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STARCH-MODIFIED THERMOSETTING MELAMINE FORMALDEHYDE ACID COLLOID AND PAPER HAVING DRY STRENGTH MADE THEREWITH

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ABSTRACT OF THE DISCLOSURE

The invention provides a starch-modified thermosetting melamine-formaldehyde acid colloid. The modified colloid is cationic and water-soluble, and imparts excellent dry strength to paper without imparting more than a negligible amount of wet strength. It is preferably employed as a beater additive but may be applied to preformed paper.

The present invention relates to a modified thermosetting melamine-formaldehyde acid colloid. The invention includes such modified colloid, process for the preparation thereof, paper manufacturing processes which employ the modified colloid, and paper having a content of the modified colloid.

An advance of outstanding importance occurred in the papermaking art when it was discovered that the polymethylol melamines, when allowed to age at an acid pH, polymerize to a colloidal cationic state; that the resulting colloid has a substantive affinity for cellulose fibers in aqueous suspension; and that paper made by a process which included the step of adding an aqueous solution of the colloid to the furnish to the papermaking machine possesses a high degree of wet strength. This wet strength develops while the wet web undergoes normal drying in the process of becoming paper; see U.S. Patents Nos. 2,345,543, 2,559,220 and 2,986,489.

In many instances, it is desirable for paper to possess high dry tensile strength while not possessing more than a negligible amount of wet tensile strength. The principal kinds of paper in which this combination of properties is desirable are book paper, office form paper and shelf paper. It is frequently desired to re-pulp paper of these categories, but this step cannot be performed easily when the paper possesses high wet strength, and a special method employing steam jets is needed, cf. U.S. Pats. Nos. 2,394,273 and 2,423,097.

Paper is deemed to possess high wet strength when, as a practical matter, it cannot be pulped without treatment with special chemicals or with special machinery. As a rule of thumb, at a basis weight of 50 lbs. per 25 x 40 x 500 ream, paper can be pulped readily without need for special treatment when it has wet strength of less than about 3 lbs. per inch, and such paper is generally considered to possess negligible wet strength.

The discovery has now been made that the wet-strength imparting properties of melamine-formaldehyde acid colloid are substantially entirely annulled without significant effect upon the dry-strength imparting properties of the colloid, when the colloid is reacted with a major amount of a water-soluble starch. In preferred instances, the starch-melamine formaldehyde colloid reaction product has caused an increase in dry tensile strength of the paper (as determined by bursting strength) of more than 40%, while the resulting paper has no more than negligible wet strength.

The amount of starch which is needed to effect this surprising transformation is substantial and in general is 5 to 50 times the weight of the melamine-formaldehyde acid colloid. Best results are obtained when the weight of the starch is about 10 to 20 times the weight of the colloid but it is practical to use larger or smaller amounts depending upon the extent to which it is desired to suppress wet strength while still achieving a high degree of dry strength. The reaction product is water-soluble and cationic, and when added to a dilute aqueous suspension of cellulose papermaking fibers is substantially adsorbed by the fibers. The composition develops its dry strengthening properties during the time required for the wet waterlaid web to dry when passed, as is customary, over drums heated by steam at temperatures between 190° F. and 250° F.

The reaction product of the present invention is prepared by mixing an aqueous solution of any water-soluble papermaker's starch with an aqueous solution of a partially polymerized positively charged (i.e., cationic) melamine-formaldehyde acid colloid. Colloidal solutions of this type have long been used as wet strengthening agents by the principal paper mills of the world, and are described in U.S. Pats. Nos. 2,345,543, 2,417,014 and 2,986,489. Typically the solutions are mixed at solids contents of 2%–10% by weight, but this is not critical. The reaction product forms within a few hours at room temperature, and the resulting milky or opalescent solution is then ready for use. The chemical structure of the product has not been ascertained.

The duration of the reaction varies with temperature and pH, and with the ratio of the starch to the melamine, and with the concentration of the reagents in the solution. It can readily be found by determining the wet strengthening efficiency of the reaction mixture from time to time. The reaction is substantially complete when the dry strengthening efficiency of the solution substantially ceases to increase.

The melamine-formaldehyde acid colloid solution may be prepared by any convenient method. One such method is that shown in U.S. Pat. No. 2,345,543 wherein a 12% by weight solution of trimethylol melamine is acidified to pH 3 with hydrochloric acid and the solution is allowed to age at room temperature until a colloidal haze develops. If preferred, the method of U.S. Pat. No. 2,986,489 (which employs excess formaldehyde) may be followed.

The starch solution may be prepared by boiling any of the commercially available papermaking starches (potato starch, corn starch, oxidized starch, etc.) until the granules of the starch have burst, after which the starch may be modified. Thus the invention includes the use of amine-reacted and cyanamide-reacted starches.

The two solutions are mixed so as to provide between about 5 and 50 parts by weight of starch (dry basis) on the weight of melamine colloid present. The solutions may be mixed hot, but if mixed hot, should be used at once. Preferably, they are mixed cold.

The solutions of the reaction product are employed in paper-making by adding the reaction product to the paper machine furnish at any convenient point, for example at the fan pump, or upstream therefrom. Adsorption of the reaction product on the fibers takes place rapidly and retention is excellent.

There does not appear to be a threshold value associated with the use of this reaction product in papermaking, and consequently even very small amounts may be added with some benefit. Moreover, large amounts may be added with increasing benefit, although at a declining rate per unit weight of the reaction product added. The greatest improvements in strength per increment of the reaction product added occurs when the amount thereof is in the range of about 0.2%–2% (dry weight basis).

Amounts in this range are consequently preferred. The optimum economic amount in each instance can be readily

determined by following the methods shown in the examples.

The pH of the furnish may vary from strongly to mildly acidic (i.e., from about pH 3 to about pH 6 or more), so that the process is capable of exerting its improvement under near-neutral conditions.

Frequently, the strengthening effect of the complex is improved when the fibers are pre-treated or mordanted with alum. This treatment is effected by adding alum or its equivalent in amounts from one-third to three times the weight of the complex to the furnish prior to the addition of the complex. When alum is used in this manner the pH of the fibrous suspension both before and after the addition of the melamine-starch reaction product is about 4–5.

The invention will be further illustrated by the examples which follow. These examples are preferred embodiments of the invention and are not to be construed as limitations thereon.

EXAMPLE 1

The following illustrates manufacture of melamine-colloid starch reaction products according to the present invention.

Reaction Product A

To 25 g. of spray-dried trimethylol melamine dissolved in 135 ml. of 0.5 N HCl is added 46.8 g. of 37% aqueous formaldehyde solution. After 8 hours of standing at 25° C. the solution is diluted to 5% solids by addition of water. To 100 cc. of this solution is added at room temperature 1 liter of a 5% by weight solution of pearl corn starch, prepared by boiling 50 g. corn starch in 1000 cc. of water for 10 minutes. This provides 10 parts of starch per part of melamine-formaldehyde colloid.

Reaction Product B

The foregoing is repeated except that 1.5 the amount of corn starch solution is added to the melamine colloid solution so that the starch:melamine colloid ratio is 15:1.

Reaction Product C

The procedure for the preparation of Reaction Product A is repeated except that twice the amount of starch solution is added, so that the starch:melamine colloid ratio is 20:1.

All three are mobile, slightly hazy solutions.

EXAMPLE 2

The following illustrates the manufacture of paper which possesses substantially improved dry strength while possessing substantially no wet strength, according to the present invention.

An aqueous suspension of well-beaten Northern kraft fibers is adjusted to pH 5 and 2% of alum based on the dry weight of the fibers is added with stirring to mordant the fibers.

Aliquots are taken. One is left untreated as primary control. To others is added starch; to still others is added melamine-formaldehyde colloid solution in amounts shown in the table below. To other aliquots are added the amounts of the reaction products A, B and C shown in the table below.

The aliquots are gently stirred to distribute the additives through the fibrous suspension, after which handsheets are formed from the suspension at pH 5 and at 49–51 lbs. basis weight (25"–40"/500 ream). The handsheets are dried for one minute at 240° F. and conditioned at 50% relative humidity and 71° F. for 24 hours, and are then

tested to determine their dry and wet strengths. Results are as follows:

Run No.	Agent added: Desig.	Percent [1]	Composition [2]	Paper: Dry burst [3]	Wet tensile [4]
Controls					
1				20.8	0.8
2		0.5	Starch	23.4	0.8
3		1.0	Starch	26.3	0.9
4		1.5	Starch	24.8	1.0
5		0.05	Melamine colloid	23.3	1.5
6		0.1	Melamine colloid	24.4	1.7
7		0.15	Melamine colloid	24.2	2.1
Examples of invention					
8	C	0.5	Starch-melamine colloid (ratio 20:1).	25.5	1.1
9	C	1.0	Starch-melamine colloid (ratio 20:1).	29.1	1.5
10	C	1.5	Starch-melamine colloid (ratio 20:1).	29.3	1.6
11	B	0.5	Starch-melamine colloid (ratio 15:1).	25.3	1.3
12	B	1.0	Starch-melamine colloid (ratio 15:1).	28.5	1.
13	B	1.5	Starch-melamine colloid (ratio 15:1).	29.0	1.8
14	A	0.5	Starch-melamine colloid (ratio 10:1).	26.9	1.3
15	A	1.0	Starch-melamine colloid (ratio 10:1).	28.0	1.6
16	A	1.5	Starch-melamine colloid (ratio 10:1).	30.3	2.0

[1] Based on dry weight of the fibers.
[2] For description see text above.
[3] Lb./sq-in.
[4] Lb./inch.

We claim:

1. An aqueous acidic colloidal solution of a cationic reaction product of a cationic thermosetting melamine-formaldehyde acid colloid with 5 to 50 times its weight of a water soluble starch.

2. A solution according to claim **1** having a pH in the range of 3–5.

3. A solution according to claim **1** wherein the weight of starch in the reaction product is 10 to 20 times the weight of the melamine-formaldehyde acid colloid therein.

4. Paper of above normal dry strength but of negligible wet strength composed of cellulose fibers bonded together by an adsorbed content of a reaction product according to claim **1.**

5. Paper according to claim **4** wherein the weight of the reaction product is 0.2%–2% of the dry weight of the fibers.

6. Process for the preparation of an aqueous acidic colloidal solution of a cationic reaction product of a cationic thermosetting melamine-formaldehyde acid colloid with 5 to 50 times its weight of a water-soluble starch, which comprises mixing an aqueous solution of a cationic melamine formaldehyde acid colloid with an aqueous solution of a water-soluble starch in proportion to supply between 5 and 50 parts by weight of said starch (dry basis) on the weight of said colloid, and allowing the resulting solution to stand until the dry strengthening efficiency of the solution substantially ceases to increase.

7. A process according to claim **6** wherein the solutions are mixed at solids contents of 2%–10% by weight.

8. A process according to claim **6** wherein the resulting solution is at room temperature when allowed to stand.

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106—213; 127—33; 162—175; 260—15

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Norman Thorndike Woodberry

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

Column 4, line 17 in the Table, last column "1. " should be -- 1.6 --.

Signed and sealed this 9th day of November 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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