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PRODUCTION OF SIZED ALKALINE PAPER

Walter F. Reynolds, Jr., Stamford, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to the production of sized paper by applying to the fibers thereof a novel class of sizing agents characterized by their high sizing efficiency and their ability to make sized paper under neutral and alkaline conditions. The invention includes the application of the novel sizing agents to paper, either in the presence or absence of alkaline fillers, as well as the novel papers sized therewith, as will hereinafter be more fully described.

The manufacture of a sized alkaline paper has heretofore presented a definite problem. Ordinary sizes, such as rosin size precipitated on the paper fibers by alum, cannot be applied in the presence of alkalies. Similarly alkaline fillers such as calcium carbonate-type fillers cannot be successfully incorporated into aqueous suspensions of paper pulp to which rosin size and alum have already been applied; when this is attempted the sizing action of the rosin size is lost. The principal difficulty arises from the fact that such alkaline fillers impart a relatively high pH to the paper pulp suspensions, on the order of 9.0, whereas rosin sizing is carried out at pH values between 5 and 6. Similar difficulties are encountered when papers are made alkaline which contain ordinary wax sizes precipitated on the paper pulp by the use of alum. A serious problem in sizing paper containing carbonate fillers is the formation of foam and bubbles when the stock is treated with alum to develop the sizing properties.

The present invention is based on the concept of applying to aqueous paper pulp suspensions a class of compounds containing a long chain aliphatic radical having a sufficiently great chain length to impart the necessary water resistance and ink resistance to cellulosic paper fibers sized therewith, these compounds being higher aliphatic amines condensed with epichlorhydrin in such a manner that the condensation products are water-soluble or water-dispersible but substantive to cellulosic paper fibers in dilute aqueous suspension. In the practice of the present invention aliphatic monoamines having hydrocarbon chain lengths of 16 or more carbon atoms are reacted with epichlorhydrin in a quantity sufficient to form products containing from 1 to 2 mols of epichlorhydrin condensed with each mol of amine.

In practicing the process of my invention a water-soluble or water-dispersible higher aliphatic amine-epichlorhydrin condensation product of the class described is added to a dilute aqueous suspension of cellulosic papermaking fibers in quantities of from about 0.1 to 3–5% by weight under neutral or preferably under acid conditions. After the condensation product has been absorbed by the cellosic fibers the stock suspension is made alkaline, as by the addition of an alkaline filler such as finely divided calcium carbonate, aqueous sodium silicate or the like. The stock is then made into paper by any suitable forming procedure, as on a Fourdrinier machine or on a cylinder machine, and the paper is heated in the usual manner to remove excess moisture. During this heating, which is usually carried out by passing the paper over or between steam-heated drying rolls having temperatures between 200° F. and 300° F. for a time of about 0.5–3 minutes, the sizing properties of the condensation product are developed on the fibers and a well-sized paper is obtained.

My invention presents a number of important advantages both in sized but unfilled paper and in the production of sized paper containing alkaline fillers. Sized papers that are neutral or alkaline in character, instead

of acid, serve a number of important purposes. Thus, bag stock made from kraft fibers develops its greatest mechanical strength under alkaline conditions; this is particularly important in the manufacture of multi-wall paper bags. Sulfite pulp and other pulps are frequently bleached with alkaline bleaching agents, and a paper capable of retaining its water-resistance, ink-resistance, and other properties of a sized paper, after bleaching with alkaline bleaching agents, is of considerable value. The sizing agents of the present invention are particularly well adapted for use in processes wherein the paper is bleached on the papermaking machine, or immediately thereafter, and prior to the complete drying thereof. Papers sized in accordance with the present invention are also well suited for impregnation with commercial sodium silicate solutions, as for example by calender sizing, to provide better strength, printability and grease or oil resistance. Sodium silicate is also used as an adhesive in making boxboard.

Among the alkaline fillers for paper, finely divided calcium carbonate is by far the most widely used. However, other fillers such as Raffold (calcium carbonate-magnesium hydroxide), calcium sulfite, etc. are applied to aqueous paper pulp suspensions under alkaline conditions and present much the same problem. These fillers are usually applied in quantities ranging from 5–50% up to 100% or more of the dry weight of the paper fibers in order to obtain paper containing from 2% to 30% of its weight of filler. It is another important advantage of the process of my invention that the aliphatic amine-epichlorhydrin condensation products enhance the retention of finely divided alkaline fillers by the paper pulp while, in turn, the water resistance and ink resistance imparted to the fibers by the condensation product are not materially decreased by the filler content of the sheet.

