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BEATER SIZING OF PAPER WITH KETENE DIMERS

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8 Claims. (Cl. 92—21)

This invention relates to a process of beater sizing paper with higher organic ketene dimers.

In the sizing of paper it is conventional to add a sizing agent, such as, usually, rosin size, and, occasionally, wax, asphaltic material, or the like to the pulp slurry before the sheet is formed. These sizing materials are precipitated on the pulp by the addition of papermaker's alum which is added to the pulp slurry to bring the pH to 4 to 4.5. This is termed the beater sizing process. The bulk of sized paper prepared in this country is beater sized. A much smaller amount of paper is sized by applying a sizing agent to the surface of the paper sheet.

Recently, in U. S. Patent 2,627,477 to William Downey, it is disclosed that ketene dimer emulsions are useful in the surface sizing of paper. The emulsions are not substantive to the cellulose fibers so that heretofore it has not been practical to use these emulsions in beater sizing.

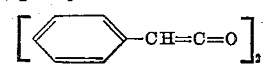
There has now been discovered a practicable process whereby aqueous emulsions of ketene dimers, as described in the said patent to Downey, may be used in a beater sizing process. In this process ketene dimer emulsions are added to the beater at a concentration of from about 5 parts of ketene dimer per million parts of water to about 200 parts of ketene dimer per million parts of water, and the pH of the pulp slurry is adjusted to within the range of 5 to 9, inclusive. The pulp is then formed into a sheet and dried. 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 minutes. However, this is not necessary as adequate sizing develops on mere standing at room temperature for a few hours. Furthermore, if the sheet is prepared at a relatively high pH, such as about 8.5 or higher, a sheet will be sized as it comes off the machine so that additional curing is not needed.

This process has several advantages. Thus, it has been found that even though the emulsions are not naturally substantive to cellulose they are retained by the cellulose fibers in much greater amounts than their concentration in the water would indicate. Further, at the low concentrations used in the process of the instant invention, the amounts lost in the discarded white water are very small. While the ketene dimer emulsions can be used at the pH's normally used in paper manufacture, it has been found that the use of the critical pH range reduces almost in half the amount of ketene dimer needed to obtain a given degree of sizing.

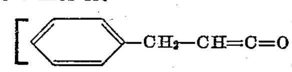
The aqueous emulsions when used in this process are stable over the entire pH range of the process and are even stable when subjected to the vigorous mechanical action found in the beater. The discovery that the ketene dimer emulsions are stable under these extreme conditions is truly unusual and surprising. Further, the process of the instant invention obviates the necessity of using alum to fix the size on the paper fibers. The aqueous emulsions of ketene dimers do not cause foam in the papermaking system, thereby permitting faster machine speeds in those systems where foam is the limiting factor. The process of the instant invention, in permitting the

use of slightly acid and alkaline pH's in the paper system, gives greatly improved initial strength to the sheet as well as improved permanence.

The ketene dimers which are used in the instant process 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. Thus, a mixture of stearic and oleic acids gives a ketene dimer which is very easily emulsified. A mixture which is particularly preferred is the mixed tetradecyl-, hexadecyl ketene dimer prepared from a mixture of stearic acid and palmitic acid, particularly a mixture of these two acids in approximately equal proportions. The emulsions used in this process are prepared as set forth in the said patent to William Downey.

When there is 0.1% hexadecyl ketene dimer in the paper, based on the dry weight of the paper, only one hydroxyl group in about every nine thousand present in the cellulose is reacted with the ketene dimer. No method is known by which such minuscule amounts of ketene dimer can be determined quantitatively in the presence of such a large amount of cellulose. Accordingly, the amount of ketene dimer on the paper was determined mathematically in Examples 1–11. This method is as follows: The conditions of preparation are kept constant. Thus, a Noble and Wood handsheet machine is used. A given amount of water was added to the deckle box and to this was added a given amount of ketene dimer emulsion. Wet 2:1 water to pulp sheets were added to the deckle box and the squeezings from the squeeze rolls were caught and poured back to the deckle box to keep the amount of water constant. The percent of the ketene dimer present in the water which is abstracted by the pulp in the formation of a paper sheet will be fairly uniform. However, as the amount present in the water decreases as more sheets are formed, the amount actually on the sheet will decrease. Thus, for instance, assume that the diluted paper pulp is treated with X grams of ketene dimer, and assume further that the amount of ketene dimer retained on each sheet formed is Y% of that present in the water, then the first sheet prepared will contain X times Y grams of ketene dimer, the second sheet will contain (X—XY)Y grams of ketene dimer, etc. This being a simple geometric progression, the number of grams of dimer on the n^{th} sheet X_n is given by $X_n = X_0Y(1-Y)^{n-1}$ where X_0 is the number of grams of dimer originally added to the pulp.

