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PROCESS FOR FORMING WATER-
RESISTANT GLUE FILMSJohn R. Hubbard, Gowanda, N. Y., assignor to
Peter Cooper Corporations, Gowanda, N. Y.No Drawing. Application November 8, 1940,
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7 Claims. (Cl. 106—135)

This invention relates to a process for enhancing the wet-strength and water resistance of fibrous materials, such for example as paper pulp fibers, webs of paper or textile materials.

In this process and composition of matter, an animal glue or suitable protein is established upon or within a fibrous material or web as a film or a reinforcement in differentiation from the more common use of animal glue or protein as an adhesive as in the joining of wood blocks and other materials.

The procedure heretofore employed for the purposes outlined was a two-step process comprising:

(1) Description of a protein film upon or within the web;

(2) Treatment of said protein film so deposited by formaldehyde, various polymers of formaldehyde or related materials and/or metallic or organic tanning salts.

In increasing the wet-strength or water resistance of paper webs, the more common procedure has consisted in:

(1) Running the paper from the paper machine through a protein tub size, followed by a squeeze for removal of excess size;

(2) Running of the sized paper (either before or after drying) through a second tub containing a formalin solution, squeezing to remove excess hardening agent, followed by suitable drying. Alternatively the second step of this procedure is effected by subjecting the sized web to fumes of formalin vapor, or by spraying a hardening agent on the sized web.

By means of these processes as heretofore employed and in variations thereof, it was difficult to obtain uniform results because:

(1) Case hardening of the outer surface of the protein film resulted when the concentration of the hardener was too strong, which resulted in having the inner portions of the protein film unchanged;

(2) Incomplete hardening of the film, if the concentration of the hardener was too low;

(3) Lack of uniform depth and degree of tannage throughout the thickness of the protein film.

Heretofore it has been impractical to add a hardener, such as formalin, directly to the protein size solution in sufficient amounts to satisfactorily harden the protein film without causing a coagulation of premature hardening of the protein before it could be applied to the web of fibrous material. For practical use under mill operating conditions, the size solution must

remain stable with constant fluidity over periods of time from a few hours to a day or two, and in some cases this "working life" of the size solution must be even longer. When a hardener of the correct concentration and quantity is added to a protein size solution, progressive tannage of the protein takes place, and, consequently, the working life of such a solution is too short, and thus the two-step process hereinbefore referred to had to be used.

One object of this invention is to provide an improved process of producing a fibrous web of materially increased wet strength. A further object is to produce a single step process for applying a sizing solution with a hardener mixed therewith to a fibrous material to produce a web of increased wet strength.

A further object of this invention is to provide an improved sizing process for producing a fibrous material of improved water resisting properties. Another object is to provide an improved process for providing a uniform depth and degree of tannage of the dried protein film. It is also an object of this invention to provide a process including the use of a sizing solution containing a volatile organic acid, a hardener and an alkali or buffer salt, and so proportioning these ingredients that upon volatilization of the acid from the size film, the film will have a pH sufficiently high to ensure very efficient hardening of the glue.

Other objects of this invention will appear from the following description and claims.

The following procedure results in producing a size film which under some conditions produces the desired wet strength of a fibrous web and this procedure is first described, since it is of simple form and serves to illustrate the principle upon which my invention operates:

In accordance with this procedure, a solution of glue or other suitable protein is made in the usual manner, for example, by adding approximately 30 parts by weight of glue, such for example as Peter Cooper Standard IX, to 300 parts by weight of water. To this solution, I add from 1½ to 3 parts by weight of an organic acid, preferably an acid which is volatile, such for example, as an 85% formic acid. This acid materially lowers the pH of the glue solution, and a hardening or tanning agent may then be added to the solution without causing the solution to become quickly coagulated. If formalin is used as a hardening agent, it is first diluted with 3 to 5 equivalent volumes of water and is then added to the glue solution, the amount of formalin be-

ing 1 to 3 parts by weight. The solution may contain from 5% to 10% of formalin based on the weight of dry glue used in making the solution, and this quantity of formalin is adequate to insure proper hardening of a protein size film formed by the use of this solution. This glue solution is preferably kept at a temperature of about 100° F. to 125° F. and will remain stable for a period of from 48 to 72 hours, thus insuring adequate working life of the solution for commercial use. Greater or smaller quantities of formalin may be used to suit varying condition, and in such cases, the quantity of formic acid is varied accordingly.

In place of formic acid, acetic, or propionic acid, other suitable weak organic acids may be employed and preferably acids which are volatile are chosen, for the purpose of immobilizing the action of the hardener upon the protein size solution during storage or use of the same. On drying of the size film and the subsequent loss of water, the concentration of the glue in the film is increased, and as the organic acid volatilizes the resistance of the protein to the hardening action of the formalin decreases, so that the formalin serves to harden the protein film deposited upon or within the web.