Papermaking fibers impregnated or coated with from 0.1% to 1.5% or more of the higher aliphatic amine-epichlorhydrin condensation products can also be further sized with wax sizes, with starch or other amylaceous sizing agents, or with proteins or gums in amounts of from 0.1% to 3% or more prior to forming them into paper. It should be noted, however, that rosin sizes or other forms of abietic acid should not be used along with the condensation products, as they appear to destroy the sizing action. For this reason wax sizes containing rosin soaps as emulsifying agents should not be employed, although other soap-type wax emulsions are suitable.

The higher aliphatic amine-epichlorhydrin condensation products used in practicing the invention are obtained by heating either an aliphatic amine or a salt thereof with a quantity of epichlorhydrin sufficient to form a condensation product containing from 1 to 2 mols of combined epichlorhydrin for each mol of aliphatic amine. When epichlorhydrin and a free higher aliphatic amine are used the proper proportion of reagents to be mixed together is from equimolecular quantities up to slightly more than 2 mols of epichlorhydrin for each mol of amine. When amine salts are used the molar ratio of epichlorhydrin can be considerably higher, extending up to about 3:1. This difference appears to result from the fact that the amine salts do not react with epichlorhydrin as readily or as completely as do the free amines themselves; therefore, a larger proportion of epichlorhydrin may be used. The fact appears to be that no more than 2 mols of epichlorhydrin can be reacted with 1 mol of a higher aliphatic monoamine such as octadecylamine, regardless of the excess of epichlorhydrin in the reaction mixture; the unreacted epichlorhydrin appears to form glycerol dichlorohydrin that does not function as a sizing agent.

In general, therefore, the condensation products suitable for use in practicing the invention are those containing from 1 to 2 mols of epichlorhydrin condensed with 1 mol of higher aliphatic amine or amine mixture having an average molecular weight corresponding to a hydrocarbon chain length of from 16 to 22 carbon atoms. The preferred aliphatic monoamines used are those of about 16–18 carbon atoms, since these are obtainable commercially at reasonably low cost. It will be understood that either alkyl amines (i. e., amines of

saturated character) or alkenylamines (unsaturated amines) may be employed; however, it is preferred that at least 50% of the amine hydrocarbon be fully saturated.

In preparing the condensation products the amine is preferably dissolved in a solvent such as ethanol, propanol, butanol or the like, and the epichlorhydrin is added slowly at temperatures below about 90° C. After all the epichlorhydrin has been added the solution is heated until a water-soluble or water-dispersible condensation product is formed. The solvent can then be removed by distillation at reduced pressure and the sizing agent obtained as a waxy material. In carrying out the condensation, care should be taken to use relatively mild reaction conditions, such as temperatures not substantially higher than 100° C., and to stop the reaction when an initial condensation product has been formed. If the reaction is carried out for too long a time, or if excessively high temperatures are used, there is danger of forming a polymerized condensation product that has greatly reduced efficiency as a sizing agent and that is not readily dispersed in water.

The quantity of condensation product to be employed depends on the type of paper pulp used, on the water resistance and ink resistance desired, and on the heating times and temperatures to be employed in drying the paper. I find that as little as 0.2% to 1% can be employed, based on the dry weight of the paper pulp, when the paper is dried by contact with drying rolls heated to 130–150° C. for 1 minute, or at 115–130° C. for 2 minutes. Larger quantities of the sizing agent, within the range of 1–2% on the dry weight of the paper pulp, will produce good results when heating times and temperatures of 115–130° C. for 0.5–1.5 minutes are employed. Still larger quantities of sizing agents, up to 3% or in extreme cases up to 5%, may be used; however, amounts of more than 3% are seldom advisable. When wax sizes, starches, gums or other materials are employed, they are usually used in quantities of from 0.1% to 0.5% up to about 1% based on the dry weight of the paper. Ordinarily, the optimum quantities of such mixed sizing agents are about 0.5% to 1% of the condensation product along with 0.1% to 0.5% of the wax size or other auxiliary size, based on the weight of the paper.

From the foregoing it will be seen that my invention consists in the production of paper having the novel characteristic of retaining under alkaline conditions its water resistance, ink resistance and other properties of a sized sheet. This is accomplished by impregnating the cellulosic paper fibers, while in dilute aqueous suspension, with a small quantity of the condensation product of from 1 to 2 mols of epichlorhydrin with 1 mol of an aliphatic amine containing at least 16 carbon atoms, forming the treated fibers into paper or other similar water-laid product, and heating the paper while the pH of the stock is 7 or higher, and preferably 7.5–10.0, at temperatures of 100–150° C. or higher and for a time sufficient to dry the paper and develop the sizing properties of the condensation product thereon. The paper stock may also be impregnated with an alkaline sizing material, such as calcium carbonate, prior to the forming step without interfering with the sizing properties of the condensation product. Starches, gums and hydrocarbon wax sizes may also be added.

