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GLYOXAL TREATMENT OF ABSORBENT PAPER TO IMPROVE WET STRENGTH

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This invention relates to the production of wet-strengthened absorbent products of unwoven, felted cellulose fibers and more particularly to a method of treating an absorbent paper to produce a product having relatively high wet and dry strengths, as well as good moisture absorbing properties and resistance to linting. This application is a continuation-in-part of our prior application Serial No. 561,506, filed November 1, 1944, now abandoned.

One of the principal problems encountered in the manufacture of absorbent papers, such as paper toweling, absorbent tissue, paper diapers and the like, arises out of the fact that such papers when wet normally possess relatively little strength, and hence tear or rupture easily. Numerous efforts have been made to overcome this difficulty and various substances have been proposed for improving the wet strength of absorbent papers, either by incorporation of the substance in the paper stock during its preparation or by its application to preformed sheets. In general, these prior processes have been open to one or more of several objections. Thus in some cases they have excessively decreased the absorbency or adversely affected other desirable properties of the sheet. In other cases they have been excessively expensive. In still other cases the treating agents proposed have been acid media that tended to corrode the paper-making equipment or to decrease the strength of the cellulose fibers or both. In other cases the nature of the wet strengthening process and the reagents used have been such that the resulting product could not be readily disintegrated by alkalis, and thus effective re-use of the "broke" was precluded.

It is accordingly an object of the invention to provide a process for improving the wet strength of an absorbent paper with a minimum decrease in the absorbency thereof. It is a further object of the invention to provide a process of this type which uses reagents that do not adversely effect the paper-making machinery or "tender" the cellulose fibers. It is still another object of the invention to provide a wet-strengthened absorbent paper that is capable of being readily disintegrated by alkalis for re-use in the paper-making process. Other objects of the invention will be in part obvious and in part pointed out hereafter.

We have discovered that the foregoing objects can be achieved by applying to a preformed absorbent sheet of paper an aqueous solution of a solute consisting essentially of glyoxal, and then

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heating the treated sheet to a temperature sufficient to cause the glyoxal to react with the cellulose. We have found that, contrary to certain prior teachings, it is not necessary to utilize a mixture of glyoxal and another reagent capable of reacting with the glyoxal to produce wet strengthening of the paper, but on the contrary that by following the procedure described hereafter, the desired wet strengthening of the paper may be achieved by employing an aqueous solution of glyoxal wherein glyoxal alone is the agent producing wet strength.

The glyoxal used in carrying out the present process may be either the pure compound or the technical grade. However, where the technical grade is used it is commonly quite strongly acid, and hence before a solution of technical grade glyoxal is applied to the paper its acidity is preferably reduced by addition of sufficient alkali to produce an approximately neutral solution. The pH of a solution of technical grade glyoxal may be adjusted with a suitable alkali, such as sodium hydroxide, to a pH between about 4.0 and 8.0.

It has been found to be important that the absorbent paper, after the application of the aqueous glyoxal solution thereto, be heated to a temperature sufficient to cause the glyoxal to react with the cellulose of the paper to produce the desired degree of wet-strengthening. In general, the temperature used in the present process is higher than that used in certain prior processes which depend for their wet strengthening effect upon a reaction between glyoxal and another reagent capable of condensing with the glyoxal to produce a water-resistant condensation product. Thus in the present process the treated paper is preferably heated for a period of time sufficient to reduce the moisture content to say 3% to 7% and to a temperature of not less than about 212 °F. While the upper temperature limit is not particularly critical it should, of course, be below the temperature which produces decomposition or excessive dehydration of the paper. In general, the temperatures ordinarily used at the drying end of a paper-making machine are suitable for use in the present process.

Our experiments indicate that glyoxal is unique in its capacity to increase the wet strength of absorbent papers. The unique and unexpected efficacy of glyoxal for this purpose and the failure of chemically related compounds to give a comparable result under the same conditions, is brought out by the data given in Tables I and II

below. In the experiments which form the basis of Table I, preformed sheets of absorbent paper were immersed in aqueous solutions containing about 1% by weight of the treating agent and were squeezed to remove excess solution, after which they were dried on a drier whose surface temperature was 240° F. In each case the dry and wet strengths of the sheet were determined by the well-known Schopper tensile test. The data given in Table I represent average values obtained by treating several samples with each treating agent.

The data given in Table II were obtained using the same procedure as in Table I, but the paper used in the second set of tests had a greater initial tensile strength and therefore the data of Table I cannot be directly compared with the data of Table II.

