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SIZED PAPER

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The present invention relates to paper and other cellulosic webs composed of fibers sized by a uniformly adsorbed content of certain alkanolamine-fatty acid reaction products, and to methods for manufacturing such paper.

The present invention is based upon the concept of contacting papermaking cellulosic fibers while in dilute aqueous suspension with a salt of a high molecular weight composition prepared by reacting a dialkanolamine or trialkanolamine with a long chain fatty acid at at least an esterification temperature, the proportion of fatty acid to the hydroxyl groups of the amine and the extent of the reaction being controlled so that the products, when formed into a salt, are on the borderline between solubility and insolubility. The products formed are sufficiently hydrophilic that when agitated with water they form stable colloidal or semi-colloidal dispersions therein, yet are sufficiently hydrophobic that when present on cellulosic fibers they impart thereto a high degree of water-resistance, thereby acting as sizing agents. A most important feature is that when dispersed in water the salts of the compounds mentioned are cationic and are substantively adsorbed by cellulose fibers. They thus do not require precipitation thereon by the addition of any supplementary material.

A further important feature of the invention is that the sizing agents, when once adsorbed, are not desorbed from the fibers or otherwise rendered ineffective when the fibers either in aqueous dispersion or after formation into a paper sheet, are made alkaline, or exposed to alkaline conditions. As a result, after addition of the sizing agent and its adsorption on the fibers large amounts of calcium carbonate or other alkaline filler may be added so as to raise the pH of the suspension up to about 9, resulting in formation of alkaline paper containing from 2% to 30% of alkaline filler by weight. Moreover, with or without the filler the paper may be employed in contact with such alkaline materials as soap.

Broadly, the paper or other cellulosic webs of the present invention consists essentially of cellulosic fibers sized by a uniformly adsorbed content within the range of about 1% to 4% (based on the weight of the fibers) of a product corresponding to that formed by heating an amine selected from the group consisting of the water-soluble dialkanolamines, the water-soluble trialkanolamines and mixtures thereof with a saturated monocarboxylic fatty acid of 16-20 carbon atoms (at least 1 molecule of fatty acid being supplied for each three hydroxyl groups present in the amine at an esterification temperature up to about 225° C. until reaction of the fatty acid with the alkanolamine is at least about 50% complete.

The foregoing paper is advantageously manufactured by a process which includes the steps of forming a dilute aqueous suspension of papermaking fibers, adding thereto between 1½% to 5% or more (based on the dry weight of the fibers) of the above-described reaction product as a water-dispersible salt in colloidal cationic aqueous dispersion whereby the reaction product in large part is

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substantively adsorbed by the fibers, sheeting the fibers to form paper or other cellulosic web, and heating the web at a temperature between about 200° F. and 260° F. for about ¼ to 5 minutes to dry the same and develop the sizing properties of the reaction product thereon. A large part of the added size is adsorbed, the fibers as sheeted having a content of from about 1% to 4% thereof. During the drying no significant chemical effect takes place and development of water-resistance is believed due to fusion and flow of the reaction product along the fibers, thereby greatly increasing the fiber area protected.

The invention is applicable to any of the common pulps including bleached and unbleached northern and southern kraft pulps, sulfite pulps and soda pulps, and mixtures of the two. General commercial practice is to sheet these pulps at an acid pH and the sizing dispersion may be added without adjusting the pH of such pulps. If desired, however, the size may be added while the pulp has an alkaline pH up to about 9, somewhat better water-resistance however being imparted when the pulp has a pH in the normal range between 4.5 and 6. In the latter event, a still further improvement is obtained when a small amount of alum, from 50% to 150% of the weight of the size, is added subsequent to the addition of the size.

Only a small amount of the reaction product composition is needed to produce effective sizing. A commercially valuable sizing effect has so far always been obtained when the amount added is in the range of about 1½%. However, there is a threshold value below which no sizing takes place. Numerous experiments have shown that this value is about 1% of the size based on the weight of the fibers. The sizing effect rises rapidly as increasing amounts are added, but the sizing imparted per increment of size falls off beyond 4%, although water-repellence continues to increase when as much as 5% or more of the size is added, all percentages being based on the dry weight of the fibers. While the present invention includes the addition of from the threshold value of about 1% to 5% of size, we prefer to have present the intermediate amount of between about 2% to 3½% as in this range the sizing effect imparted per unit weight of size is at the maximum.

More in detail, the sizes are most advantageously prepared by mixing a suitable alkanolamine and fatty acid in desired proportions and heating the two at an esterification temperature up to about 225° C. until reaction of the fatty acid is at least 50% complete. Esterification temperatures are those at which water is evolved by the reaction, but it is probable that a part of the water results from some amide formation. We prefer to employ temperatures between about 175° C. and 200° C., this range providing a product which affords best water-repellence while minimizing formation of the less effective amide material. The course of the reaction may be followed by acid number determinations or by collecting and determining the amount of water evolved. The material assumes value as a paper size when about 50% of the fatty acid has thus reacted, but substantially better results are obtained when 75% of the fatty acid has reacted. Results improve as the reaction continues and we therefore prefer that the fatty acid be at least 90% reacted by way of esterification.