The invention will be further described by the following specific examples. It should be understood, however, that although these examples may describe certain features of the invention in detail, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

A solution of 103.7 grams (0.371 mol) of "Armeen D," a commercial octadecylamine having a molecular weight of 279,5, in 150 cc. of ethanol was converted into the hydrochloride by adding 13.7 grams (0.371 mol) of concentrated hydrochloric acid. The solution was heated to 70° C. and 68.6 grams (0.742 mol) of epichlorhydrin was added with cooling at the rate of about 5–8 cc. per minute while maintaining the temperature below 70° C. The mixture was then boiled under a reflux condenser for 4 hours, the solvent removed by distillation and the product was stripped under a partial vacuum. The residue was an opaque, dark brown soft wax containing 1.3 mols of combined epichlorhydrin for each mol of amine.

This product was tested as a sizing agent in calcium carbonate-filled paper by the following procedure. A beaten stock composed of 40% sulfite and 60% soda pulp was diluted with demineralized water to 0.6% consistency and separated into a number of portions. To these the higher aliphatic amine-epichlorhydrin condensation product was added. Corn starch and wax size were also added to some of the portions. In the table below the percentages of these sizes are based on the dry weight of the fibers.

A quantity of finely divided calcium carbonate filler equal to the dry weight of the paper fibers was then added and the stock having a pH of 9.0 was made into paper on a Nash laboratory handsheet machine. The handsheets were couched onto blotting paper and dried at the temperature and during the times shown in the table below. The dried sheets were analyzed for calcium carbonate content and tested for sizing (water resistance) by the Currier size tester (slack scale) and for ink resistance on the B. K. Y. tester. The test results, expressed in seconds, are shown in the following table:

Percent Cond. Prod.	Percent Other Size	Percent $CaCO_3$ in Sheet	Dried 1 min. at 130° C.		Dried 2 min. at 130° C.	
			Currier	B. K. Y.	Currier	B. K. Y.
1	None	15.8	8	23	19	300
1	1% Corn Starch	14.7	54	>300	51	300
0.9	do	14.0	33	>300	35	300
0.8	do	14.3	13	35	28	300
0.8	None	13.4	11	12		
1	1% Wax Size	15.5	30	>300	43	300
1	1% Borax-Solubilized Mannogalactan Gum.	26.2	15	>300	29	300
2.5	None	20.7	32	>300		
1.5	do	16.4	23	>300		
Drying Temperature 150° C. for 1 Min.						
0.65	None	13.6	34	>300		
0.85	do	15.7	28	>300		
1	do	16.4	30	>300		

Example 2

A solution of 496 grams (1.84 mols) of octadecylamine in 700 cc. of ethanol was neutralized by adding 155 cc. (1.84 mols) of concentrated hydrochloric acid. It was then heated to 65° C. and 511 grams (5.52 mols) of epichlorhydrin was added during a 50 minute period at the rate of 5–8 cc. per minute. During this addition the reaction mixture was cooled to a maximum temperature of 74° C. Fifteen minutes after the addition was complete the solution was heated to boiling and refluxed 4 hours. After removing volatiles the condensation product was obtained as a light brown clear syrup which cooled to a soft tan paste.

This product was added to samples of an aqueous paper pulp suspension which were then sized by adding 100% of calcium carbonate and made into handsheets. These handsheets were dried and tested in the usual manner with the following results:

Percent Sizing Agent	Percent $CaCO_3$ in sheet	Dried 1 min. at 130° C.		Dried 2 min. at 130° C.	
		Currier	B. K. Y.	Currier	B. K. Y.
1	15.5	20	64	40	>300
2	16.1	27	>300	44	>300

Example 3

A. A condensation product was prepared from octadecylamine and epichlorhydrin in the molar ratio of 1:1.2. This was done by dissolving 146 grams (0.5 mol) of a commercial octadecylamine in 125 cc. of alcohol, heating to 65° C. and adding 55.5 grams (0.6 mol) of epichlorhydrin during 10 minutes, followed by boiling the mixture under a reflux condenser for 4 hours. The solvent was distilled and the residue stripped of volatiles by heating at reduced pressure, whereupon the solid condensation product was obtained as a light tan colored wax.

B. A similar condensation product was prepared by adding the epichlorhydrin to the octadecylamine solution in the molar ratio of 1.4:1. A solution of 146 grams of octadecylamine in 125 cc. of alcohol was used and 64.8 grams (0.7 mol) of epichlorhydrin was added during 15 minutes. The mixture was then refluxed 4 hours and stripped of solvents in the usual manner.

C. Following the same procedure, 146 grams (0.5 mol) of commercial octadecylamine was reacted with 83.2 grams (0.9 mol) of epichlorhydrin to form a condensation product.

D. A solution containing 146 grams (0.5 mol) of commercial octadecylamine in 150 cc. of ethanol was prepared and heated to 65° C. To this solution 92.5 grams (1 mol) of epichlorhydrin was added uniformly during 12 minutes, the temperature being maintained below 75° C. The resulting mixture was boiled 4 hours under a reflux condenser, the solvents removed by distillation at reduced pressure and the residue stripped of volatiles in the usual manner. There was obtained 223.2 grams of octadecylamine-epichlorhydrin condensation product as a light, brittle, tan colored wax.

E. A solution of 292 grams (1 mol) of commercial octadecylamine in 300 cc. of ethanol was prepared and 232 grams (2.5 mols) of epichlorhydrin were added over a 48 minute period. The mixture was refluxed 4 hours and stripped of solvent and volatiles in the usual manner.

These condensation products were dissolved in water and added to aqueous paper pulp suspensions in amounts of 1%, based on the dry weight of the fiber. A quantity of calcium carbonate filler equal to the dry fiber weight was then added and handsheets were made and tested, the procedure being the same as that described in Example 1. The test results were as follows:

Prepn.	Epi:Amine	Percent $CaCO_3$ in Sheet	Dried 1 min. at 130° C.		Dried 2 min. at 130° C.	
			Currier	B. K. Y.	Currier	B. K. Y.
A	1.2:1	10.9	18	28	42	>300
B	1.4:1	11.5	26	72	43	>300
C	1.8:1	14.5	17	23	38	>300
D	2.0:1	14.8	7	12	30	>300

These results show that condensation products of from 1 to 2 mols of epichlorhydrin with 1 mol of a higher aliphatic amine are good sizing agents for paper. It will be noted from Example 2 that good sizing agents can also be prepared using higher molecular ratios of aliphatic amine salts.

Example 4

A solution of 110 grams (0.39 mol) of commercial octadecylamine in 150 cc. of ethanol was prepared and converted into the hydrochloride by adding 33 cc. (0.39 mol) of concentrated hydrochloric acid. The solution was then agitated at 70–78° C. while 109 grams (1.18 mols) of epichlorhydrin were added during 15 minutes. The solution was then refluxed 4 hours and the condensation product recovered as in Example 1.

A furnish consisting of 60% bleached sulfite and 40% bleached soda pulp was suspended in water, beaten to a Green freeness of 475 and divided into portions. To these there was added 1.5% of the above-described condensation product. The pH was then adjusted to 7.0 or to 9.0 by adding aqueous sodium hydroxide after which the consistency was adjusted to 0.6% by adding buffered demineralized water. The stock so prepared was made into handsheets on a Nash laboratory handsheet machine and the sheets were dried for 1 minute at 130° C. on a laboratory drum dryer. Tests for water and ink resistance were then made with the following results:

pH	Currier (slack)	B. K. Y.
7.0	4	10
9.0	32	70

The sizing action of the condensation products in the absence of calcium carbonate or other alkaline fillers is evident. It is clear, however, that this sizing action is most fully developed when the stock is made alkaline after the sizing agents have been added thereto.

Example 5

A beaten 100% unbleached kraft pulp was diluted with water to 0.6% consistency and portions were treated with the condensation product of Example 3–B in amounts varying from 0.25% to 1.5% based on the dry weight of the fiber while other portions remained untreated. In all cases a sufficient quantity of sodium hydroxide solution was then added, after first adding the octadecylamine-epichlorhydrin condensation product, to raise the pH to 9.0.

The treated and untreated pulps were made into handsheets on a Nash laboratory handsheet machine. The handsheets were couched onto blotting paper, pressed between wool felts in a laboratory rotary press and dried on a drum dryer for 1 minute at 115° C. Handsheets were tested for water resistance by the Currier size tester (hard scale) and for ink resistance by the B. K. Y. tester. The results are given in the following table wherein the figures mean seconds of time required to penetrate the paper except where otherwise indicated.

Percent Sizing Agent	Water Resistance	Ink Resistance
None	<2	<5.
0.25	2	5.
0.5	5	150.
0.75	12	270.
1.0	27	over 5 min.
1.5	30	Do.