Table I

Treating Agent	Dry Tensile Strength, lbs./in.	Wet Tensile Strength, lbs./in.	Ratio: wet dry $\times 100$
Untreated.....	12.9	0.99	7.65
Glyoxalic acid.....	12.6	0.72	5.7
Glycollic acid.....	12.8	0.56	4.4
Glyoxal.....	13.7	2.43	17.7

Table II

Treating Agent	Dry Tensile Strength, lbs./in.	Wet Tensile Strength, lbs./in.	Ratio: wet dry $\times 100$
Untreated.....	19.5	2.2	11.3
Benzil.....	16.0	2.1	13.7
Methylglyoxal.....	17.5	1.7	9.7
Formaldehyde.....	17.9	1.3	7.3
Glyoxal.....	18.1	8.1	44.8

From the foregoing tables it is apparent that such substances as formaldehyde, glyoxalic acid, glycollic acid, methylglyoxal and benzil, when used under the same conditions as glyoxal, either do not increase the ratio of wet strength to dry strength at all or increase it only very slightly, whereas when glyoxal is used the wet strength-dry strength ratio is increased between two- and four-fold. Thus glyoxal is strikingly superior to these other substances in improving the wet strength of absorbent papers.

In order to point out more fully the nature of the present invention, the following specific example is given of an illustrative procedure that may be used in carrying out the invention:

A 45 lb. basis sheet was prepared containing approximately 50% ground wood and 50% unbleached sulphite pulp. The sheet was pressed and dried before application of the treating agent thereto.

After drying, the sheet was completely immersed for approximately 20 seconds in an aqueous solution of a commercial grade of glyoxal containing 1.6 ml. of the glyoxal, 29.1 ml. of 0.05 normal sodium hydroxide, and 69.3 grams of water, the pH of this solution being about 7.5. The sheet appeared to be completely saturated at the end of 20 seconds and was removed from the solution, placed between blotters, and pressed for one minute at 120 lbs. per sq. in. pressure. It was found that this manner of pressing reduced the moisture content of the sheet to about 50%, based on the air-dry weight of the sheet. After the excess solution had been expressed in this manner, the sheet was dried for seven minutes on a drier whose surface temperature was 240° F. When tested by the Schopper tensile test, this sheet

showed a dry tensile strength of 13.7 lbs./in. and a wet strength of 2.49 lbs./in. Thus the ratio of wet strength to dry strength was 18.3 ($.183 \times 100$) which is about two and one-half times as great as the corresponding ratio for this paper when untreated.

It is of course to be understood that the foregoing example is illustrative and that the various operating conditions set forth may be modified within the scope of the invention. For example, the concentration of glyoxal in the treating solution may be varied within relatively wide limits. It has been found that the improvement in wet strength depends primarily upon the amount of glyoxal retained in the paper, rather than upon the concentration of the treating solution. However, there does not appear to be any selective absorption of the glyoxal from the solution, and hence the amount of glyoxal retained in the paper before drying depends upon the amount of solution associated with the paper after it has been pressed or squeezed, and upon the concentration of the glyoxal in the solution associated with the paper after it has been squeezed. In general, a useful degree of improvement in wet strength may be achieved by applying to the sheet a quantity of glyoxal such that between 0.3 and 3.0% of glyoxal, based on the dry weight of the sheet, is retained on the sheet. Within this range, and for relatively constant drying conditions, the improvement in wet strength appears to be an approximately linear function of the amount of glyoxal applied. It has been found that about 10% to 20% of the glyoxal is lost during drying depending on the drying temperature, and hence the amount of glyoxal applied from solution should be somewhat greater than the indicated percentage to provide for retention of 0.3 to 3% on the paper after drying. Quantities of glyoxal less than 0.3% and greater than 3% may be used in particular cases, although where less than 0.3% is used the improvement in wet strength is ordinarily relatively slight, and in cases where more than 3% is used the additional increase in wet strength may not be economically worthwhile.

In cases where the solution is applied by saturating the sheet and then expressing the excess solution, the desired concentration of glyoxal in the sheet may be achieved within limits by varying either the proportion of solution expressed from the sheet, or the concentration of the treating solution, or both. Usually it will be desirable to use a treating solution containing between 0.1% and 5% by weight of glyoxal. It will, of course, be understood that the solution may be applied in other ways than by saturating the sheet, as for example, by spraying a controlled quantity of the solution onto the sheet.

As pointed out above, since in the present process glyoxal is used in the absence of any added reagent capable of condensing therewith, it is important that the treated paper be heated to a temperature sufficient to cause the glyoxal to react with the cellulose of the paper. The drying is preferably effected by heating the sheet to a temperature of 240° F. to 250° F. with a drying period of about 15 to 60 seconds. As indicated above, the treated sheet should be heated to a temperature of at least 212° F., since the improvement in wet strength is significantly greater when such temperatures are used than it is when relatively lower temperatures are used.

The use of glyoxal in accordance with the present process appears to improve the wet strength of papers made from all different types

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of pulps. Our tests have shown significant increases in the wet strength of papers prepared from both bleached and unbleached sulphite and kraft pulps, bleached soda, alpha, and ground wood pulps. The improvement in the wet strength of papers prepared from ground wood pulps is particularly striking.

