to adjust its polyvinyl alcohol concentration to 3.5% and an additional part of 85% phosphoric acid were added to give the solution a final pH of about 4.8.

This solution was then applied to a web of 42 lb. unbleached kraft having a moisture content of 5.0 at the rate of 200 ft./min. by means of an air knife to provide 0.3 lb. of coating per 1000 square feet of web. The solution was at a temperature of 140° F. when applied and the web was then dried at a temperature of 150° F. to a final moisture content of 5.0%. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

Treatment	Vanceometer gloss (microamperes NCS-12 oil)		
	5 secs.	20 secs.	60 secs.
None (base stock)	51	27	17
Example X	89	89	89

EXAMPLE XI

This example illustrates the preparation of a sizing composition and the treatment of a web of 42 lb. unbleached kraft in accordance with the process of this invention.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 96.5 parts of water at a temperature of 75° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of one part 85% phosphoric acid. The slurry was then cooked with agitation for 25 min. at 200° F. Water was then added to the solution thus produced to adjust its concentration to 4.0% and additional 85% phosphoric acid was added to give the solution a final pH of about 4.8.

This solution was then applied to a web of 42 lb. kraft having a moisture content of about 5.0% at the rate of 725 ft./min. by means of a water box on the calender stack. The solution was at a temperature of 145° F. when applied and the web was then dried at a temperature of about 185° F. to a final moisture content of 5.0%. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer gloss (microamperes, NCS-12 oil)		
	5 secs.	20 secs.	60 secs.
Untreated	18	14	12
Example XI	48	28	18

EXAMPLE XII

This example illustrates the preparation of a sizing composition and the treatment of a web of unbleached kraft in accordance with the process of this invention.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 96.5 parts of water at a temperature of 75° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of one part 85% phosphoric acid. The slurry was then cooked with agitation for 25 min. at 200° F. Water was then added to the solution thus produced to adjust its concentration to 3.5% and an additional part of 85% phosphoric acid was added to give the solution a final pH of about 4.8.

This solution was then applied to a web of unbleached kraft having a moisture content of 5.0% at the rate of 100 ft./min. by means of a size press to provide 0.2 lb.

of polyvinyl alcohol per 1000 square feet of web. The solution was at a temperature of 77° F. when applied and the web was then dried at a temperature of 180° F. to a final moisture content of 5.0%. The surface of the thus-treated web was then tested with the Vanceometer Absorption Tester, and the following results were obtained:

	Avg. Vanceometer gloss (microamperes, NCS-12 oil)		
	5 secs.	20 secs.	60 secs.
Untreated base stock.....	32	19	16
Example XII.....	71	69	62

EXAMPLE XIII

This example illustrates the use of the invention to lay fibers. A solution having a concentration of 1-3% and a boric acid-polyvinyl alcohol ratio from 0.5 to 0.9:3.0 parts polyvinyl alcohol was prepared in the following manner.

0.5 part of boric acid and 3.0 parts of Vinol 165 were added slowly to 50.4 parts of water at a temperature of 100° F. and thoroughly mixed. The resultant slurry was adjusted to a pH of approximately 4.7 by the addition of 85% phosphoric acid. The slurry was then cooked with agitation for 25 min. at 200° F. Water was added to adjust the percent solids to 2% and an additional phosphoric acid was added to give the solution a final pH of about 4.8.

This solution was then applied to a web by means of a size press.

It will be apparent to those skilled in the art that various changes and modifications may be made in the embodiments described above without departing from the invention, as defined in the appended claims. It is intended, therefore, that all matter contained in the foregoing description and in the drawings shall be interpreted as illustrative only and not as limitative of the invention.

We claim:

1. A process for treating a paper web to apply polyvinyl alcohol thereto with minimum penetration of the polyvinyl alcohol into the web which comprises preparing an aqueous composition containing said polyvinyl alcohol in admixture with boric acid in the amount of more than 15% and up to 50% by weight of the polyvinyl alcohol, said composition having a pH of at most 6.0, applying said composition to said web at a temperature up to about 210° F., and drying said web with the polyvinyl alcohol thereon.

2. A process for treating a paper web to apply polyvinyl alcohol thereto with minimum penetration of the polyvinyl alcohol into the web which comprises preparing an aqueous composition containing said polyvinyl alcohol in admixture with boric acid in the amount of more than 15% and up to 50% by weight of the polyvinyl alcohol, said composition having a pH of at most 6.0 and containing at least about 0.5% of polyvinyl alcohol, applying said composition to said web at a temperature up to about 210° F., and drying said web with the polyvinyl alcohol thereon.

3. A process for treating a paper web to apply polyvinyl alcohol thereto with minimum penetration of the polyvinyl alcohol into the web which comprises applying to said web an aqueous composition containing said polyvinyl alcohol in admixture with boric acid in the amount of more than 15% and up to 50% by weight of the polyvinyl alcohol, said composition having a pH of at most 6.0, said composition being applied to said web at a temperature up to about 210° F., and drying said web with the polyvinyl alcohol thereon.