It is evident from these results that an appreciable degree of sizing is obtained when as little as 0.25% of the higher aliphatic amine-epichlorhydrin condensation product is used, and that quantities of 0.5% to 1.5% may be applied commercially.

Example 6

Handsheets were made by the usual procedure from a beaten 100% unbleached sulfite pulp treated at 0.6% consistency with 1.5%, based on the dry fiber weight, of the condensation product of Example 3–B and made alkaline to a pH of 9.0 by adding NaOH solution. The handsheets were dried on a heated drum for 4 minutes at 115° C.

Portions of these handsheets were subjected to peroxide bleaching by impregnating the sheets with an alkaline aqueous peroxide bleaching solution containing 0.5% hydrogen peroxide and 0.75% trisodium phosphate. A 6% pickup of bleaching solution was realized. The impregnated sheets were dried on a heated drum at 105° C. for 2 minutes. The "brightness" (per cent reflectance at 454 millimicrons) and water resistance were determined for the bleached and unbleached sheets. The Currier size tester (hard scale) was employed for the water resistance size test. The test results are shown in the following table:

Treatment	Brightness	Currier Size Test, Seconds
Peroxide bleached	57.7	69
No bleaching	53.2	87

Under similar circumstances, a rosin sized sheet would lose practically all its water resistance on being subjected to an alkaline bleaching solution.

What I claim is:

1. A method of producing paper sized by an absorbed content of an epichlorohydrin-amine condensation product which comprises preparing a dilute aqueous suspension of cellulosic papermaking fibers, adding thereto a small quantity of a water-soluble initial condensation product of from 1 to 2 mols of epichlorhydrin with 1 mol of an aliphatic amine containing at least 16 carbon atoms, whereby said condensation product is absorbed by said fibers, forming the treated fibers into paper, and heating the paper at a pH higher than 7.0 to dry the same and develop the sizing properties of the condensation product thereon.

2. A method according to claim 1 in which the condensation product is formed by condensing from 1 to 3 mols of epichlorhydrin with 1 mol of aliphatic primary amine of from 16 to 22 carbon atoms.

3. A method according to claim 1 in which the quantity of condensation product added to the papermaking fibers is within the range of from 0.2% to 5%.

4. A method of producing paper sized by an absorbed content of an epichlorohydrin-amine condensation product containing an alkaline filler which comprises preparing a dilute aqueous suspension of collulosic papermaking fibers, adding therto a small quantity of a water-soluble initial condensation product of from 1 to 2 mols of epichlorhydrin with 1 mol of an aliphatic amine containing at least 16 carbon atoms, whereby said condensation product is absorbed by said fibers, mixing a finely divided alkaline filler with the suspension of fibers so treated, forming the resulting furnish into paper and heating the paper at a pH higher than 7 to dry the same and develop the sizing properties of the condensation product thereon.

5. A method according to claim 4 in which the alkaline filler is calcium carbonate.

6. A method according to claim 4 in which the quantity of condensation product added to the papermaking fibers is within the range of from 0.2% to 3%.

7. A method of producing paper sized by an absorbed content of an epichlorohydrin-amine condensation product and containing a member of the group consisting of starches, gums and hydrocarbon waxes which comprises preparing a dilute aqueous suspension of cellulosic papermaking fibers, adding thereto a small quantity of a water-soluble initial condensation product of from 1 to 2 mols of epichlorhydrin with 1 mol of an aliphatic amine containing from 16 to 22 carbon atoms, whereby said condensation product is absorbed by said fibers, adding to the fibers so treated a quantity of an aqueous dispersion of a member of the group consisting of starches, gums and hydrocarbon waxes sufficient to deposit about 0.1% to 3% of the dry fiber weight thereon, forming the resulting furnish into paper and heating the paper at a pH higher than 7 to dry the same and develop the sizing properties of the condensation product thereon.

8. A method according to claim 7 in which the quantity of condensation product added to the cellulosic fibers is within the range of from 0.1% to 1.5%.

9. Paper composed of felted cellulosic fibers sized by an absorbed content of about 0.1% to 5% of their dry weight of a water-soluble initial condensation product of from 1 to 2 mols of epichlorhydrin with 1 mol of an aliphatic amine containing from 16 to 22 carbon atoms and heated at about 100–150° C. for about 0.5 to 3 minutes to develop the sizing properties thereof.

10. Paper as defined in claim 9 carrying about 5–30% of an alkaline filler.

11. Paper as defined in claim 10 in which the alkaline filler is a calcium carbonate filler.

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