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SIZED PAPER AND METHOD OF MAKING SAME

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4 Claims. (Cl. 162—158)

This invention relates to improvements in the internal sizing of paper with aqueous ketene dimer emulsions.

It is known that ketene dimers are effective sizing agents for paper. These materials, as such, are insoluble in water and, in order to facilitate their use in the paper industry, they have been mixed with emulsifying agents which make them readily dispersible in water for the formation of aqueous emulsions. These emulsions, however, are usually nonionic and when used for the internal sizing of paper, the retention of the ketene dimer by the cellulose fibers is not complete, with the result that some of the material goes to waste with the discarded white water.

A principal object of the present invention is the provision of a process for the internal sizing of paper with aqueous emulsions of ketene dimers wherein improved retention of the ketene dimer by the paper fibers is obtained with resultant economies in operation.

In accordance with the invention, it has been found that in the internal sizing of paper with ketene dimers wherein an aqueous emulsion of ketene dimer is added to a dilute aqueous pulp suspension and the pulp then sheeted and dried, improved retention of the dimer by the paper fibers may be obtained by incorporating in the aqueous pulp suspension from about 0.001% to about 0.2% by weight, based on the weight of pulp, of polyvinylamine. By virtue of this increased retention, it is possible to obtain a greater degree of sizing with the same amount of ketene dimer added or an equivalent degree of sizing utilizing less of the ketene dimer. Moreover, these results are obtained with a smaller loss of ketene dimer in the discarded white water.

In a preferred procedure for carrying out the invention, the aqueous emulsion of ketene dimer containing the polyvinylamine admixed therewith, is added to an aqueous suspension of cellulosic papermaking fibers, as in the beater of a papermaking system and the pulp then formed into sheets or webs in the conventional manner. Optimum results are obtained if, during sheet formation, the aqueous suspension is maintained at a pH within the range from about 4.5 to about 8 and preferably within the range from about 4.5 to about 5.5.

The polyvinylamine is preferably added to the aqueous emulsion of ketene dimer in the form of an aqueous solution or dispersion and just prior to the introduction of same into the aqueous suspension of papermaking fibers. The addition should, of course, be accompanied with sufficient agitation or stirring to insure thorough admixture of the polyvinylamine solution with the aqueous emulsion.

While it is preferred, as indicated, to add the aqueous emulsion of ketene dimer and polyvinylamine to the aqueous suspension of pulp in admixture with each other, it is also possible to add the two separately. Thus, the polyvinylamine, preferably in the form of an aqueous solution, may be added before, after or along with the aqueous ketene dimer emulsion. As in the case of the preferred procedure, optimum results are obtained if the

pH of the aqueous pulp suspension is maintained within the indicated range.

Some sizing of the paper by the ketene dimer will usually be developed during drying of the paper web in accordance with conventional drying procedures utilized in the art. If desired, the sheet may be cured by heating to a relatively elevated temperature, say about 100° C., for a short period of time such as about 10 or 15 minutes. However, this is not necessary as adequate sizing develops on mere standing or storage at room temperature for a day or two.

Having described the invention generally, the following examples are given in illustration but not in limitation of the invention. All parts and percentage are by weight unless otherwise specified.

EXAMPLES 1–3

A polyvinylamine hydrochloride was prepared by the method set forth by Reynolds and Kenyon, J. Am. Chem. Soc. 69, page 911 (1947). Polyvinylphthalimide was prepared by polymerization of N-vinylphthalimide in water rather than in ethylene dichloride-methanol solution as recommended by Reynolds and Kenyon. The resin hydrochloride contained 15.6% nitrogen as primary amine as determined by the Van Slyke test and 15.6% total nitrogen as determined by the Kjeldahl test, and 39.6% chlorine. A 0.1% solution of a polyvinylamine hydrochloride was made up in distilled water.

Ten parts of alkylketene dimer, prepared from a mixture of approximately equal parts of stearic and oleic acids by forming the acid chlorides thereof and then reacting the acid chlorides with a tertiary amine, were mixed with two parts of G1096 (sorbitol-ethylene oxide condensate esterified with oleic acid), a product of the Atlas Powder Company, the mixture heated to about 130° F., and then poured slowly into 488 parts of water at 130° F. to form an aqueous emulsion.

Three portions of the alkylketene dimer emulsion were mixed with varying amounts of the polyvinylamine hydrochloride solution and each of the three mixtures then added to an unbleached kraft pulp, the proportions of ingredients being such as to provide 0.2% of the ketene dimer based on the pulp and 0.001, 0.003 and 0.005% of polyvinylamine hydrochloride based on the pulp. The unbleached kraft pulp, in each instance, had been beaten to 750 SR freeness and then diluted in the proportioner of a Noble and Wood handsheet machine to a concentration of 0.25%. In each case, the ketene dimer emulsion and the polyvinylamine hydrochloride solution were mixed five minutes before being added to the pulp.