In size solutions as heretofore made, when formalin was added directly to the protein size solution without first adding an acid, the amount of formalin which could be added without rapid coagulation of the composition under practical mill conditions was in the range of about 1% or less, based on the weight of the dry glue used in the solution. This small ratio of formalin to dry glue is insufficient to adequately harden the protein size film. If from 5% to 10% of formalin, based on the weight of the glue present in the solution, is added to the solution without first adding acid thereto, the resulting composition coagulates and jells within ten to fifteen minutes at a temperature of 120° F.

The volatile weak organic acid in my composition is added to cause a change of the normally negatively charged protein to a positively charged protein. While positively charged, the glue protein is for all practical purposes inert to the hardening agent under the dilution usually employed for making sizing solutions and at the temperatures under which this solution is generally employed, which temperatures are generally from 100° to 125° F.

While any acid may be used to effect a positively charged protein ion so as to render it resistant to the action of a hardening agent, it is obvious that it is not desirable to use strong mineral or organic acids, since these cause hydrolysis of the protein, thus destroying its properties of being effectively hardened by the hardener. For this reason, I prefer to use weak organic acids for this purpose and preferably such acids which are also volatile are employed to permit removal of excess acid from the protein film on drying, and thus to permit the positively charged protein ion (acid) to become less positively charged as the acid volatilizes and in many cases to become negatively charged, under which condition, the protein is far more reactive with the hardener.

Animal glue proteins are thought to be neutral or electrically devoid of charge at pH 4.7. When less acid, or in a pH range of 4.7 to 8.5, for example, the protein becomes progressively more negatively charged as the pH rises toward pH 8.5. In the pH range of 4.7 to 1.0, for ex-

ample, the glue protein becomes progressively more positively charged as the pH decreases toward pH 1.0. The normal glues of commerce run in a pH range of 7.4 to 6.0, and are therefore strongly negatively charged, and are very reactive to the formalin hardener.

The pH of my improved glue composition hereinbefore stated has a pH of 3.2 to 3.5 so that the protein therein is positively charged and practically inert to the action of the hardener under the conditions described.

The composition hereinbefore described may be modified and improved by the addition thereto of buffer type alkalis, such for example as borax, and when thus modified, the wet strength or water resistance of the film is increased. When a buffer type alkali is added, an increase in the amount of volatile acid is necessary to neutralize the original alkali value of the buffer salt. On volatilizing the excess volatile acid in the composition, the alkaline buffer salt serves to bring the pH of the size film above 4.7, thereby forming a negatively charged protein which is far more reactive to the hardener present in the film. If desired, a plasticizer, such as glycerine, may also be added to the solution.

The following example illustrates how a buffer salt may be added to the solution for the purpose of producing a superior hardening effect on the resulting film.

Example I

	Parts by weight
1XM glue	30
Water	300
Formic acid	2 1/4
Formalin	3
Borax	3.6

The following example illustrates a sizing solution having a plasticizer incorporated therein:

Example II

	Parts by weight
1XM glue	30
Water	300
Formic acid	1 1/4
Formalin	3
Glycerine	15

In Example III, I have incorporated both a plasticizer and a buffer salt:

Example III

	Parts by weight
1XM glue	30
Water	300
Formic acid	2 1/4
Formalin	3
Borax	3.6
Glycerine	15

The foregoing examples are merely illustrative of some of the many formulas embodying my invention, and it will be obvious that additional formulas can be readily worked out by persons skilled in the art. It is not intended to limit the invention to the particular examples herein given.

I am aware of the fact that volatile organic acids have been used in connection with glue solutions containing materials which per se are not tanning agents, but which are activated by the acid into tanning agents. In accordance with this invention, however, I use as tanning agents only materials which per se are active in hardening proteins, and in accordance with my invention, the acid is employed for the purpose of retarding the action of the per se tanning agents. Formalin is a tanning agent per se which does

not require any acid to activate it. Other per se tanning agents may be employed in place of formalin, such for example as chromic compounds wherein the chromium is in the basic radical and certain aluminum salts.