4. A process for treating a paper web to apply polyvinyl alcohol thereto with minimum penetration of the polyvinyl alcohol into the web which comprises applying to said web an aqueous composition containing at least about 0.5% of polyvinyl alcohol in admixture with boric acid in the amount of more than 15% and up to 50% by weight of the polyvinyl alcohol, said composition having a pH of at most 6.0, said composition being applied to said web at a temperature up to about 210° F., and drying said web with the polyvinyl alcohol thereon.

5. A process for treating a paper web to apply polyvinyl alcohol thereto with minimum penetration of the polyvinyl alcohol into the web which comprises applying to said web an aqueous composition containing 0.5% to 35% of polyvinyl alcohol in admixture with boric acid in the ratio of 0.5 to 1.3 parts by weight of boric acid per 3 parts of polyvinyl alcohol, said composition having a pH of at most 6.0, said coating being applied to said web at a temperature up to about 210° F., and drying said web with the polyvinyl alcohol thereon.

6. An aqueous polyvinyl alcohol composition for application to a cellulosic fibrous web and effective to deposit polyvinyl alcohol on said web with minimum penetration of polyvinyl alcohol into the web, comprising water, polyvinyl alcohol, and boric acid, said boric acid being present in the amount of more than 15% and up to 50% by weight based on the polyvinyl alcohol and said composition having a pH of at most 6.0.

7. An aqueous polyvinyl alcohol composition for application to a cellulosic fibrous web and effective to deposit polyvinyl alcohol on said web with minimum penetration of polyvinyl alcohol into the web, comprising water, polyvinyl alcohol, and boric acid, said polyvinyl alcohol being present in the amount of 0.5% to 35% and said boric acid being present in the amount of more than 15% and up to 50% by weight based on the polyvinyl alcohol, and said composition having a pH of at most 6.0.

8. An aqueous polyvinyl alcohol composition for application to a cellulosic fibrous web and effective to deposit polyvinyl alcohol on said web with minimum penetration of polyvinyl alcohol into the web, comprising water, polyvinyl alcohol, and boric acid, said polyvinyl alcohol being present in the amount of 0.5% to 35% and said boric acid being present in the ratio of 0.5 to 1.3 parts by weight of boric acid per 3 parts of polyvinyl alcohol, and said composition having a pH of at most 6.0.

9. A paper web having a dried film of polyvinyl alcohol thereon deposited from a composition comprising water, 0.5% to 35% of polyvinyl alcohol, and boric acid, said boric acid being present in the ratio of 0.5 to 1.3 parts by weight of boric acid per 3 parts of polyvinyl alcohol, and said composition having a pH of at most 6.0.

10. A paper web having a dried film of polyvinyl alcohol thereon deposited from a composition comprising water, 0.5% to 35% of polyvinyl alcohol, and boric acid, said boric acid being present in the amount of more than 15% but at most 50% by weight based on the polyvinyl alcohol, and said solution having a pH of at most 6.0.

11. A dry blend adapted to be added to water to form an aqueous polyvinyl alcohol composition for application to a cellulosic fibrous web and effective to deposit polyvinyl alcohol on said web with minimum penetration of the polyvinyl alcohol into the web, comprising polyvinyl alcohol, boric acid, and an acid effective to adjust the pH of said solution, said boric acid being present in an amount more than 15% and up to 50% by weight based on the polyvinyl alcohol and said second-named acid being present in an amount sufficient to give said composition a pH of at most 6.0.

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12. A dry blend adapted to be added to water to form an aqueous polyvinyl alcohol composition for application to a cellulosic fibrous web and effective to deposit polyvinyl alcohol on said web with minimum penetration of the polyvinyl alcohol into the web, comprising polyvinyl alcohol, boric acid, and an acid effective to adjust the pH of said solution, said boric acid being present in the ratio of 0.5 to 1.3 parts by weight of boric acid per 3 parts of polyvinyl alcohol, and said second-named acid being present in an amount sufficient to give said composition a pH of at most 6.0.

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117—121, 161; 260—29.6, 91.3

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,438,808 Dated April 15, 1969

Inventor(s) Raymond L. Hawkins and George Davidowich

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

Column 2, line 4, "gelatin" should read -- gelation --.
Column 5, line 52, "viescosity" should read -- viscosity --;
line 58, "this" should read -- that --.
Column 7, line 39, "light" should read -- like --.
Column 9, line 18, "75°" should read -- 75°F --; line 35, before
"gloss" should read -- percent --.
Column 10, line 7, "of" should read -- for --.
Column 11, line 39, "descirbed" should read -- described --.
Column 15, line 4, "penerta-" should read -- penetra- --.

SIGNED AND
SEALED
FEB 24 1970

(SEAL)

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