

UNITED STATES PATENT OFFICE

2,683,089

BIBULOUS SHEET

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No Drawing. Application June 10, 1952,
Serial No. 292,720

11 Claims. (Cl. 92—3)

1

2

The present invention relates to the manufacture of bibulous cellulosic paper and tissues and paper of improved adsorbency for water. More particularly, the present invention relates to a process for the manufacture of bibulous paper and tissues of improved water absorbency by a process wherein a substantially non-ionic water-soluble alkylene oxide adduct of a hydroxyalkylamide of a carboxylic acid of 14-22 carbon atoms is added to a stock of cellulosic fibers in aqueous suspension and the suspension is aged until adsorption of the adduct by the fibers is substantially complete. The invention includes the use of these adducts in conjunction with hydrophilic cationic wet strength resins and further includes the formation of bibulous paper and paper tissues from the adduct-treated fibers with or without the wet strength resin.

The manufacture of bibulous papers, particularly papers and tissues such as blotting paper, paper napkins and paper towels is an important and rapidly growing specialty of the paper industry. These papers are characterized by their lack of odor, open texture, and especially by their high absorbency for water. Unsized papers are not acceptable under modern standards for these purposes, as they retain sufficient of the natural resins present in the wood from which they are made to impart a distinct and most disadvantageous degree of water repellency to the fibers, and it is therefore necessary to neutralize this water repellency or "desize" the fibers before they can be formed into paper of satisfactory quality for the uses intended.

In the past, numerous proposals have been advanced for desizing cellulosic papers and tissues. At the present time, it is general commercial practice to defer desizing until the fibers have been formed into a web. The web is desized by sprinkling a dilute solution of appropriate wetting agent thereon, or by passing the web through a bath containing the agent. When the web is dried, the agent is deposited on the fibers, and reduces the surface tension of any water subsequently added, permitting the water to permeate the sheet rapidly by capillary action.

It has also been proposed to apply desizing agents to cellulosic fibers while in aqueous suspension by adding an appropriate surface active agent to the slush stock, and substantively adsorbing the agent on the fibers. Up to the present, the only desizing agents known which are substantively adsorbed by cellulosic fibers while in aqueous suspension are the cationic surface active agents. It has not proved practical to use

these agents as they are prohibitively expensive in cost, not being readily formed from commercially available raw materials. It is a primary object of the present invention to provide a series of agents which are substantively adsorbed by cellulosic fibers in aqueous suspension, which have high desizing effectiveness, and which can be prepared from readily available raw materials by a simple and direct synthesis.

The discovery has now been made that bibulous tissues and paper of the types described can be prepared by forming a stock of cellulosic fibers in the ordinary way, adding to the stock a very small proportion of a water-soluble alkylene oxide adduct of a hydroxyalkyl amide of a carboxylic acid having between about 14 and about 22 carbon atoms, aging the stock for a few minutes until adsorption of the adduct is substantially complete, sheeting the stock at an appropriate basis weight, and drying the water-laid sheet thus formed. As a result of the addition of the adduct, the natural water repellency of the fibers is much reduced and papers of increased absorbency are obtained.

Cellulosic fibers in aqueous suspension are negatively charged, and in the past it has been generally believed that such fibers are substantive only to positively charged or cationic particles. The amide adducts of the present invention, however, are almost if not entirely non-ionic in nature. The reason why these adducts are substantively adsorbed in so rapid a manner by cellulosic fibers is therefore unknown, and I do not wish to be limited to any particular theory.

The further discovery has been made that after adsorption of the adduct by the fibers is complete, the fibers possess substantially unimpaired substantivity for cationic, hydrophilic, wet strength resins. It has been found that after the fibers have been treated with a small proportion of the adduct within the range specified above, and while still in aqueous suspension, they may be treated with a small proportion of a cationic, hydrophilic, wet strength resinous colloid and then sheeted and cured at an elevated temperature in accordance with ordinary practice to develop the properties of the wet strength resin. A paper of substantially the expected wet strength is thereby obtained. This order of addition, it has been found, may be reversed with substantially equivalent results.