The amount of fatty acid used is of importance. In every case the amount should be at least ⅓ of the amount which is stoichiometrically equivalent to the hydroxyl groups of the alkanolamine, so that there is supplied at least one fatty acid molecule or the equivalent for every three amine hydroxyl groups present. Thus, in the case of diethanolamine at least ⅔ of a mol. of fatty acid should be employed per mol. of the amine, and in the case of triethanolamine at least 1 mol. of the fatty acid. Lower

amounts of fatty acid yield reaction products which are of negligible value as sizing agents for paper. At the other extreme, the amount of fatty acid should not exceed the stoichiometrical equivalent of the hydroxyl groups as when a larger amount is used the products are unduly difficult to disperse in water and therefore are not practical for papermaking purposes, and in practice the convenient maximum from the point of view of dispersibility is about $\frac{1}{10}$ of this value, particularly in the case of tertiary amines. Thus, in the case of a dialkanolamine such as diethanolamine the maximum amount of fatty acid is best limited to about 1.8–2.0 mols and in the case of a trialkanolamine such as triethanolamine to about 2.7 mols.

The results improve as the ratio of fatty acid to the amine hydroxyl groups is increased over the minimum value of 0.33 mentioned above. A sharp improvement results when the amount of fatty acid is 50% of the stoichiometric equivalent of the hydroxyl groups of the alkanolamine, and a plateau is reached when the amount of fatty acid is between about $\frac{2}{3}$ and $\frac{1}{2}$ of the stoichiometric equivalent. Thus, in the case of diethanolamine best results are obtained by the use of between 1.3 and 1.7 mols of fatty acid per mol of the amine, and in the case of triethanolamine between 2.0 and 2.5 mols.

As alkanolamines there may be employed in the practice of the present invention any of the water-soluble short-chain secondary and tertiary alkanolamines, that is, alkanolamines having no chain longer than 6 carbon atoms. Suitable secondary amines include diethanolamine diisopropanolamine, 3,3'-iminobis-1-propanol, 4,4'-iminobis-1-butanol, and 6,6'-iminobis-1-hexanol. Suitable tertiary amines include such N-alkyl dialkanolamines as N-ethyl-diethanolamine, N-propyl-dipropanolamine, and N-methyl-diisopropylamine and trialkanolamines such as triethanolamine, tributanolamine, triisobutanolamine, and trihexanolamine. The monoalkanolamines yield poor sizing results and these are therefore not included within the scope of the present invention. The alkyl or alkanol chains may be of the same or different length and may be branched; moreover, the hydroxyl groups may be primary as in the case of diethanolamine, secondary as in the case of diisopropylamine, or tertiary as in the case of the iminobis-t-butanol. We have found, however, that the reaction of fatty acids with primary hydroxyl groups is more rapid than with secondary or tertiary hydroxyl groups and therefore the former type of compound is preferred.

As fatty acids there may be employed straight chain saturated acids such as hexadecanoic acid and octadecanoic acid and similar but branched acids obtained by petroleum oxidation. It is only necessary for the acid to have a sufficiently long carbon chain to render the ester composition as a whole sufficiently hydrophobic for papermaking purposes, and the invention is not limited to the particular acids mentioned. Unsaturated fatty acids are undesirable but are tolerated in minor amounts.

Neither the particular alkanolamine nor the particular fatty acid is therefore a primary feature of the present invention.

While the fatty acids are preferred, nevertheless esters such as ethyl stearate and acid chlorides such as stearoyl chloride may be used. After reaction similar ester compositions are obtained and correspond to those obtained by the use of free fatty acid, the use of the acid chlorides however rendering subsequent addition of a solubilizing acid unnecessary.

It will be understood that the reaction products described above are generally complex mixtures. In the first place, the invention permits employment of mixed amines and mixed long chain fatty acids, which of itself leads to mixed products. Moreover, fatty acid or fatty acid equivalent reacts according to a normal distribution curve so that on the assumption that only esterification occurs, the product is a mixture of mono and diesters,

where dialkanolamines are employed, and are mono, di and triesters where trialkanolamines are employed. Since not all of the fatty acid need react by way of esterification or amidation, the product may contain a variable amount of the fatty acid salt of the alkanolamine ester. Further, there is evidence that where secondary amines are employed some amide formation may take place resulting in the presence of alkanolamides or alkanolamide esters. As a result, the products are most conveniently described in terms of their preparation.

