A - SODIUM ALUMINATE + HCl USED IN BEATER SUBSTANTIALLY FREE OF BIVALENT ANIONS

B - ALUMINUM SULFATE USED IN BEATER

% MELAMINE-FORMALDEHYDE RESIN (BASED ON BONE-DRY PULP)
UNITED STATES PATENT OFFICE

METHOD OF MAKING HIGH WET STRENGTH PAPER

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5 Claims. (Cl. 92—21)

1. This invention relates to the preparation of high wet strength paper having good flexibility, by first mixing with paper pulp in the beater an ordinary paper sizing, and either (1) aluminum chloride, nitrate or acetate or (2) an alkali metal aluminate plus hydrochloric, acetic or nitric acid; polyvalent inorganic acid ions being always substantially absent from the system employing either (1) or (2); after the pulp has been reduced to final readiness for paper a wet strength-imparting melamine-formaldehyde resin or melamine-monoureide-formaldehyde resin is incorporated therein.

The obtaining of paper having a high wet strength without detrimentally affecting the other properties thereof has been given considerable attention in recent years. In many of the proposed means of maintaining or increasing the wet strength of the paper, the paper has been rendered brittle or the properties were otherwise altered so that the increased wet strength has been obtained by the sacrifice of some other desirable property.

The preparation of high wet strength paper has been described in U. S. Patents Nos. 2,291,079 and 2,291,080 of Hofferbert. In these patents the high wet strength of the paper is obtained by the use of amino triazine-aldehyde condensation products applied as a tub sizing to the paper (i.e., after the paper is formed and dried) and the final product which is obtained, while having an increased wet strength, exhibits a much lower flexibility than the paper originally treated. As an improvement over the process of the Hofferbert patents it has been suggested that melamine-formaldehyde resin be first dissolved in hydrochloric acid and aged for at least 12 to 24 hours followed by using the resulting product as a beater sizing in the regular beater furnish i.e. with alum (aluminum sulfate) as a flocculent. This procedure has resulted in a paper showing some improvement in wet strength without any serious decrease in the flexibility of the paper. I have found, however, that by employing my invention vastly improved wet strengths may be obtained over the wet strengths obtained by the procedure referred to and yet the flexibility properties of the paper are not adversely affected.

It is an object of my invention to produce a high wet strength paper having good flexibility properties and generally, good stability toward photographic emulsions without adversely affecting the other properties of the paper. Other objects of my invention will appear herein.

My invention in its broader aspects comprises a process of making paper of high wet strength particularly adapted to photographic purposes in which paper pulp is mixed in the beater with paper sizing and either (1) an alkali metal aluminate and sufficient hydrochloric, nitric or acetic acid to precipitate the sizing or (2) sufficient aluminum chloride, nitrate or acetate, to precipitate the sizing, and before the paper stock is brought to the paper machine, there is incorporated therein a small proportion of a wet strength-imparting melamine-formaldehyde resin or melamine-monoureide-formaldehyde resin, care being taken to carry out the process in the absence of polyvalent inorganic acid radicals.

In the preferred aspect of my invention there is first incorporated in the pulp in the beater one of the usual beater sizings which is acidified to a pH of 4 to 5 by the addition of an alkali metal aluminate and hydrochloric, nitric or acetic acid or by the addition of an aluminum salt of one of those acids. After the pulp has been reduced and before being brought to the paper machine there is added and uniformly distributed throughout a wet strength-imparting melamine-formaldehyde resin or melamine-monoureide-formaldehyde resin. While I have mentioned a pH of 4 to 5 as being the preferred range of acidity for precipitating the usual beater sizings, it will be understood that the principle involved in such acidification is to introduce the right amount of specified acid to precipitate the sizing without having either too much acidity or too little acidity. Obviously no advantage is to be gained by having the furnish more acid than necessary as this simply results in excess acidity. At the other extreme, it is not wise to have too little acidity in the furnish for the reason that incomplete precipitation of the sizing will be effected, with accompanying loss of economy and quality.

In making paper in accordance with my invention, hydrochloric is the preferred acid for use with the alkali metal aluminate, being less expensive and readily available. Nitric acid may be employed; however, it is more expensive than
hydrochloric and has oxidizing tendencies which may be undesirable with some types of treatment. Acetic acid may be employed; however, more is required to impart the desired pH than is the case with hydrochloric acid.