The following examples illustrate sizing compositions in accordance with this invention containing other hardening agents and mixtures of hardening agents:

Example IV

	Parts by weight
1XM glue -----	30
Water -----	300-500
Formic acid -----	6
Aluminum sulfate -----	6
Sodium acetate -----	3
Borax -----	2

Example V

	Parts by weight
1XM glue -----	30
Water -----	300-500
Formic acid -----	2½
Aluminum sulfate -----	6
Borax -----	3

Example VI

	Parts by weight
1XM glue -----	30
Water -----	300-500
Formic acid -----	2½
Aluminum sulfate -----	6
Borax -----	3
Glycerine -----	10-30

Example VII

	Parts by weight
1XM glue -----	30
Water -----	300
Formic acid -----	2½
Chrome alum -----	2

Example VIII

	Parts by weight
1XM glue -----	30
Water -----	300
Formic acid -----	2¾
Borax -----	1
Chrome alum -----	2

Example IX

	Parts by weight
1XM glue -----	30
Water -----	300
Formic acid -----	2¾
Borax -----	1
Chrome alum -----	2
Glycerine -----	15

Example X

	Parts by weight
1XM glue -----	30
Water -----	350
Formic acid -----	2½
Formalin -----	3
Chrome alum -----	2
Aluminum sulfate -----	1.8
Borax -----	1.8

It is obvious that other possible combinations of various materials which are per se tanning or hardening agents may be used, depending upon the results desired. Formalin is a very effective tanning agent and does not color the size solution and gives easy penetration of fibrous materials by the solution. Size solutions containing formalin are sometimes difficult to control for purely surface sizing. The chrome-alum type of tanning agent as well as other chromic salts wherein the

chromium is in the basic radical produces a colored size solution, and is, consequently, useful only where a green color is not objectionable. This material provides excellent tannage and can be controlled so as to produce either a surface size or a penetration type of size. Any of the commercially available chrome-alums may be used, as well as other chromic salts, such as chromic chloride, nitrate, sulphate and hydroxide, the latter being dissolved in an appropriate acid, and such chromic salts may be substituted for chrome-alum in the foregoing examples.

Aluminum sulfate provides a fair tannage and does not color the size solution and is very easily controlled to produce a surface size, rather than a penetration type of size.

In place of aluminum sulfate, other aluminum salts, such for example as aluminum chloride and aluminum nitrate, may be employed where trivalent aluminum ions are present in solution. Any such trivalent aluminum salts may be substituted for aluminum sulfate in the examples given.

The use of aluminum sulfate in glue solutions for tub sizing of paper was well known prior to this invention. The usual formulas for such tub sizing solutions specify 5% to 10% glue solutions containing from 2½% to 5% of alum, based on the weight of the dry glue. Such size solutions produce only a slightly hardened glue film and require close control of the flowing properties due to the increase in viscosity of the size solution by the alum. If an excess of alum is added, the size solution thins satisfactorily but the resultant dry size film is inferior in wet strength or hardening action due to the excess mineral acid present in the film and paper base. This in turn is due to the fact that the paper makers' alum which is employed contains sulfuric acid. Such procedure, therefore, produces a brittle paper stock and is undesirable. My improved composition employs from 6½% to 30% of aluminum sulfate, based upon the weight of the dry glue in the solution, and the average amount of aluminum sulfate in Examples IV to VI is about 20%. This produces a marked tannage of the dried glue film and the mineral acid content of the aluminum salt present in the composition is neutralized, with borax or other alkali buffer salts. In my composition, I also employ a volatile acid for acidifying the composition to such a point that the protein is made inactive toward the tanning agent until the volatilization of the acid causes the pH to rise toward the neutral point, where the tannage is markedly superior. By varying the volatile acid content of the size solution, the viscosity and flowing properties of the solution are easily controlled.

In preparing size solutions using aluminum or chromic salts, the glue is first brought into solution at about 120° F. Preferably the organic acid is then added and mixed well with the glue solution. The hardening agents, buffers, or plasticizers may then be added in any desired order. With hardening agents other than formalin it is possible to make a mixture of the acid with the hardening agents before adding same to the glue solution; however, results are generally more satisfactory if the acid, preferably volatile, is first added to the glue solution then followed by the hardening agents.

In order to apply my invention for use under any particular mill condition, the following procedure is recommended:

1. Sample solutions are made of the glue con-

centration required and to different samples are added various quantities of formic acid or other weak organic acid, which is preferably volatile.

2. Formalin or other per se tanning agent is added to each sample in accordance with the protein content of the glue and in quantity sufficient to produce the desired degree of hardening of the glue film.

3. The working life of each sample at the temperature at which it is to be used commercially is then determined.

4. The sample containing the lowest percentage of volatile acid which satisfactorily stabilizes the size under the particular mill conditions is then selected. If buffers, alkaline salts, plasticizers, or auxiliary hardeners are used, sufficient additional volatile acid is added to neutralize the added alkali or to insure the desired stability.