Ordinarily, treatment of a fibrous cellulosic stock with a cationic, hydrophilic, wet strength resin results in the formation of a paper sheet of decreased absorptivity, as compared to a simi-

lar paper sheet prepared without the use of such a resin. The power of the amide adducts of the present invention is such that, unexpectedly, this decrease in speed of absorption can be much reduced and in numerous instances more than negated, resulting in the formation of a paper of satisfactory wet strength which is more bibulous than normal paper having substantially no wet strength at all.

It has been found that bibulous papers prepared from unpurified or only partially purified cellulosic stocks slowly decrease in absorbency with the passage of time. Ordinarily this decrease takes place steadily and uniformly and the rate of deterioration remains even after one year. Ultimately, the paper substantially loses its bibulous properties. It has been found, however, that application of the adducts of the present invention markedly reduces this rate of decrease in absorbency markedly, and this beneficial action is noted whether or not a wet strength resin is present. The present invention thus permits the shelf life of bibulous papers to be markedly extended.

The mechanism by which the adducts of the present invention overcome the water repellency of both the natural resins and the added wet strength resins is not understood, and again applicant does not wish to be limited to any particular theory.

The benefits of the present invention are not limited to any one type of cellulosic fibers, and beneficial results are obtained when the adducts of the present invention are added to such comparatively resin-free slush stocks as those made from alpha pulp and from bleached and unbleached northern kraft pulps. Very marked desizing effects have been observed even in the case of papers prepared from pulps predominantly composed of ground wood, and unbleached sulfite and semi-chemical pulps. It has been found that when highly resiniferous ground wood pulp is treated with the adducts of the present invention followed by the addition of a normal amount of a cationic hydrophilic wet strength resin, in certain instances the paper obtained has better water absorbency than paper made from ground wood directly.

Cellulosic papers and tissues prepared by the use of these adducts, in the absence of any wet strength resin, find use as toilet paper, blotting paper, diaper fillers and paper intended for similar applications. Paper produced by the use of these adducts followed by treatment with a wet strength resin find use as paper napkins, paper tablecloths and paper towels.

Adducts suitable for the practice of the present invention may be produced by known means by a variety of processes. Preferably, they will be prepared by a two-step process in which a hydroxyalkyl amide is formed first by the reaction of a hydroxyalkylamine with an appropriate acid, followed by reaction of the amide with an alkylene oxide such as propylene oxide or butylene oxide. Ethylene oxide is preferred. In the first step, the acid is agitated with a slight excess of a primary or secondary hydroxy-alkylamine at about 200° C. until the calculated amount of water has evolved. Any excess or unreacted amine remaining in the reaction mixture is then stripped off. The residue is reacted with the alkylene oxide, preferably ethylene oxide, at about 120° C. in the presence of strong aqueous sodium hydroxide as catalyst, until sufficient alkylene oxide has combined to impart water-solubility. A similar

method is disclosed and claimed in copending application serial No. 177,776 filed on August 4, 1950 by J. J. Carnes et al, now abandoned.

Any fatty acid saturated or unsaturated, containing about 14–22 carbon atoms may be used either in pure form or admixed with similar acids. Acids of this type are represented by such monobasic acids as coconut, palmitic, oleic, and stearic acids, and by abietic acid and resin acids. Since mixtures may be used, both refined and crude tall oil fall in this class, crude tall oil consisting of about 40%–60% of fatty acids, 5%–10% of unsaponifiables, chiefly lignins and sterols, and the balance abietic and other rosin acids. Refined tall oil is crude tall oil from which the unsaponifiables and frequently a part of the abietic and rosin acids have been removed. Since crude tall oil constitutes the most readily available source of fatty acids and yields results substantially equal to the results obtained by the use of the less readily available types of acid mentioned, crude tall oil is the raw material of choice for the practice of the present invention. In general, the preferred acids are those selected from the group of acids consisting of the fatty acids and rosin acids of about 14 to about 22 carbon atoms. In addition, certain of the di- or polybasic acids formed by dimerizing or polymerizing one or more of the unsaturated monobasic acids of the class described have given comparable results. The cost of these acids, however, is prohibitively high, and therefore these acids fall outside the preferred group of acids set forth above.

The hydroxyalkylamines used in the synthesis described above are the short-chain amines having a chain length not in excess of 4 carbon atoms, for example, 4-aminobutanol, 4,4'-iminodibutanol and 2,2'-iminodiethanol. Generally, however, superior results are obtained by the use of the more readily available mono and diethanolamines. By the use of these amines, as described above, suitable substituted amides may readily be prepared from the acids mentioned.