A given number of sheets are prepared in this manner, say, 100, and numbered consecutively in the order of preparation. These sheets are then tested for sizing as described in the above examples. As the amount of ketene dimer actually present on the sheet is continually decreasing, there will be a point after which the sizing will be very poor. Let us say that this occurs after thirty sheets have been prepared. Now the system is cleaned out and treated with a different amount of ketene dimer, say, 2X grams. Again, a series of handsheets are prepared, say, one hundred, numbered consecutively in the order of preparation and tested for sizing. Let us assume that the fifty-first sheet is the first one that shows a poor degree of sizing corresponding to the thirty-first sheet prepared from the system which was originally treated with X grams of ketene dimer. Knowing X, it is now possible by simple mathematics to compute what fraction would have to be abstracted in the formation of each sheet (that is, Y) in order for the thirty-first sheet and fifty-first sheet of the above runs to show the same degree of sizing. Knowing this percent, it is then possible to compute the amount of ketene dimer actually present on any particular sheet.

The following examples are presented in illustration but not in limitation of the invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLES 1 THROUGH 5

An emulsion was prepared by melting 100 parts of hexadecyl ketene dimer and adding thereto 10 parts of methyl oleate and 30 parts of polyoxyethylene sorbitol laurate sold by Atlas Powder Company under the trade name of "Atlox 1045." To the solution thus prepared was added water at a temperature of 70° C. First, a water-in-oil emulsion was formed, but as the amount of water increased, the emulsion inverted to form an oil-in-water emulsion.

A lightly beaten unbleached kraft pulp was diluted with water so that its concentration was 2.5 parts of pulp per 10,000 parts of water. To this was then added enough of the ketene dimer emulsion prepared above to give the concentration of ketene dimer indicated in Table I. The pulp was then made into handsheets on a Noble and Wood handsheet machine and dried on a steam roll. The sheets were then cured at 105° C. for about 10 minutes. The pH of the pulp slurry was varied by adding varying amounts of hydrochloric acid or sodium hydroxide, depending on the pH desired. This was done prior to addition of the ketene dimer.

The sizing on the sheets was tested by dipping a strip of paper in a solution of blue-black ink for 15 seconds, then washing the strip in running water, and air-drying the strip. The color on the strip then denoted the degree of sizing, an even light-blue color denoting excellent sizing, the color becoming darker as the sizing became poorer. The amount of ketene dimer on the sheet necessary to give good sizing as determined by this test was then determined for a series of pH's. The results are set forth in Table I.

Table I

Example No.	pH	Percent of Ketene Dimer in Paper Based on the Dry Weight of Paper	Initial Ketene Dimer Concentration (Parts Per Million Parts of Water)
1	4	0.136	20
2	5	0.078	10
3	7	0.072	10
4	9	0.081	11
5	10	0.164	35

Thus, within the pH range of 5 to 9 only about half as much ketene dimer is needed to obtain good sizing as is necessary at a pH of 4 or 10.

EXAMPLES 6 THROUGH 11

An aqueous emulsion of hexadecyl ketene dimer was prepared as in Examples 1 through 5. A series of different types of pulps were then made into handsheets as set forth in Examples 1 through 5 with the exception that the pH in these examples was held at 7. In each example the initial concentration of ketene dimer was 10 parts of dimer per million parts of water. The amount of ketene dimer on the sheet necessary to give good sizing was determined for the various pulps as set forth in Examples 1 through 5. The nature of the pulp and the amount of dimer needed for good sizing are set forth in Table II.

Table II

Example No.	Nature of Pulp	Percent of Ketene Dimer in Paper Based on the Dry Weight of the Pulp
6	Unbleached kraft	0.042
7	Bleached kraft	0.060
8	Semikraft	0.060
9	Bleached sulfite	0.092
10	80% Ground wood 20% Bleached sulfite	0.162
11	80% Ground wood 20% Bleached kraft	0.135

Thus, it may be seen that aqueous emulsions of ketene dimers may be used to size a wide variety of pulps. The minimum amount needed to size a particular pulp varies with the nature of the pulp as may be seen from the above data.

The effectiveness of any particular emulsion of a given ketene dimer with a given emulsifier depends on the mechanical treatment of the emulsion, the temperature of preparation, etc. Hence, if portions of the same emulsion are used in a series of experiments, the results will generally be comparable. Thus, only one emulsion was used for the different runs constituting Examples 1 through 5, and another emulsion was used for the different runs constituting Examples 6 through 11. Therefore, the results within each table are fully comparable to other results within the same table but are only qualitatively comparable to results in any other table.