One thousand parts of each of the thus-treated pulps were diluted to 10,000 parts in the deckle box of the handsheet machine and then formed into 8 x 8 handsheets. A series of 12 sheets was made in this manner from each of the treated pulps and with the exception of the first sheet, each successive sheet was diluted with white water drained away from the preceding sheet.

The sheets were dried on a steam roll and then cured at 105° C. for about 15 minutes. Sheets 1, 2, 3, 4, 7 and 12 were tested for sizing by noting the resistance in seconds to Superchrome Ink. The results are set forth in Table 1 below:

Table 1

Example No.	Percent Poly inyl-amine Hydro-chloride	Resistance in Seconds to Superchrome Ink—Sheet No.					
		1	2	3	4	7	12
1	0.001	1	37	63	82	96	136
2	0.003	2	58	77	58	79	145
3	0.005	66	74	78	112	104	122

The sizing results obtained in Examples 1–3 are superior to those which are obtained with sheets similarly prepared and tested but without the addition of polyvinylamine hydrochloride thus indicating a greater degree of retention of the ketene dimer by the cellulose fibers.

EXAMPLES 4–6

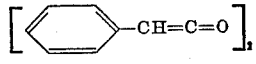
Samples of bleached kraft pulp were treated, formed into sheets and tested as in Examples 1–3 except that the proportions of ketene dimer and polyvinylamine hydrochloride were varied to provide 0.3% of the ketene dimer, based on the pulp, and 0.005, 0.01 and 0.05% of the polyvinylamine hydrochloride based on the pulp. The results are set forth in Table 2 below:

Table 2

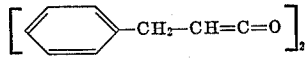
Example No.	Percent Poly inyl-amine Hydro-chloride	Resistance in Seconds to Superchrome Ink—Sheet No.					
		1	2	3	4	7	12
4	0.005	2	7	20	50	205	274
5	0.01	2	26	130	136	300	311
6	0.05	201	230	278	328	410	610

As will be evident, Examples 4–6 show an even greater improvement in sizing, and thus in retention, than Examples 1–3. Optimum improvement is obtained when the amount of polyvinylamine utilized is from about 0.05% to about 0.1% by weight, based on the weight of the pulp and hence this is the preferred range. As previously indicated, however, the amount of polyvinylamine may vary from about 0.001% to about 0.2%.

The ketene dimers which are particularly useful in the process of the present invention are dimers having the formula $[RCH{=}C{=}O]_2$ where R is a hydrocarbon radical, such as alkyl having at least 8 carbon atoms, cycloalkyl having at least 6 carbon atoms, aryl, aralkyl and alkaryl. In naming ketene dimers, the radical "R" is named followed by "ketene dimer." Thus, phenyl ketene dimer is:



benzyl ketene dimer is:



and decyl ketene dimer is: $[C_{10}H_{21}{-}CH{=}C{=}O]_2$. Representative ketene dimers whose emulsions may be used in the process of the instant invention include octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, tetracosyl, phenyl, benzyl, β-naphthyl and cyclohexyl ketene dimers, as well as the ketene dimers prepared from montanic acid, naphthenic acid, $\Delta^{9,10}$-decylenic acid, $\Delta^{9,10}$-dodecylenic acid, palmitoleic acid, oleic acid, ricinoleic acid, petroselinic acid, vaccenic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, parinaric acid, tariric acid, gadoleic acid, arachidonic acid, cetoleic acid, erucic acid and selacholeic acid, as well as ketene dimers prepared from naturally occurring mixtures of fatty acids, such as those mixtures found in coconut oil, babassu oil, palm kernel oil, palm oil, olive oil, peanut oil, rape oil, beef tallow, lard (leaf) and whale blubber. Mixtures of any of the above-named fatty acids with each other may also be used.

Aqueous emulsions of alkylketene dimers suitable for use in the process of the present invention are fully described in U.S. Patent No. 2,627,477 to William Downey. However, particularly preferred are those emulsions which are prepared using a nonionic emulsifier. In addition to the nonionic emulsifiers specifically disclosed by Downey, those nonionic emulsifiers which have been found to be particularly useful include polyoxyethylene sorbitan trioleate, sold by the Atlas Powder Company under the name "Tween 85"; polyoxyethylene sorbitol hexaoleate, sold by the Atlas Powder Company under the trade name "Atox 1086"; polyoxyethylene sorbitol laurate, sold by the Atlas Powder Company under the trade name "Atlox 1045"; and polyoxyethylene sorbitol oleate-laurate, sold by the Atlas Powder Company under the trade name "Atlox 1045."