The amount of alkylene oxide reacted should be at least sufficient to form an adduct which is freely soluble in ten times its weight of water at 20° C. forming a clear transparent solution therewith. Ordinarily to secure this result more than about 10 mols of the alkylene oxide must be reacted. When somewhat less than sufficient alkylene oxide is reacted to impart solubility, the adduct is hydrophilic and readily dispersible in water, but appearance of the dispersion is cloudy. When still less alkylene oxide is reacted the adduct is not hydrophilic at all. When a dispersion is formed of the adduct in this non-hydrophilic stage, on standing the particles of adduct coalesce and sink. At the other extreme there appears to be no maximum to the amount of alkylene oxide which may be reacted.

In the case of the mono-amides prepared from crude tall oil, an adduct effecting maximum improvement in absorbency takes place when about 12 mols of the alkylene oxide have been reacted. In the case of amides prepared from stearic acid, peak results are attained by the use of about 16 mols of the oxide. With other amides still larger amounts of the oxide are necessary for optimum results, but in no case has this peak been found to require the use of more than 50 mols of the alkylene oxide.

The adducts prepared as described above may be viscous or waxy solids, and it is advantageous to use them as 5% or even more dilute water solutions thereof to facilitate metering and to

ensure their rapid and uniform distribution through the stock.

A noticeable increase in absorbency results when as little as 0.02% of one of the adducts is added, based on the weight of the dry fibers. The improvement in absorbency continues rapidly through the range of roughly 0.5-1.5%. The addition of further amounts of the adduct cause an additional increase in absorbency, but this generally is less than proportional to the amount of additional amide added. Beyond 2%, the improvement effected is comparatively slight, and the maximum proportion of adduct which can be used to advantage in most instances appears to be about 3%, based on the weight of the fibers.

As a result, it is preferred to add between about 0.05% and 0.2% of the adduct based on the weight of the fibers, this proportion yielding very satisfactory increases in water absorbency while minimizing the consumption of the adduct.

The consistency of the slush stock will be at a normal value between 0.5% and 5% during addition of the amide. Thereafter, the stock is aged. In numerous instances, depending chiefly on the character of the pulp and the adduct, a few seconds are sufficient for this purpose, whereas in other instances, 10-15 minutes should be allowed. For maximum efficiency the aging should be extended until adsorption of the adduct is substantially complete, any unadsorbed adduct being wasted with the white water without benefit to the paper.

The pH of the stock is not critical as adsorption of the adduct takes place with the stock in any normal condition, somewhat better results, however, being obtained with the stock on the acid side. The pH of the stock may be as low as 2 and may be as high as 9 or higher. As a result, the pH of the stock will depend primarily on other considerations such as the character of the stock and its tendency to foam, and the presence or absence of wet strength resins or sensitive fillers or colorants. Thus it is possible to produce an alkaline paper containing an adduct of the present invention and also pH sensitive fillers and colorants. A suitable wet strength resin which yields an alkaline paper is produced by the reaction of ammonia with epichlorohydrin as disclosed and claimed in copending application Serial Number 277,741 filed on March 20, 1952 by J. H. Daniel Jr., et al.

After sheeting, the adduct treated sheets need only be dried, as the adducts of the present invention are not benefited by subjecting them to curing conditions. The waterlaid sheets will therefore ordinarily be dried at about 200° F. as is normal, the duration of the drying depending principally on the basis weight of the sheet. Where, however, a thermosetting wet strength resin has been added, the temperature and duration of the drying should be such as will develop the wet strength properties of the resin. While this varies with the specific wet strength resin employed, good results are generally obtained in the case of ordinary paper when the resin is cured at 200° F. to 260° F. for 1/2 to 3 minutes. In the case of light papers and tissues, the heating time is reduced, decreasing to about 1 second in the case of facial tissues.

The water-absorbency or bibulousness of paper is determined by conditioning the sheet at 73° F. for 24 hours at 50% relative humidity and allowing a 0.03 g. drop of distilled water to fall upon the sheet at that temperature and

humidity. The time required for the drop to be completely absorbed is measured by a stopwatch.