The alkali metal aluminate (with acid) and the aluminum chloride, nitrate or acetate (without acid) perform the function in the furnish of supply the necessary aluminum floc to agglomerate the precipitated sizing, this function of aluminum floc being well known in the art. It is desirable with the commercial melamine-formaldehyde resins to first age them in solution in hydrochloric acid before incorporating in paper pulp in accordance with my invention. Some resins of this type require considerable aging such as standing of their hydrochloric acid solution for 24 hours or longer, while in the case of other resins of this type standing but a short time such as 3 hours is sufficient; such aging is understood by the trade. Aging may be carried out, for example, by dissolving 100 lbs. of commercial melamine-formaldehyde resin in a mixture of 50 gallons of water and 48.6 lbs. of commercial hydrochloric acid at a temperature of 130°-140° F., long enough to make 100 gallons and allowing the mass to stand at a temperature less than 100° F. for the desired time, such as approximately 3 to 24 hours.

Melamine-monomoureide-formaldehyde resin is described in some detail in U. S. Patent No. 2,312,668 of D'Alelio dated March 2, 1943. It is conveniently prepared by first reacting melamine with an equal number of moles of urea followed by reaction of the melamine urea formed, with formaldehyde. For example, 2000 grams of concentrated HCl containing 20 moles of hydrochloric acid were added to 10 liters of distilled water and 1200 grams of urea (20 moles) were dissolved in this solution. By reacting 2520 grams of practical grade melamine (20 moles) therewith at an elevated temperature a product consisting essentially of melamine monoureide may be obtained. The melamine-monomoureide was isolated from the reaction mixture by crystallization and then dried. 2000 grams (11.83 moles) of the melamine-monoureide thus obtained were dissolved with rapid stirring in a mixture consisting of 16.8 liters of water and 5.6 liters (75 moles HCHO) of commercial 40% formalin, the mixture being brought to a temperature of 80° C. before adding the ureide. When the ureide had all dissolved, the solution was rapidly cooled to room temperature. It had a pH of 2.9.

Resins having various molar ratios of formaldehyde to melamine may be employed as the melamine-formaldehyde resin. For instance, resins prepared using molar ratios of formaldehyde to melamine of from 1:1 up to 6:1 or even higher can be used. Ordinarily, the resins prepared using a molar ratio of formaldehyde to melamine between 2:1 and 4:1 are most suitable for this operation.

In making paper in accordance with my invention, the pulp is placed in the beater and, in the beating operation, is sized with one of the usual sizing materials among which may be mentioned rosin, hydrogenated rosin, or stearic acid, which has been saponified with caustic soda or the like. Ordinarily, the size may be prepared from the resin, hydrogenated rosin or stearic acid by treating with 1/4 of its weight of caustic soda. The soap thus formed can be used in any dilution desired. The use of larger amounts of caustic soda in preparing the soap merely necessitates the employment of larger proportions of acid in the beater sizing operation and has other disadvantages. When the sizing is added to the beater, there is also added sodium aluminate and an acid such as hydrochloric acid in a sufficient amount to precipitate the sizing material and to impart the proper acidity to the paper. Instead of adding sodium aluminate and acid, the aluminum salt of the monovalent acid may be added such as, for instance, aluminum chloride or aluminum nitrate. If the aluminum salt added is not of sufficient acid strength to impart the desired acidity to the paper when used in small quantity, the addition of acid is also necessary in the beater. The size of the desired amount is incorporated in the beater mass to bring the mass to the acidity desired. It is desirable, particularly if the paper being prepared is to be used for photographic purposes, to reduce the acidity of the pulp to a pH of approximately 4 to 5.

After the beating operation is completed and the pulp has been reduced so as to be ready for forming paper, such as after the pulp has been put through the Jordan, a small amount of a wet strength-imparting resin above specified is added thereinto in proper proportion. The paper stock is then conditioned for deposit on the web of the paper machine and paper is prepared therefrom.

