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[54] **WATER-SOLUBLE QUATERNIZED MELAMINE-ALDEHYDE RESINS AND THEIR APPLICATION IN THE PAPER INDUSTRY**

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[58] **Field of Search** ....162/164, 166; 260/67.6, 71, 260/17.3 R, 249.6

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[57] **ABSTRACT**

A water-soluble resin is prepared by condensing 1 to 6 moles of an aldehyde compound such as glyoxal with 1 mole of melamine and reacting the resulting product with 0.2 to 0.5 moles of a quaternization agent such as dimethyl sulfate per mole of said melamine.

11 Claims, No Drawings

WATER-SOLUBLE QUATERNIZED MELAMINE-ALDEHYDE RESINS AND THEIR APPLICATION IN THE PAPER INDUSTRY

The present invention relates to water-soluble resins, especially intended to impart good strength to paper in the wet state. The invention also relates to a method of preparation of the said resins and also to a method of manufacture of the paper in which they are employed.

It is known that paper is composed of an assembly of cellulose fibers feebly bound to each other, which results in a low strength of this material, especially in the moist state. The strength of the paper can be increased by various methods which vary from the improvement of refining to the introduction into the paper of natural or synthetic products which increase the adherence of the fibers to each other.

Improvement of the strength of the paper in the moist state has been especially effected up to the present time by the addition to the pulp in the pulping machine of various resins, amongst which the melamine-formaldehyde resins have proved to be particularly effective. These resins, in the state in which they are obtained by condensation of melamine with formaldehyde, are generally insoluble in water, and they are employed either in the form of hydrochlorides dispersable in water or in the form of colloidal aqueous solutions. The strength given by these resins to the moist paper is known as permanent because it is maintained even after prolonged immersion of the paper in water.

For other applications, such as the manufacture of papers for sanitary uses, towels, handkerchieves, napkins, etc., it has been sought to give the paper a so-called temporary strength in the wet state, in the sense that this disappears at the end of a more or less long immersion of the paper in water, which permits easier destruction of the paper after use. The problem of obtaining this strength in the wet state is solved at the present time by the action of glyoxal on the sheet of paper, this dialdehyde giving the paper in fact a good temporary strength in the wet state. Glyoxal is however very soluble in water and does not have any particular affinity for papermaking fibers, so that it is not possible to introduce it into the pulping machine; it is considered sufficient to treat the paper produced in sheet form by glyoxal, which substantially complicates the process of manufacture.

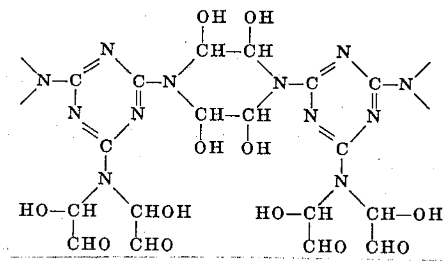
The object of the present invention is to resolve in a satisfactory manner the general problem of the strength of paper in the wet state. The applicants have in fact found that new resins obtained by the condensation of amino-triazines and more particularly of melamine with glyoxal, or with mixtures of glyoxal and formaldehyde, followed by quaternization of the condensation product obtained, resulted, when they were added to the paper pulp in the pulping machine, in an increased strength of the paper sheet in the wet state, and in the maintenance of this improvement in the strength of the paper during a more or less long immersion which can be regulated at will by varying the composition of the resin, and especially, all other things being equal, by modifying the respective proportions of glyoxal and formaldehyde.

The utilization in the paper industry of the resins according to the invention has the following advantages:

- The resin can be obtained in the form of a powder soluble in water which provides convenience of transport and stability during storage;
- The use of the resin is very flexible as a result of the possibility of introducing it into pulps having pH values v varying from 4.5 to 8;
- The resin produces a substantial increase in the strength of the paper in the dry state and an increase in strength in the wet state, this strength having a more or less long duration, depending on the composition of the condensation product of the amino-triazine with glyoxal and formaldehyde.

According to the invention, the condensation products of amino-triazine and more particularly of melamine with glyoxal or glyoxal and formaldehyde are prepared under pH conditions in the vicinity of neutrality, and such resins are generally insoluble or only slightly soluble in water; they are converted to water-soluble products by the action of an appropriate quaternization agent.

The mechanism of the condensation of melamine with glyoxal has not been fully explained; it may however be assumed that the following linkage system is formed to a more or less considerable extent:



containing alternately melamine cycles and piperazine cycles.