Where fatty acids or fatty acid esters are employed as raw materials for the reaction, the reaction products are converted before use to water-dispersible condition by addition of a mineral or organic, water-soluble, non-oxidizing acid having a dissociation constant not materially less than that of acetic acid. Suitable acids include hydrochloric acid, hydrobromic acid, nitric acid, formic acid, phosphoric acid, acetic acid, the chloroacetic acids, propionic acid, and glycolic acid. Alternatively, materials such as epichlorohydrin and dimethylsulfate and alkyl halides such as ethyl chloride may be used which form acid or acid equivalent during their reaction with the ester composition. In practice we prefer to use acetic acid or hydrochloric acid, these acids being readily available, non-toxic, and having the particularly desirable property of forming salts of desirably low softening point so that the step of dispersing the salts in water may be performed without need of autoclave equipment. The acid is advantageously stirred into the ester composition while in molten condition and at least sufficient is added to render the composition dispersible upon agitation with hot water. Alternatively, the reaction product in molten form may be slowly poured into rapidly agitated hot water, that is, water having a temperature above the softening point of the reaction product. In the case of acetic acid we add from 1 to 2 mols per nitrogen atom of the alkanolamine and preferably about $1\frac{1}{4}$ to $1\frac{1}{2}$ mols, too little acetic acid causing the sizing results to fall off. In the case of hydrochloric acid only between about $\frac{1}{4}$ and $\frac{3}{4}$ mols is necessary and addition of about $\frac{1}{3}$ of a mol produces a composition of about the best sizing effectiveness. An excess does not inactivate the size. Where fatty acid chlorides are employed, generally no acid need be separately added.

The acids are best added in concentrated form so as to minimize the amount of water introduced, thereby minimizing hydrolysis of the esters.

The process of the present invention does not preclude the addition of the materials customarily added in the course of paper manufacture. Included among these are melamine-aldehyde, urea-aldehyde and other cationic resins to improve wet strength, starch, gums, and partially hydrolyzed polyacrylamides to improve dry strength, and pigments and dyes.

The invention will be more particularly described by the examples which follow. The examples illustrate embodiments of the invention and are not to be construed in limitation thereof.

Example 1

The following illustrates the preparation of various sizes according to the present invention.

The sizes were prepared by charging technical stearic acid and the indicated alkanolamine into a three-necked flask fitted with a mechanical stirrer, nitrogen inlet tube, and thermometer. In each instance 1 mol of the alkanolamine was taken, and the number of mols of stearic acid is shown in the table below. The reaction mixtures were heated to 200° C. in 45–60 minutes and maintained at that temperature at least until the acid number dropped to 15, and generally below 10. Terminal acid numbers are shown in the table. During the reactions, nitrogen gas was passed through the flask to minimize discoloration and to sweep out the water formed.

The products were cooled to about 125° C. and salt-forming material stirred in as shown in the table below.

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The ester salts thus formed were dispersed by slowly pouring the products into rapidly agitated water at 95° C. so as to form dispersions containing 5% solids, which were homogenized hot and then cooled. Details of the method by which the sizes were prepared are shown in the following table.

Size No.	Amine ¹	Fatty Acid Mols ²	F. A. Ratio ³	Hours Reacted	Acid No.	Acid Added	
						Name	Mols ⁴
1.....	TEA	2.5	0.83	5.25	6.9	HCl	0.35
2.....	TEA	2.0	0.67	4.25	2.2	HCl	0.35
3.....	TEA	1.5	0.60	1.25	6.9	HCl	0.25
4.....	TEA	1.5	0.60	1.25	5.9	HAc ⁵	1.0
5.....	TEA	1.5	0.60	1.25	5.9	Me ₂ SO ₄	0.5
6.....	DEA	2.0	1.0	1.5	1.5	HCl	0.25
7.....	DEA	1.5	0.75	1.5	2.5	HAc ⁵	1.0
8.....	DEA	1.0	0.60	1.0	1.1	HAc ⁵	1.0
9.....	TIPA	2.0	0.67	7.5	13.7	HCl	0.5

¹ DEA = diethanolamine; TEA = triethanolamine; TIPA = trisopropanolamine.

² Per mol of amine.

³ Mols fatty acid divided by number of hydroxyl groups of amine.

⁴ Per mol of amine taken.

⁵ HAc = acetic acid.

Example 2

The sizes of Example 1 were diluted to 1.5% solids by addition of water and were evaluated as follows.

A 60%:40% bleached sulfite-soda pulp mixture beaten to a Green freeness of 350 ml. was diluted to a consistency of 0.6% and adjusted to a pH of 4.5. Aliquots were withdrawn and treated with the materials shown in the table, the pH after addition of the material or materials being adjusted to the value shown by the addition of NaOH or HCl as required. The aliquots were gently stirred for five minutes to allow adsorption of the size to take place, after which sheets were formed on a Nash handsheet machine, dried for one minute at 240° F., conditioned at 73° F., and 50% relative humidity for at least 24 hours, and tested for their water and ink resistance by the Currier and BKY methods respectively.