I have found that the papers resulting from treatment with the wet strength-imparting resins herein specified, when substantially free of polyvalent inorganic acid ions, possess wet strengths considerably higher than paper in which those ions are present. I have also found that to obtain a specified wet strength a much less quantity of the resin is necessary when sodium aluminate and hydrochloric, nitric or acetic acid are employed or when their aluminum salt is employed, than in those cases in which polyvalent inorganic acid ions are employed in any of the operations in sizing the pulp in the beater. For instance, a high wet strength paper prepared in accordance with my process, using sodium aluminate and hydrochloric acid together with the sizing material in the beater, and adding 3% of wet strength-imparting melamine-formaldehyde resin before placing on the wire of the paper machine, the operation carried out in such a manner as to produce a paper weighing 24 lbs. per 1000 square feet, gave a product having a wet strength of 11 1/2% pounds per square inch whereas a similar pulp using the same sizing material but employing only aluminum sulfate (the conventional material) to precipitate the size in the beater and then adding 3% of the resin before placing on the wire of the paper machine gave a paper, when of the same base weight, having a wet strength of only 8 pounds per square inch. In another instance in which only 1 1/2% of the resin was employed, the paper in which the sodium aluminate and monovalent acid was used (polyvalent inorganic acid ions being absent) gave a wet strength of 11 whereas, when aluminum sulfate only was employed for acidifying the beater size, the other conditions being the same, a wet strength of only 5% was obtained.

The drawing is for the purpose of illustrating the distinction between the wet strengths of paper sized with or without polyvalent inorganic acid ions and those in which an aluminum sulfate is employed in the beater. It may be seen from this graph that to obtain a wet strength of 6 a considerably less proportion of the wet strength-imparting resin is necessary in the case wherein polyvalent inorganic acid ions are excluded than in the case where aluminum sulfate
is used. The data employed for this graph was obtained by processing beater stock and handling over the paper machine in a regular manner except that in one case the stock was prepared using, in the beater to acidify the pulp, sodium aluminate and hydrochloric acid and in the other aluminum sulfate. The beater compositions for the two cases were as follows:

<table>
<thead>
<tr>
<th>Sodium Aluminate Treatment</th>
<th>Aluminum Sulfate Treatment</th>
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<tr>
<td>1100 gals. water.</td>
<td>1100 gals. water.</td>
</tr>
<tr>
<td>600 lbs. sulfite pulp.</td>
<td>600 lbs. sulfite pulp.</td>
</tr>
<tr>
<td>5.5 lbs. sodium aluminate.</td>
<td>2.5 lbs. sodium stearate.</td>
</tr>
<tr>
<td>45 lbs. cooked corn starch.</td>
<td>1.1 lbs. aluminum stearate.</td>
</tr>
<tr>
<td>11.1 lbs. gelatine.</td>
<td>16.7 lbs. aluminate.</td>
</tr>
<tr>
<td>30 lbs. hydrochloric acid (sp. gr. =1.16)</td>
<td></td>
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</table>

The paper sheets prepared in each case had a base weight of 20 lbs. per 1000 square feet.

The resin employed was a melamine-formaldehyde resin marketed as Paper Maker's Resin No. 607 which had been aged by allowing the solution of the 50% hydrogenated hydrochloric acid (5% normal) to stand for approximately 3 hours. The acid-resin solution was added to the stock, after the Jordonation operation in every case.

It may be seen from the attached graph that even a very small proportion of resin will increase the wet strength. In accordance with my invention, in most cases it is preferred to use at least 3% of resin. Ordinarily, not more than 5% is necessary to give the desired wet strength although a further amount such as up to 10% or even more may be incorporated if desired. Normally 3% of resin based on the bone dry weight of the pulp is the preferred operating range. Other materials than those listed such as starch, glues, dyes and the like may be added as an addition to the paper pulp provided they do not introduce any substantial amount of sulfate radical or some other polybasic inorganic acid radical to the mass. The sole criterion as to the amount of polyvalent acid radical which can be tolerated is that which does not materially affect the wet strength of the paper which is obtained. It has been my experience that some polyvalent inorganic acids are less liable to lower the wet strength of the paper obtained than are other acids of this nature. It is to be understood that the term "substantially free of polyvalent inorganic acid ions" when applied to paper is to be understood to mean that polyvalent acid ions are not present in an amount to exert any more substantial effect upon the wet strength than would be obtained by their complete omission.

Roughly the same wet strength is obtained when using the same proportions of melamine-formaldehyde resin in the system under the same conditions, as is described above and illustrated in the graph in the case of melamine-formaldehyde resin.

The wet strengths referred to in this application were determined by means of an Ashcroft tester, the values being in pounds per square inch. In determining these values, the paper was first soaked in water for two hours at 70°F, before being tested.

The invention may be carried out using any customary paper pulp. Although high α-cellulose sulfite pulp was employed in most of the operations described herein, other types of wood pulp or rag stock or recovered waste fiber may be employed as the starting material for making paper in accordance with my invention. The sizing material is usually used in an amount on the order of 1% of the bone dry weight of the pulp although this proportion may be varied as desired. The acid employed to precipitate the sizing is preferably any strong monobasic acid particularly if the acid has no detrimental effect upon the properties of the paper.

As related above, in some cases it may be desirable to employ the aluminum salt of a monobasic acid to acidify the pulp in the beater. For instance, aluminum chloride is eminently suitable for this purpose and eliminates the difficulty of handling large volumes of acid in the paper making operation. Instead of aluminum chloride, aluminum nitrate or acetate may be employed. Sometimes it may be desirable to supplement the salt with an addition of hydrochloric acid to supply the desired degree of acidity.

The following examples illustrate my invention:

**Example 1**

A refined sulfite wood pulp was placed in a hollander or beater to which was added approximately 1% of hydrogenated resin size and approximately 1% of sodium aluminate, the percentages being based upon the bone dry weight of the pulp. The hydrogenated resin size employed was prepared by saponifying hydrogenated resin with approximately ½ its weight of caustic soda. Approximately 5% (based on the bone dry weight of the pulp) of 35% hydrochloric acid was added to the beater, thus precipitating the sizing materials of the pulp. After the beating treatment had been completed and after the pulp had been put through a Jordonation operation but before the paper stock was brought to the paper machine, there was added thereto 1% (based on the weight of the bone dry pulp) of an acid-aged wet strength imparting melamine-formaldehyde resin (No. 607) in solution in hydrochloric acid. The paper stock was then applied to the wire of the paper machine and paper was prepared therefrom and passed through the remainder of the machine in the conventional manner. The paper having a base weight of 20 lbs. per 1000 sq. ft. exhibited a wet strength of 12 lbs. per square inch.

**Example 2**

600 pounds of sulfite pulp in suspension in 1100 gallons of water were mixed in the beater with 10 pounds of sodium stearate, 45 pounds of corn starch and 15 pounds of aluminum chloride, the materials being added to the water in the beater in the order given. After the beating treatment had been completed and the pulp had been put through a Jordonation operation, acid-aged melamine-formaldehyde resin (No. 607) in solution in hydrochloric acid was added to the stock in an amount ½% of the bone dry pulp. The resultant stock was then processed over a paper machine in the conventional manner. The wet strength of this paper was determined by soaking for two hours in water at 70°F, and testing in an Ashcroft tester. The wet strength of the paper was found to be 25 pounds per square inch. The paper processed in an identical manner but using aluminum sulfate to impart acidity in the beater gave a wet strength of approximately 10 pounds per square inch. The papers compared both had a base weight of 52½ pounds per 1000 square feet.

**Example 3**

600 pounds of sulfite pulp in suspension in 1100
gallons of water were mixed in the beater with the following added in the order given:

- 5.6 lbs. of sodium aluminate
- 9.6 lbs. of sodium stearate
- 3.0 lbs. of gelatin
- 45.0 lbs. of cooked corn starch
- 4.5 gallons of hydrochloric acid (24%)

After the beating had been completed and the pulp had been Jordanned, melamine-monomeride-formaldehyde in solution in hydrochloric acid was added to the stock in an amount ½% of the weight of bone dry pulp. A paper sheet was formed therefrom (base weight 20 pounds per 1000 square feet) which exhibited a wet strength of 38 pounds per square inch.

There are, of course, types of paper which do not require sizing and, in fact, in which sizing is not even desired such as, for instance, paper towelling and the like which need to be highly water absorptive but at the same time must maintain high wet strength. My invention is as useful for such un sized papers as it is for photographic paper, for instance, where a sizing is customary. In producing most paper stock, it is desirable to have the furnish on the acid side to prevent foaming et cetera, and it might be thought that one could produce such unsized papers by merely omitting the sizing and by employing the customary aluminum sulfate to obtain the desired acidity. However, I have found that even in the absence of sizing, one does not obtain as high wet strength when employing aluminum sulfate as the acidifier as one obtains by omitting substantially all polyvalent inorganic acid radicals from the furnish and using either hydrochloric acid, nitric acid, or acetic acid as the acidifier in conjunction with the resins which I have above outlined as being wet strength-imparting resins. Thus a water absorptive high wet strength unsized paper can be produced by a furnish make-up consisting of water, suitable paper pulp and a melamine-formaldehyde resin or melamine-monomeride-formaldehyde resin, with a strong monobasic acid such as hydrochloric acid, nitric acid, or acetic acid as the acidifier, all polyvalent inorganic acid ions being substantially absent from the furnish. An example of the preparation of such a furnish is as follows:

**Example 4**

600 pounds of sulfite pulp in suspension in 1100 gallons of water were mixed in the beater with ½% of aqueous hydrochloric acid (24% concentration) reducing the pH of the mass to approximately 4.5. After the beating treatment had been completed and the pulp had been put through a Jordonning operation 3% (based on the bone dry weight of the pulp) of acid-aged melamine-formaldehyde resin (No. 607) in solution in hydrochloric acid was added to the stock. The resultant stock was then processed on the paper machine in the conventional manner to form a paper sheet highly absorbent to water. The paper sheet had a weight of 14 pounds per 1000 square feet and when tested with the Abbe Rood tester exhibited a wet strength of 18 pounds per square inch. Normal paper making pH is ordinarily within the range of 4-6.5 and in order to obtain this pH an acidifying agent is added to the beater. In my invention this acidifying agent is sodium chloride, aluminum nitrate, or aluminum acetate. The pH obtained by this addition is conducive beth to precipitation of the beater sizing and condensation of the resin added to impart higher wet strength in paper making operations. This is true with respect to all of the resins which I have advocated employing herein. The strength of the strong monobasic acid in the furnish is sufficient to give to the furnish a pH of 4 to 6.5.

It is to be understood that the strong monobasic acid desired although usually supplied by direct addition to the pulp mass where acidification is desired, may also be supplied by addition of an acid salt of a strong monobasic acid. This is illustrated by the use of aluminum chloride which supplied both hydrochloric acid and aluminum floc. Other salts of strong monobasic acids which impart a lower pH to the mass such as ammonium chloride, et cetera may be employed for this purpose if desired.

If desired the operator may employ alum for the acidification of the pulp followed by treatment with barium, calcium or strontium chloride to precipitate the sulfate ions and thus assure the absence of sulfate ions in the final product. It is to be observed that such a procedure also comes within the scope of my invention as defined by the appended claims.

I claim:

1. A method of making high wet strength paper which comprises beater sizing paper pulp with an acid precipitable sizing material, adding there to in sufficient amount to precipitate the sizing and impart a pH of 4-6.5 an aluminum material selected from the group consisting of an alkali metal aluminate plus hydrochloric acid, an alkali metal aluminate plus acetic acid, an alkali metal nitrate plus nitrous acid, alimiuim chloride, aluminum nitrate and aluminum acetate, incorporating in the pulp ¼-5%, based on the bone dry weight of the pulp, of a wet strength-imparting resin selected from the group consisting of the melamine-formaldehyde resins and the melamine-monomeride-formaldehyde resins and forming paper therefrom.

2. A method of making high wet strength paper which comprises beater sizing paper pulp with an acid precipitable sizing material, adding there to in sufficient amount to precipitate the sizing and impart a pH of 4-6.5, incorporating in the pulp ¼-5%, based on the bone dry weight of the pulp, of a wet strength-imparting resin selected from the group consisting of the melamine-formaldehyde resins and the melamine-monomeride-formaldehyde resins, and forming paper therefrom.

3. A method of making high wet strength paper which comprises beater sizing paper pulp with an acid precipitable sizing material, adding there to in sufficient amount to precipitate the sizing and impart a pH of 4-6.5, incorporating in the pulp ¼-5%, based on the bone dry weight of the pulp, of a wet strength-imparting resin selected from the group consisting of the melamine-formaldehyde resins and the melamine-monomeride-formaldehyde resins, and forming paper therefrom.

4. A method of making high wet strength paper which comprises beater sizing paper pulp with an acid precipitable sizing material, adding there to in sufficient amount to precipitate the sizing and impart a pH of 4-6.5, following by incorporating in the pulp ¼-1% (based on the bone dry weight of the pulp) of a melamine-formaldehyde wet strength-imparting resin and forming paper from the pulp.

5. A method of making high wet strength paper which comprises beater sizing paper pulp with an
acid precipitable sizing material, adding thereto aluminum chloride in sufficient amount to precipitate the sizing and impart a pH of 4 to 6.5, incorporating in the pulp ½–1% based on the bone-dry weight of the pulp of melamine-formaldehyde wet strength-impacting resin and forming paper therefrom.

FRED W. BOUGHTON.

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