The aqueous emulsions and/or suspensions are added to the paper pulp in amounts such as to produce a concentration of the ketene dimer in the aqueous pulp suspension of from about 0.01% to about 1% by weight based on the weight of dry pulp. The preferred concentration of ketene dimer is from about 0.1% to about 0.5% by weight based on the weight of dry pulp.

The polyvinylamine contemplated for use herein should have a molecular weight of at least about 10,000. Chemically pure polyvinylamine is difficult to produce and is not necessary for the efficient realization of the process. Thus, this process includes not only pure polyvinylamine but also the various impure polyvinylamines produced by the hydrolysis of polymeric N-vinylimides of dicarboxylic acids so long as the polyvinylamine contains at least 40% of the nitrogen present as primary amino groups as indicated by the Van Slyke test. The production of such impure polyvinylamines by the hydrolysis of N-vinylimides of dicarboxylic acids is shown, for instance, by Hanford and Stevenson in U.S. 2,365,340 wherein they are designated by them as polymeric solvolytic products of N-vinylimides of organic dicarboxylic acids. Other processes for the hydrolysis of polymeric N-vinylimides of dicarboxylic acids which may be used to obtain impure polyvinylamines having the required amount of primary amino groups include hydrolysis with aqueous ammonia, a combination of aqueous alkali and acid, and so on. The term "polyvinylamine" as used herein includes, then, both chemically pure polyvinylamine and the various impure polyvinylamines which contain at least 40% of the nitrogen present as primary amino groups.

In utilizing the polyvinylamine in the process of the present invention, it is desirable to first dissolve it in water to form an aqueous solution and then add the desired amount of this solution to the aqueous ketene dimer emulsions or to the aqueous suspension of paper pulp, depending on the particular procedure being used. The amount of polyvinylamine utilized will vary depending on a number of factors but, in general, will be from about 0.001% to about 0.2%, and preferably from about 0.05% to about 0.1%, based on the pulp.

For convenience, the polyvinylamine in the foregoing examples was added as the hydrochloride. However, it may be added as the free amine, inorganic salt, or organic salt as availability and economic convenience dictate.

It will thus be seen that the present invention provides an improved process for the internal sizing of paper with aqueous emulsions of ketene dimers. While a preferred embodiment of the invention has been disclosed, the invention is not to be construed as limited by the specific details described except as they may be included in the following claims.

What I claim and desire to protect by Letters Patent is:

1. The process of sizing paper which comprises forming an aqueous suspension of paper pulp, admixing with the aqueous suspension of paper pulp an aqueous ketene dimer emulsion and polyvinylamine, the aqueous ketene dimer emulsion being added in an amount such that the concentration of ketene dimer in the aqueous suspension of paper pulp is from about 0.01% to about 1% by weight, based on the weight of dry pulp, the polyvinylamine being added in an amount such that the concentration thereof in the aqueous suspension of paper pulp is from about 0.001% to about 0.2%, based on the weight of dry pulp, and then forming the thus treated paper pulp into sheets.

2. The process of claim 1 wherein the ketene dimer

has the formula $[RCH=C=O]_2$ where R is a hydrocarbon radical selected from the group consisting of alkyl groups having at least 8 carbon atoms, cycloalkyl having at least 6 carbon atoms, aryl, aralkyl and alkaryl groups.

3. The process of sizing paper which comprises forming an aqueous suspension of paper pulp, admixing with the aqueous suspension of paper pulp a sufficient amount of an aqueous alkylketene dimer emulsion to supply from about 0.01% to about 1% alkylketene dimer based on the weight of dry pulp, said aqueous alkylketene dimer emulsion containing from about 0.001% to about 0.2% of polyvinylamine based on the weight of dry pulp, and then forming the thus-treated paper pulp into sheets.

4. Paper sized with from about 0.01% to about 1% of ketene dimer and from about 0.001% to about 0.2% of polyvinylamine, said ketene dimer having the formula $[RCH=C=O]_2$ where R is a hydrocarbon radical selected from the group consisting of alkyl groups having at least 8 carbon atoms, cycloalkyl groups having at least 6 carbon atoms, aryl, aralkyl and alkaryl groups.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,961,366 November 22, 1960

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, Table 1, second column thereof, in the heading, line 2, for "Poly inyl-" read -- Polyvinyl- --; column 4, line 2, for '"Atox 1086"' read -- "Atlox 1086" --; line 6, for '"Atlox 1045"' read -- "Atlox 1045A" --.

Signed and sealed this 25th day of April 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents