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MANUFACTURE OF SIZED PAPER

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The present invention relates to the manufacture of sized paper by use of emulsions of hydrophobic isocyanates. The invention includes the papermaking processes involved and the paper itself.

At the present time the manufacture of paper, paperboard, etc. (hereinafter referred to as "paper") of high lactic acid resistance is an important specialty of the papermaking art. Such paper is used for the wrapping of butter, margarine and cheese, and as containers for liquid milk and buttermilk. Customarily the lactic acid resistance of such paper is determined by the penescope method wherein the paper or paperboard is first painted with methyl orange on one side and, after the methyl orange has dried, the paper is contacted with 20% aqueous lactic acid at 100° F. This lactic acid resistance is taken as the time required for the solution to penetrate the paper and produce five red spots. When tested in this manner, first-quality rosin sized paper resists penetration for 300–400 seconds.

The discovery has now been made that paper of very satisfactory lactic acid resistance is produced by a process which comprises adding a colloidal emulsion of a hydrophobic organic isocyanate directly to a dilute aqueous suspension of papermaking fibers, sheeting the fibers to form a wet web, and heating the sheets for 1 to 3 minutes at 200°–250° F. The sizing is thus in substantial part developed while the paper is on the machine.

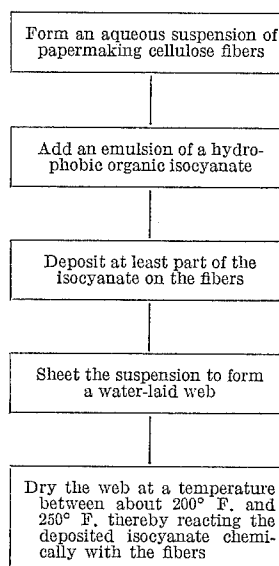
I have further discovered that best results are obtained when the isocyanate is added as an anionic emulsion, and particularly when the isocyanate is deposited on the fibers and the fibers are sheeted in the absence of dissolved polyvalent metal ions.

According to the present invention, a beater pulp of papermaking cellulose fibers is prepared at any convenient consistency, for example, between about 0.5% and 5%. To this is added a small amount of the colloidal isocyanate emulsion more particularly described below. The suspension is agitated gently to distribute the emulsion particles uniformly therethrough.

The aqueous suspension of fibers is then sheeted, preferably at a pH between 4.5 and 6, to form a wet waterlaid web containing emulsified isocyanate droplets, and the web is dried on steam-heated rolls, likewise in accordance with conventional practice. The sizing properties of the isocyanate in substantial part are developed during the drying step, the isocyanate droplets reacting chemically with the cellulose of which the fibers are composed.

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A simplified flow diagram of the process is as follows:



A feature of the invention is that the isocyanate size causes a slight but definite increase in the wet strength of the paper produced. This result is surprising because rosin size, wax size and other sizes commonly used to produce lactic acid resistance impart no such strength and in fact usually have a weakening action.

The paper obtained consists essentially of cellulose fibers having one or more higher alkyl isocyanates uniformly reacted therewith. The paper exhibits very satisfactory resistance to penetration by aqueous lactic acid, ink and water.

As sizing agents good results are obtained with alkyl isocyanates containing at least 10 carbon atoms. The isocyanate grouping is mono-valent and the invention includes the use of di- or poly-isocyanates. Thus the invention includes such isocyanates as 2-ethyldecyl isocyanate, 9-phenylhexadecyl isocyanate, and 6-cyclohexyldodecyl isocyanate. There may be also used poly-isocyanates such as 1,18-octadecyl diisocyanate and 1,12-dodecyl diisocyanate, wherein one long chain alkyl grouping connects two isocyanate radicals and imparts hydrophobic properties to the molecule as a whole. Considerably better results are obtained where the alkyl radicals are straight chain. Accordingly, I prefer to use isocyanates such as decyl isocyanate, hexadecyl isocyanate and octadecyl isocyanate.

The isocyanates used in the process of the present invention are liquid or solids having low melting points and are thus readily emulsified. A suitable procedure comprises slowly pouring the isocyanate into a rapidly agitated volume of water containing an anionic dispersing agent to form a crude or primary emulsion which can then be converted to a colloidal emulsion by known means, for example, by passage through a homogenizer until the dispersed isocyanate particles or droplets (hereinafter for convenience generically referred to as "droplets" have been reduced to substantially colloidal dimensions, so that the emulsion shows substantially no tendency to "cream" on standing. As non-ionic emulsifying agents there may

be used, for example, the condensation products of ethylene oxide with long chain alkyl phenols, the higher fatty amides, or the fatty acid polyhydric alcohol esters; as anionic emulsifying agents there may be used the soaps of fatty acids with alkali hydroxides, the higher alkyl sulfates and sulfonates, and the aryl and alkaryl sulfonates as such or after reaction with formaldehyde. In practice, the non-ionic agents and the polyalkaryl naphthalene sulfonate dispersing agents are preferred as these agents are stable both at acid and alkaline pH values eliminating

at a basis weight of about 50 lbs. and 200 lbs. per 25" x 40"/500 ream. The light sheets are dried for one minute at 240° F. and the heavy sheets for 3 minutes at 240° F.

The handsheets are conditioned for 24 hours at 73° F. and 50% relative humidity. The thick sheets are tested for their water absorption and resistance to penetration by hot 20% aqueous lactic acid solution (penescope method) and the thin sheets for their wet strength and their resistance to penetration by ink. Results are as follows:

Run No.	Octadecyl Isocyanate		pH ²	Lactic Acid Resist., Sec. ³	Ink Resist., Sec. ⁴	H ₂ O Abs., Percent ⁵	Wet Tensile, Lb./in.
	Emul. Type	Percent Alum Added ¹					
Control			4.5	0	0	124.8	0.4
1	Non-ionic	0.75	4.5	0	0	60.3	0.6
2		0.75	4.5	2,400	154	33.8	0.9
3	Anionic	0.35	4.5	>1,000	676	35.5	1.1
4		0.35	4.5	>1,000	318	36.1	1.0
5		0.60	4.5	>1,000	1,340	32.4	1.2
6		0.60	4.5	>1,000	633	33.4	
7		0.60	4.5	550		33.6	

¹ On dry weight of fibers.

² Before sheeting.

³ By penescope.

⁴ Optical.

⁵ Increase in weight after 15 minutes of total immersion.

need for precise pH control. However, the invention does not depend on the particular emulsifying agent selected.

The emulsion is uniformly added to the fibrous suspension at any convenient solids content. I prefer, however, to add the emulsion in dilute free-flowing form, i.e., at a solids content of 5% to 15% by weight, so as to facilitate uniform distribution of the colloidal droplets throughout the suspension.

The invention will be described more particularly by the examples which follow. These examples represent specific embodiments of the invention and are not to be construed as limitations thereon.

Examples 1-7

The following illustrates the results obtained by the process of the present invention of a pulp which is normally very difficult to size. The results are shown in comparison with those obtained in control experiments.

An aqueous suspension of well-beaten bleached 100% hardwood kraft pulp is prepared at 0.6% consistency and is adjusted to a neutral pH. The sizing agent is prepared by rapidly agitating 10 gm. of octadecyl isocyanate with 150 ml. of water and 0.2 gm. of a mixture of sodium diisopropyl naphthalene sulfonate and sodium triisopropyl naphthalene sulfonate to form an anionic emulsion which is homogenized three times in a laboratory homogenizer. A stable colloidal suspension is obtained.

A non-ionic emulsion is prepared in the same manner using a p-nonylphenol-ethylene oxide emulsifying agent in place of the anionic agents shown above.

Aliquots of pulp are withdrawn and treated as shown in the table below, after which the aliquots are gently stirred to distribute the colloidal sizing agent uniformly therethrough. The aliquots are then adjusted to pH 4.5 with hydrochloric acid, sheeted on a Nash handsheet machine, and formed into handsheets in accordance with usual laboratory practice. The handsheets are prepared

The results show that good sizing can be obtained with alum present, but that best results are obtained when the papermaking process is performed by use of an anionic emulsion in the absence of any polyvalent metal salt.

I claim:

1. A method of manufacturing sized paper which comprises forming an aqueous suspension of papermaking cellulose fibers, adding thereto an emulsion of a hydrophobic organic isocyanate, depositing at least part of said isocyanate on said fibers, sheeting the suspension to form a waterlaid web, and drying said web at a temperature between about 200° F.-250° F. whereby said deposited isocyanate chemically reacts with the fibers.

2. A method according to claim 1 wherein the isocyanate is octadecyl isocyanate.

3. A method according to claim 1 wherein the emulsion is anionic and the isocyanate is deposited on the fibers by the action of alum.

4. A method according to claim 1 wherein the emulsion is anionic and the isocyanate is deposited on the fibers and the fibers are sheeted in the absence of dissolved polyvalent metal ions.

5. A method according to claim 1 wherein the fibers are sheeted at a pH between about 4.5 and 6.

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