The effect of the present process upon the absorbency of the treated paper is more favorable than that of certain prior processes. In general, all processes for wet-strengthening paper decrease the absorbency of the paper in some degree. In the case of many of the prior processes, the absorbency of the treated paper continues to decrease as a function of time until at the end of a period of months the absorbency has dropped to the point where the paper is substantially useless for its intended purpose. Where the present process is used, on the other hand, there is an initial relatively small decrease in absorbency during the first week or two after treatment, and thereafter there appears to be no further material decrease in absorbency.

Our tests have further shown that the wet strength of paper treated by the present process improves over a period of time. Also the nature of the treated product is such that it is capable of being disintegrated by strong alkali so that the broke normally accumulating as an incident of the paper-making process can be readily disintegrated and reprocessed.

From the foregoing description it is apparent that the present process is capable of achieving the several objects set forth above. The application to an absorbent paper of a small quantity of an aqueous solution of a solute consisting essentially of glyoxal produces a striking improvement in the wet strength of the paper. The treating solution may be applied in any suitable and convenient manner, such as by dipping the paper in a body of the solution or by spraying the solution onto the paper. Since the solution is approximately neutral, it does not corrode or otherwise damage the paper-making machinery or "tender" the cellulose fibers. The absorbency of the paper is more nearly preserved and the nature of the process is such that any broke that is formed during the paper-making process can be readily and effectively reused.

We claim:

1. The process of producing an absorbent paper having improved wet strength, comprising the steps of; applying to a preformed sheet of absorbent paper an aqueous solution containing glyoxal as its sole essential active ingredient to deposit on said sheet a quantity of glyoxal equal to between 0.3% and 3% by weight of said sheet, and heating said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

2. The process of producing an absorbent paper having improved wet strength, comprising the steps of; applying to a preformed sheet of absorbent paper a treating agent which is an aqueous solution containing glyoxal as its sole essential active ingredient, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

3. The process of producing an absorbent paper having improved wet strength, comprising the steps of; applying to a preformed sheet of absorbent paper an aqueous solution containing glyoxal as its sole essential active ingredient to

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deposit on said sheet a quantity of glyoxal equal to between 0.3% and 3% by weight of said sheet, said solution having a pH of at least 4.0, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

4. The process of producing an absorbent paper having improved wet strength, comprising the steps of; spraying on a preformed sheet of absorbent paper an aqueous solution containing glyoxal as its sole essential active ingredient and having a pH of at least 4.0 to deposit in said sheet a quantity of glyoxal equal to between 0.3 and 3% by weight of said sheet, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

5. The process of producing an absorbent paper having improved wet strength, comprising the steps of; dipping a preformed sheet of absorbent paper into an aqueous solution containing between 0.1% and 5% by weight of glyoxal as its sole essential active ingredient and having a pH of at least 4.0, squeezing excess solution from said sheet, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

6. The process of producing an absorbent paper having improved wet strength, comprising the steps of; applying to a preformed sheet of absorbent paper a treating agent which is an aqueous solution containing glyoxal as its sole essential active ingredient, said solution having a pH between 4.0 and 8.0 and a glyoxal content between 0.1% and 5.0% by weight, and drying said sheet by heating it for between 15 and 60 seconds to a final temperature of about 250° F. to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

7. As a new article of manufacture, a felted sheet of absorbent paper having a high wet strength resulting from the application thereto of a treating agent which is an aqueous solution containing glyoxal as its sole essential active ingredient and having a pH between 4.0 and 8.0 to deposit in said sheet a quantity of glyoxal equal to between 0.3% and 3% by weight of said sheet, and the subsequent drying of said sheet at a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper and thereby produce said improvement in the wet strength of said sheet.

8. The process of producing an absorbent paper having improved wet strength comprising the steps of applying to a preformed sheet of absorbent paper a treating agent which is an aqueous solution containing from 0.1% to 5% by weight of glyoxal as its sole essential active ingredient and having a pH of at least 4.0, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

9. The process of producing an absorbent paper having improved wet strength comprising the steps of applying to a preformed sheet of absorbent paper a treating agent which is an

aqueous solution containing from 0.1% to 5% by weight of glyoxal as its sole essential active ingredient and having a pH between 4.0 and 8.0, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said paper.

10. The process of producing an absorbent paper having improved wet strength comprising the steps of applying to a preformed sheet of absorbent paper a treating agent which is an approximately neutral aqueous solution containing from 0.1% to 5% by weight of glyoxal as its sole active ingredient, and heating said sheet to a temperature between 212° F. and the decomposition temperature of said sheet to cause said glyoxal to react with the cellulose of said paper to improve the wet strength of said sheet.

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