When melamine is condensed with glyoxal alone, the molecular proportions of glyoxal with respect to the melamine may vary from 1 to 6. The most condensed and most advantageous products are obtained with a molecular ration of glyoxal to melamine in the vicinity of 4; after quaternization, they give the most viscous solutions. When the molecular ration is lower than 3, the condensation products are difficult to quaternize, and the resins obtained are generally only slightly soluble in water. When the molecular ratio is higher than 4, on the other hand, there are obtained condensation products which are soluble in water but which have very low viscosity after quaternization and which therefore are probably only slightly condensed.

When a part of the glyoxal is replaced, during condensation, by formaldehyde, the proportions possible of the various reactants become very numerous. The most advantageous are between 2 to 4 molecules of glyoxal and 0.5 to 3 molecules of formaldehyde for one molecule of melamine, the preferred ratios being 3 molecules of glyoxal and 1 to 3 molecules of formaldehyde per molecule of melamine.

The condensation of melamine with the aldehydes is carried out in an aqueous solution at a pH value varying from 5 to 8, preferably from 5 to 7, without it being necessary to utilize a buffer mixture in order to stabilize the pH value. The temperature of the condensation is less then 100° C. The products of condensation of melamine and glyoxal or melamine-glyoxal-formaldehyde according to the invention are generally insoluble or only slightly soluble in water and have very little or no affinity for cellulose fibers. The purpose of quaternization is to render them soluble and to give them a greater affinity for the fibers. The condensation products according to the invention cannot be rendered dispersable in water by the addition of hydrochloric acid as is usually done in the case of the melamine-formaldehyde resins applied to the paper industry. There is in fact produced with the resins, according to the invention, an acid hydrolysis which results in a characteristic reduction in the viscosity of the solutions.

According to the invention, the products of condensation of the amino-triazines and more particularly of melamine with glyoxal or glyoxal and formaldehyde, which possess a basic character, are converted to quaternary ammonium salts by the action of a quaternization agent. Dimethyl sulphate is generally employed, but any other quaternization agent may generally be employed, such as the alkyl halides or the esters of aryl-sulphonic acid.

The proportion of dimethyl sulphate may vary from 0.2 to 0.5 mol per molecule of melamine.

Whereas the condensation products of melamine and formaldehyde generally give, after quaternization, products which are insoluble in water, the condensation products, according to the invention, are soluble in water, after quaternization, the presence of glyoxal increasing the solubility of the resins in an unexpected manner.

The quaternized resins of the invention are obtained in the form of yellowish aqueous solutions having a viscosity variable according to the degree of condensation and the degree of ripening or curing. In fact, this viscosity increases with time, but less rapidly than for the melamine-formaldehyde resins, and the resins according to the invention maintain their solubility in water for several months.

The quaternized aqueous resin solutions according to the invention may be evaporated at low temperature in order to give powders which are stable at ordinary temperatures and can be employed by simply dissolving in water, which constitutes an advantage with respect to the melamine-formaldehyde resins usually employed in papermaking which, if they are sold ready for use, have a very limited storage life, while if they are sold in the form of trimethylol-melamine in powder, compel the user to prepare his resin himself and to allow it to ripen.

The resins according to the invention may be introduced into the pulping machine in doses from 1 to 10 percent, preferably from 2 to 4 percent calculated by weight of dry resin with respect to the dry pulp. The resin is absorbed by the fiber, which results in a neutralization of the zeta potential of the fiber. It is not necessary to employ additional adhesion products such as rosin or aluminum sulphate.

After shaping and drying of the paper sheet, there is observed a considerable increase in the dry strength of the paper as compared with a sample sheet which does not contain the resin according to the invention. The strength of the paper in the wet state is also greatly increased, and when the paper is immersed in water, this strength is maintained for a period which increases when a part of the glyoxal is replaced by formaldehyde.

This advantageous property makes it possible to adapt the resin to the application for which it is intended.

The following examples are given by way of illustration and not in any limitative sense. In these examples, the strength of the paper has been determined by measuring the resistance to bursting, following the Müllen method.

The results obtained by carrying out the measurements on dry paper are expressed as a percentage of increase in resistance to bursting as compared with the paper which does not contain resin.

The measurements of resistance to bursting of the wet paper are carried out after 30 seconds and after 30 minutes immersion of the paper in water. The wet resistance is expressed as a percentage of the resistance of the same paper treated and dry, as a percentage of the resistance of the sample paper dry, not containing resin, and also with respect to the wet strength of a specimen paper which does not contain resin.

EXAMPLE 1

50.4 grams of melamine (0.4 mol) are introduced with stirring into 232 grams of an aqueous solution of glyoxal at 40 percent (1.6 mols) and the temperature is brought up to 60° C. The initial pH value is about 5 to 6. After the melamine has dissolved, a gradual thickening of the medium takes place. The mixture is kept at 60° C. for 3 hours.