In the preferred form of my process as herein described, a paper web, for example, is taken directly from the paper machine and led into the usual size tub containing a composition in accordance with this invention. The sized paper is then run through squeeze rolls to remove excess size, and then to a drying machine or air dryers. A similar procedure may be followed for sizing other fibrous webs. Other uses of my improved size composition may, however, be made, such for example as floating the web on the solution, immersion of the web, surface sizing one side of the web, and/or spraying the solution on a web.

While my invention has herein been described mainly as applied to paper or other fibrous webs, it is obvious that the same may be applied to any fibrous materials regardless of whether or not they are in the form of webs.

I claim as my invention:

1. A process of increasing the wet strength of fibrous materials by producing water-resistant size films on the fibers, which includes making a solution of water and glue of the desired concentration, adding to the solution a volatile organic acid and a material which is per se a direct hardening agent for the glue, said hardening material being from 5% to 30% by weight of the glue in said solution and being sufficient to effect substantially complete hardening of the protein content of the glue, the amount of acid present being sufficient to reduce the pH of the solution to a point below that at which hardening action progresses rapidly, applying the solution to the fibrous material, and drying the film on said fibrous material to remove volatile acid, whereby the pH of the glue film rises to a point at which hardening takes place.

2. A process of increasing the wet strength of fibrous materials by producing water-resistant size films on the fibers, which includes making a solution of water and glue of the desired concentration, adding to the solution a volatile organic acid, a material which is per se a direct hardening agent for the glue and sufficient in quantity to effect substantially complete hardening of the protein content of said glue, and a buffer alkali, the amount of acid present being sufficient to reduce the pH of the solution to a point below that at which hardening of the glue progresses rapidly and the amount of buffer alkali present being such that without said acid, the pH of said solution would be more than 4.7, applying the solution to the fibrous material, and drying the film on said fibrous material to remove volatile acid, whereby the pH of the glue film rises to a point at which hardening takes place.

3. A process of increasing the wet strength of

fibrous materials by producing water-resistant size films on the fibers, which includes making a glue solution containing approximately 10% of glue, adding to said glue solution a volatile organic acid and a material which per se has a direct hardening action on glue, the quantity of said hardening material being from 5% to 30% by weight of the glue in said solution and being sufficient to effect substantially complete hardening of the protein content of the glue, and the amount of acid present being sufficient to reduce the pH of the solution to a point below that at which hardening action progresses rapidly, and adjusting said solution so that the same without said volatile acid has a pH of at least 4.7, applying the solution to the fibrous material, and then drying the fibrous material to remove acid by volatilization.

4. A process of increasing the wet strength of fibrous materials by producing water-resistant size films on the fibers, which includes making a glue solution containing approximately 10% of glue, adding to said glue solution a volatile organic acid and a material which per se has a direct hardening action on glue, and a buffer alkali, the quantity of said hardening agent being from 5% to 30% of the weight of the glue in said solution and being sufficient to effect substantially complete hardening of the protein content of the glue, and adjusting the acid and alkali content of the solution so that the solution when ready for application to a web has a pH of approximately from 3.2 to 3.5 and so that said solution without said acid would have a pH of at least 4.7, applying the solution to the fibrous material, and then drying the fibrous material to remove acid by volatilization.

5. A process of producing water-resistant size, which includes making a solution of water and glue of the concentration desired for a size solution, adding to the solution a volatile organic acid, a material which is per se a direct hardening agent for the glue, and borax, the amount of acid present being sufficient to reduce the pH of the solution to a point below that at which hardening action progresses rapidly, the amount of borax present being such that the solution without said volatile acid has a pH of at least 4.7.

6. A process of producing water-resistant size, which includes making a solution of water and glue of the concentration desired for a size solution, adding to the solution a volatile organic acid, formalin and a buffer alkali, the amount of formalin being from 5% to 10% by weight of the glue in said solution and the amount of acid present being sufficient to reduce the pH of the solution to a point below that at which hardening action progresses rapidly, and the amount of the buffer alkali being such that said solution without said volatile acid has a pH of at least 4.7.

7. A process of producing a water-resistant self-hardening glue, which includes making a glue solution containing a volatile organic acid, formalin, and a buffer alkali, the quantity of formalin being from 5% to 10% by weight of the quantity of glue in said solution, the acid in said solution being sufficient in quantity to lower the pH of the solution to a point at which coagulation of the glue is retarded, applying the solution to a surface to form a film, and evaporating the volatile acid from said film to raise the pH thereof through the isoelectric point of said glue solution, whereupon rapid hardening of said film results.

JOHN R. HUBBARD.

CERTIFICATE OF CORRECTION.

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JOHN R. HUBBARD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 15, for "description" read --deposition--; 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 16th day of May, A. D. 1944.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.