The invention has been fully disclosed above and will be illustrated by the following examples which constitute preferred embodiments thereof, without being limitations thereon. Parts are by weight unless otherwise noted.

Example 1

A towelling stock formed of about 85% ground-wood and about 15% sulfite pulp torn into small pieces was broken up in a British disintegrator at approximately 2.5% consistency for a count of 2,000. This slush stock was then diluted to 0.6% consistency, and its pH adjusted to 5.0. An aliquot was withdrawn from the stock for use as the blank. To the remainder was added 3% of the cationic, hydrophilic melamine formaldehyde acid colloid of Example 1 of U. S. Patent No. 2,345,543 was added, based on the weight of the dry fibers. The resin was prepared by dissolving an ordinarily unpolymerized or partially polymerized but acid-soluble melamine-formaldehyde condensation product in water acidified with sufficient acid other than sulfuric acid to produce a pH of about 0.5-4.0 when measured in a 15% aqueous solution of the melamine-formaldehyde resin, followed by aging to convert the resin into the colloidal cationic condition. The stock after aging was separated into aliquots containing 5 grams of fiber. One was set apart as the control, and to each of the remainder was added a desizing agent, prepared by reacting N-2-hydroxyethylstearamide with ethylene oxide in the molar proportions shown below. Between additions the stock was aged 10 minutes. Hand-sheets were made on the British handsheet machine without recirculation pressed between dry blotters in a Noble-Wood press with two weights on the lever arm, and dried on a Paragon drum drier for 1 revolution at speed 3 with a surface temperature at 110-115° C. The desizing agents were added as 0.1% solutions thereof in water. Demineralized water was used throughout the above steps.

The testing procedure consisted of determination of the basis weight, wet tensile strength and absorbency of the handsheets thus produced. This last property was measured by the time required for a 0.03 g. drop of distilled water to be completely absorbed by a single thickness of the paper. In each instance, 10 such tests per handsheet was run and the results averaged. Results are as follows:

Test	Adduct		Basis Wt. ³	Wet Tensile Strength, Lb./in.	Water Absorb., Sec.
	Combined Ethylene Oxide ¹	Percent Added ²			
1.....		Blank ⁴	50.0	0.4	27
2.....		Control ⁵	51.0	5.2	198
3.....	11	0.1.....	51.4	5.0	62
4.....	11	0.3.....	51.3	4.8	35
5.....	16	0.1.....	50.9	4.8	74
6.....	16	0.3.....	51.1	5.0	50
7.....	48	0.1.....	50.5	5.2	81
8.....	48	0.3.....	50.5	5.2	66

¹ Mols. in combined form.

² Based on dry weight of the fibers.

³ Basis 25X40/500.

⁴ No wet strength resin or desizing adduct added.

⁵ 3.0% wet strength resin added.

Example 2

The procedure of Example 1 was repeated except that a freshly prepared slush stock was used,

7

the amount of adduct added in each instance was 0.1% of the weight of the fibers, and the hand-sheets were pressed between rubber rollers.

In the following tests, the adduct was prepared by reacting N-2-hydroxyethylpalmitamide with ethylene oxide in the same manner as described above.

Test	Adduct Reagents		Basis Wt. ³	Wet Tensile Strength, Lb./in.	Water Absorb., Sec.
	Combined Ethylene Oxide ¹	Percent Added ²			
1	Blank ⁴		48.2	0.4	18
2	Control ⁵		49.0	3.8	66
3	7	0.1	47.6	3.6	31
4	8	0.1	47.3	3.6	41
5	11	0.1	47.2	4.0	33
6	16	0.1	47.1	3.8	35
7	48	0.1	47.6	3.8	43
8	8	0.1	46.3	3.6	33

¹ Mols.

² Based on dry weight of fibers.

³ Basis 25×40/500. Sheets were pressed between rubber rolls.

⁴ No wet strength resin or desizing adduct added.

⁵ 3.0% wet strength resin added.

Example 3

The procedure of Example 1 was repeated except that only 1.0% of the melamine-formaldehyde colloid was added, based on the dry weight of the fibers, and the sheets were pressed in a Noble-Wood press with one weight on the lever arm. In this test the adduct used was the adduct formed by reacting N-2-hydroxyethyl stearamide with 11 mols of ethylene oxide, in the manner described. This adduct was added in the amount of 0.1% based on the weight of the fibers.