There is thus obtained a very viscous resin which is insoluble in water by dilution and which jellifies on cooling.

After 3 hours reaction at 60° C. there are gradually introduced at the same temperature and during 1 hour 30 minutes, 25.2 grams of dimethyl sulphate (0.2 mol) and the mixture is again maintained at 60° C. for 1 hour, after which the final concentration is brought to 40 percent by dilution with 115 grams of water.

The resin obtained is of a yellowish fluorescent color, has a viscosity of 250 poises at 25° C. and a pH value of 3.9.

This resin is incorporated in a bisulphite paper pulp having a degree of refining of 30 SR, and a pH value of 4.5, in a proportion of 2 percent. After shaping a sheet of paper and drying for 5 minutes at 90° C., followed by 30 minutes at 100° C., it is found that the resistance to bursting of the dry paper thus obtained and conditioned is increased by 24 percent as compared with a specimen paper which does not contain the resin according to the invention.

After 30 seconds immersion in water, the resistance to bursting is compared, in the first place with the resistance of the same dry treated paper. It is found that it is 25 percent of the resistance of the dry paper. It is then compared with that of a specimen paper which does not contain the resin; the resistance is 31.3 percent of that of the dry specimen paper and equal to 3.5 times the resistance of the specimen paper also immersed for 30 seconds in water. After 30 minutes immersion, the resistance to bursting is 15.5 percent of the same paper treated dry, 20.2 percent of the resistance of the specimen paper dry, and equal to 2.2 times the resistance of the specimen paper immersed for 30 minutes in water.

When the resin is introduced in a proportion of 2 percent into a pulp with a pH value of 8, the following values are obtained under the same conditions:

- Increase in the resistance of the treated dry paper as compared with the resistance of the dry specimen paper: 23 percent.
- After 30 seconds immersion:

resistance as a percentage of the resistance of the same dry treated paper 18 percent
- resistance as a percentage of the resistance of the dry specimen paper 22 percent
- resistance as compared with that of the wet specimen paper 2.4 times

After 30 minutes immersion:
- resistance as a percentage of the resistance of the same dry treated paper 11 percent
- resistance as a percentage of the resistance of the dry specimen paper 13 percent
- resistance as compared with that of the wet specimen paper 1.5 times

EXAMPLE 2

There are mixed in a water bath at 60° C., in the order given and with stirring, 25.2 grams of melamine (0.2 mol), 86 grams of glyoxal at 40 percent (0.6 mol) and 27.2 grams of formaldehyde in an aqueous solution at 44 percent (0.4 mol). The initial dispersion is at a pH value of 4.6; the pH increases gradually to 8 as and when the melamine passes into solution. The medium thickens gradually in a period of 2 hours.

The resin obtained is a gel soluble in its water of formation, insoluble by dilution or cooling.

The preparation is continued by quaternizing the resin in the following manner: 12.6 grams of dimethyl sulphate (0.1 mol) are introduced in 30 minutes at 60°–65° C., after which the stirring is still continued for 30 minutes. The viscosity diminishes during the introduction of the dimethyl sulphate and then increases. The final concentration is brought to 50 percent by diluting with 17.4 grams of water.

The resin obtained is a viscous fluorescent yellow syrup which has a viscosity after 24 hours of 50 poises at 25° C. and a pH value of 4.7.

The viscosity increases up to 20,000 poises after several months, the resin remaining however perfectly soluble in water. The 10 percent aqueous solutions are stable for several weeks at 20° C. By evaporating 50 percent solutions there are obtained powders which are stable and soluble in the cold state.

Incorporation tests of the resin in the paper pulp have also been carried out under the same conditions as in Example 1. The following results have been obtained:

- Increase of resistance to bursting of the treated dry paper with respect to the dry specimen paper S-*s*%/*s*
- Resistance to bursting of the wet-treated paper as a percentage of the resistance of the dry-treated paper H/S%
- Resistance to bursting of the wet-treated paper as a percentage of the resistance of the dry specimen paper H/*s*%
- Factor of resistance to bursting of the wet-treated paper with respect to the resistance of the wet specimen paper H/*s*

	S-s%/s	H/S	H/s%	H/h
pH = 4.5 :				
dry measurements	43%			
After 30 seconds immersion		37.0	54%	5.8 t.
After 30 minutes immersion		32.8% 32.8%	43.5%	4.8 t.