Size No. ¹	Size		Pulp pH ³	Sheet Basis Wt. ⁴	Currier, Sec. ⁵	BKY, Sec.
	Percent Added ²	Percent Alum Added ²				
1.....	3.5	Nil	4.5	43.4	66	>600
2.....	3.5	Nil	4.5	43.4	64	>600
3.....	3.5	Nil	4.5	44.1	29	353
4.....	3.5	Nil	4.5	47.4	140	>600
5.....	5.0	Nil	4.0	44.9	79	>600
6.....	5.0	Nil	4.5	46.8	67	>600
7.....	5.0	Nil	9.0	46.5	90	>600
8.....	3.5	Nil	4.5	43.4	54	>600
9.....	5.0	Nil	4.5	44.0	130	>600
10.....	5.0	3.0	4.5	45.7	145	>600
11.....	5.0	3.0	9.0	44.6	67	>600
12.....	2.0	Nil	4.5	45.1	35	440
13.....	3.5	Nil	4.5	45.5	61	>600

¹ Corresponds to sizes of table of Example 1.

² Based on dry weight of the fibers.

³ After addition of size.

⁴ Lb. per 25" x 40"/500 ream.

⁵ Slack scale.

The results indicate that an effective amount of sizing takes place both when the fibers are formed into paper at alkaline as well as acid pH values. The results with size No. 7 show that the addition of a small amount of alum enhances the sizing effect obtained.

Example 3

The following illustrates a preferred method for manufacturing two typical sizes of the present invention.

Size A.—1 mol of diethanolamine was reacted with 1.5 mols of technical stearic acid and neutralized with 1.25 mols of glacial acetic acid according to Example 1. The molten ester salt was cooled and crushed to about 10

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mesh, and soaked for 6 hours in sufficient cold water to provide a slurry having a solids content of 7%. The slurry was rapidly heated to 95° C. with rapid agitation. The slurry was cooled with continued agitation to room temperature and diluted to 5% solids by addition of water.

Size B.—This size was prepared by reacting 1 mol of triethanolamine with 2.5 mols of technical stearic acid, followed by the addition of 0.35 mol of 37% aqueous HCl, according to the method for the preparation of Size A.

The product was dispersed in water at 95° C. according to the method employed for the preparation of Size A.

When tested, both sizes gave somewhat superior results compared to the corresponding sizes of Example 1.

We claim:

1. Paper composed of cellulosic fibers sized by a uniformly adsorbent content within the range of about 1% to 4%, based on the weight of the fibers, of a product corresponding to that formed by heating 1 mol of an amine selected from the group consisting of the lower water-soluble dialkanolamines, the lower water-soluble trialkanolamines and mixtures thereof with a saturated monocarboxylic fatty acid of 16–20 carbon atoms, the molar equivalence ratio of said fatty acid to the hydroxyl groups of said alkanolamine being between about 0.33 and 1.0, at an esterification temperature up to about 225° C. until reaction of said fatty acid with said alkanolamine is at least about 50% complete.

2. Paper according to claim 1 wherein the weight of the size is between about 2% and 3½% of the weight of the fibers.

3. Paper according to claim 1 having an alkaline pH.

4. Paper composed of cellulosic fibers sized by a uniformly distributed content within the range of about 2% to 3½%, based on the weight of the fibers, of a product corresponding to that formed by heating 1 mol of a dialkanolamine with about 1.3 to 1.8 mols of a saturated monocarboxylic fatty acid of 16–20 carbon atoms at an esterification temperature up to about 225° C. until reaction of the fatty acid is at least 75% complete.

5. Paper according to claim 4 wherein the dialkanolamine and the fatty acid are heated until reaction of the fatty acid is more than 90% complete.

6. Paper according to claim 4 wherein the dialkanolamine is diethanolamine and the fatty acid is stearic acid.

7. Paper composed of cellulosic fibers sized by a uniformly distributed content within the range of about 2% to 3½% based on the weight of the fibers of a product formed by heating 1 mol of a trialkanolamine with about 2.0 to 2.5 mols of a saturated fatty acid of 16–20 carbon atoms at an esterification temperature up to about 225° C. until reaction of the fatty acid is at least 75% complete.

8. Paper according to claim 7, wherein the trialkanolamine and the fatty acid are heated until reaction of the fatty acid is more than 90% complete.

9. Paper according to claim 7, wherein the trialkanolamine is triethanolamine and the fatty acid is stearic acid.

10. Paper according to claim 7, wherein the trialkanolamine is trisopropanolamine and the fatty acid is stearic acid.

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