Test	Adduct, Percent	Resin, Percent	Basis Wt. ¹	Wet Tensile Strength, Lb./in.	Water Absorb., Sec.
1 ²			45.6	0.4	28
2 ³		1.0	47.1	1.8	54
3	1.0	1.0	46.0	1.6	24

¹ Basis 25×40/500.

² Blank.

³ Control.

Example 4

The procedure of Example 1 was followed except that only 1.0% of the melamine colloid was added, the desizing agent was the adduct formed by the reaction of 1 mol of the monoethanolamide of crude tall oil acids with 12 mols of ethylene oxide, and the pH of the stock was adjusted, subsequent to the addition of the melamine colloid, to the values shown in the table. The amount of desizing agent added was 0.1% of the dry weight of the fibers.

Test	pH of Stock ¹	Agents Added	Basis Wt.	Water Absorb., Sec.
1	5.0	Blank ²	42.9	53
2	7.0	do	43.5	53
3	5.0	Resin only	43.8	86
4	7.0	do	43.8	79
5	5.0	Resin and desizing agent	44.7	71
6	7.0	do	45.2	59

¹ During and after additions of desizing agent.

² No melamine resin or desizing agent.

Example 5

The procedure of Example 1 was repeated using a fresh batch of ground wood stock, with the exceptions that only 1.0% of the melamine resin was added and that the desizing agents

8

used were replaced with tall oil adducts formed by reacting the monoethanolamide of crude tall oil acids (Arizona Crude Tall Oil III) with ethylene oxide in the amounts shown below. The amount of desizing added in each instance was 0.1% of the dry weight of the fibers. Results are as follows:

Test	Combined Ethylene Oxide, Mols	Basis Wt., 25×40/500 lb.	Water Absorbency, Sec.
1	Blank	46.3	55
2	Control	49.7	101
3	8	48.5	89
4	12	48.8	78
5	16	48.2	81
6	20	48.0	81
7	49.7	47.6	84

Example 6

The procedure of Example 5 was repeated, using the same adducts used therein, the amounts of the particular adducts added being varied as shown.

Combined ethylene Oxide, Mols.	Percent Adduct Added	Basis Wt., 25×40/500	Water Absorbency, Sec.
Blank		46.2	80
Control		47.9	96
12	0.02	47.2	76
12	0.05	47.2	68
12	0.10	46.5	66
20	0.30	46.3	58
20	0.02	47.0	78
20	0.05	47.6	77
20	0.10	47.0	79
20	0.30	46.7	68

I claim:

1. As a new and useful composition of matter, a bibulous sheet of feited cellulosic fibers having uniformly adsorbed thereon between about 0.02% and 3.0% of their weight of a water-soluble alkylene oxide adduct of a short chain hydroxyalkylamide of an acid selected from the group of fatty acids and rosin acids of about 14 to 22 carbon atoms and mixtures thereof.

2. A sheet according to claim 1, wherein the short chain hydroxyalkylamide is a hydroxyethyl amide.

3. A sheet according to claim 2, wherein the adduct is an ethylene oxide adduct.

4. A sheet according to claim 3, wherein the mixture of acids is the mixture of acids present in crude tall oil.

5. A sheet according to claim 4, wherein the sheet is predominantly composed of groundwood.

6. As a new and useful composition of matter, a bibulous sheet of cellulosic fibers having uniformly adsorbed thereon between about 0.02% and 3.0% of their weight of a water-soluble alkylene oxide adduct short chain hydroxyalkylamide of an acid selected from the group of fatty acids and rosin acids of about 14 to 22 carbon atoms and mixtures thereof, and between about 0.1% and 4.0% of a cationic hydrophilic colloidal wet strength resin.

7. A sheet according to claim 6, wherein the short chain hydroxyalkylamide is a hydroxyethyl amide.

8. A sheet according to claim 7, wherein the adduct is an ethylene oxide adduct.

9. A sheet according to claim 8, wherein the mixture of acids is the mixture of acids present in crude tall oil.

10. A sheet according to claim 10, wherein the

sheet is predominantly composed of ground-wood.

11. A sheet according to claim 10, wherein the resin is a melamine-formaldehyde resin.

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