	S-s%/s	H/S	H/s%	H/h
pH = 8 :				
Dry measurements	25%			
After 30 seconds immersion		28.3%	31.0%	4.8 t.
After 30 minutes immersion		23.8%	28.0%	3.1 t.

EXAMPLE 3

There are mixed with stirring at 60°–65° C. and in the order given, 25.2 grams of melamine (0.2 mol), 86 grams of glyoxal at 40 percent (0.6 mol) and 41 grams of formaldehyde in solution at 44 percent (0.6 mol).

The medium thickens rapidly in 3 hours. As previously, the pale yellow resin is insoluble by dilution in water or by cooling.

Quaternization is effected by introducing in 15 minutes at 60°–65 C., 12.6 grams of dimethyl sulphate (0.1 mol). There is a partial fluidification of the medium and then a gradual thickening in 30 minutes. The concentration is brought to 50 percent by the addition of 15.6 grams of water.

There is obtained a viscous yellow syrup with a green fluorescence, very soluble in water. The viscosity is 50 poises after 24 hours at 25° C.

This resin becomes completely jellified after one month at 20° C., but remains entirely soluble in water after several months of storage.

The 10 percent solutions are stable for several weeks at 20° C.

By evaporation of 50 percent solutions at low temperature, there are readily obtained powders which are stable at the ambient temperature and soluble in water.

Incorporation tests of the resin in the paper pulp were carried out under the same conditions as in Example 1. The following results were obtained:

	Percent			
	(S–s)/s	H/S	H/s	H/h
pH=4.5:				
In the dry state	36			
After 30 seconds immersion		39.8	54	5.9 t.
After 30 minutes immersion		32.0	42	4.6 t.
pH=8:				
In the dry state	13			
After 30 seconds immersion		30.8	35.5	3.9 t.
After 30 minutes immersion		27	31.8	3.5 t.

We claim:

1. A water-soluble resin for application in the paper industry, consisting essentially of the condensation product of

melamine and an aldehyde compound, wherein the molecular ratio of the aldehyde compound to the melamine is between 1 and 6, reacted with a quaternization agent selected from the group consisting of dimethyl sulfate, alkyl halide and esters of arylsulfonic acids, in the amount of 0.2 to 0.5 moles of said quaternization agent per mole of said melamine.

2. Resin as claimed in claim 1, in which said aldehyde compound is selected from the group consisting of glyoxal and a mixture of formaldehyde and glyoxal.

3. Resin as claimed in claim 1, in which said quaternization agent is dimethyl sulphate.

4. Resin as claimed in claim 2, in which said quaternization agent is dimethyl sulphate.

5. Resin as claimed in claim 1, in which said ratio is equal to 4.

6. Resin as claimed in claim 2, in which the mixture of glyoxal and formaldehyde, referred to a molecule of the amino-triazine comprises from 2 to 4 molecules of glyoxal and from 0.5 to 3 molecules of formaldehyde.

7. Resin as claimed in claim 6, in which said mixture comprises 3 molecules of glyoxal and from 1 to 3 molecules of formaldehyde.

8. A method of preparation of resins comprising the condensation product of melamine and an aldehyde compound selected from the group consisting of glyoxal and a mixture of formaldehyde and glyoxal, reacted with a quaternization agent selected from the group of dimethyl sulphate, alkyl halide and esters of arylsulfonic acids, comprising the carrying out of the condensation reaction between said melamine and 1 to 6 moles of said aldehyde compound per mole of said melamine in an aqueous medium at a pH value between 5 and 8, at a temperature lower than 100° C. for about 3 hours; the adding of, at the same temperature, said quaternization agent in an amount of from 0.2 to 0.5 moles of said agent per mole of said melamine; the curing of the resultant product and the adjusting of the final concentration by the addition of water.

9. A method for the manufacture of soft paper having good temporary resistance to humidity, comprising

- providing an aqueous slurry of paper pulp having a neutral or slightly alkaline pH up to about 8;
- introducing into said paper pulp in the pulping machine in proportions of about 1 to 10 percent based on the dry weight of the paper pulp of a resin resulting from the condensation of melamine and an aldehyde compound selected from the group consisting of glyoxal and a mixture of formaldehyde and glyoxal, in an amount per mole of melamine of 1 to 6 moles of glyoxal, reacted with 0.2 to 0.5 moles per mole of said melamine of a quaternization agent selected from the group consisting of dimethyl sulphate, alkyl halides and arylsulfonic acid esters; and
- forming the pulp slurry into a sheet of paper and drying the paper thus obtained.

10. A method as claimed in claim 9, in which said proportion is comprised between 2 and 4 percent in dry weight with respect to the dry pulp.

11. Paper obtained by the method as claimed in claim 9.

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