While emulsions can vary in quality, which affects their efficiency, solutions are not subject to these variations and for theoretical purposes may be considered to represent monomolecular emulsions or dispersions so that data obtained when sizing with solutions in general represent the optimum sizing for the concentration of ketene dimer specified for the particular pulp used at the pH specified. Due to this freedom from internal variations which emulsions are inherently subject to, results obtained with one solution are fully comparable to results obtained with other solutions, other factors being equal. In order to clearly show the difference and effect of various types of ketene dimers, solutions were used in obtaining the results below.

EXAMPLES 12 THROUGH 28

Handsheets were prepared as set forth in Examples 1 through 5 with the exception that no sizing was added to the pulp slurry. The pulp was unbleached kraft and the pH of the pulp slurry was 9.0. After the handsheets had been dried, the appropriate ketene dimer was applied by dipping the sheet for one minute in a xylene solution of the dimer. The sheets were then cured for about 22 minutes at a temperature of 105° C. The type of ketene dimer, the amount on the paper, and the sizing obtained with that amount are set forth in Table III. The amount of dimer on the paper was determined by weighing the sheet dry and then weighing the wet sheet after dipping.

Knowing the concentration of dimer in the solution, the amount on the sheet was easily calculated.

Table III

Example	Ketene Dimer	Percent of Dimer in Paper Based on Dry Weight of Paper	Sizing Obtained
12	Ethyl	0.027	Poor, splotchy.
13	Butyl	0.029	No sizing.
14	Hexyl	0.034	Poor sizing.
15	Heptyl	0.028	Do.
16	Octyl	0.029	Fair sizing.
17	Hexadecyl	0.027	Excellent.
18	Phenylnonyl	0.063	Very good.
19	do	0.032	Do.
20	do	0.017	Do.
21	Eicosanyl	0.065	Excellent.
22	do	0.033	Do.
23	do	0.016	Do.
24	Benzyl	0.060	Good.
25	do	0.034	Do.
26	do	0.017	Fair.
27	Ketene dimer prepared from montanic acid.	0.051	Excellent.
28	Ketene dimer prepared from montanic acid.	0.006	Do.

The above data clearly show that for maximum effectiveness in sizing with an alkyl ketene dimer, only octyl and higher alkyl ketene dimers should be used. The data also clearly show that aralkyl and aryl ketene dimers are effective in sizing paper.

EXAMPLE 29

A ketene dimer emulsion was prepared by blending 100 parts of 85% active hexadecyl ketene dimer with 20 parts of xylene, 20 parts of methyl oleate and 20 parts of polyoxyethylene sorbitol laurate sold by the Atlas Powder Company under the trade name "Atlox 1045." This mixture was then melted at 70° C. and water (also at 70° C.) added thereto slowly while the mixture was stirred. This formed a water-in-oil emulsion which at about 50% total solids inverted to give an oil-in-water emulsion. Addition of water was continued until the solids were about 40% whereupon the emulsion was dumped into hot water to give an emulsion having about 1.5% solids.

Six beaters were furnished with 2200 lb. each of unbleached kraft pulp at 7% consistency. The pulp was beaten and 2.7 lb. of ketene dimer solids added to each beater together with additional water to give a pulp slurry of 4% consistency. There was thus present in the water 0.005% ketene dimer based on the water. A closed system was used and a small additional amount of the ketene dimer emulsion was added to the white water so that the concentration of ketene dimer at the wire was maintained at about 0.005% ketene dimer based on the water. The pulp was diluted with the treated white water and run out on a Fourdrinier paper machine in the usual manner. The pH of the white water was varied by adding caustic. Substantial quantities of paper were made with the pH of the white water at 6.7–7.0, 8.5, and 9.6.

The reels were stored overnight at room temperature. The paper prepared at approximately neutral pH's was not appreciably sized as it came off the machine, while that paper prepared at pH's of 8.5 and 9.6 was sized as it came off the machine. Within about two hours of storage at room temperature, sizing developed in all sheets, and by the morning after the run, all sheets were similarly hard-sized. Although agitation was quite vigorous in all of the machine chests, the amount of foam in the pulp was negligible. There was also a negligible amount of foam on the wire although the machine was run at 570 ft./min. The paper had a basis weight of 30 lb. per ream and was Yankee dried. It was well sized and on specification in every respect.

EXAMPLE 30

In another run a 50-lb. unbleached kraft sheet was made on a Fourdrinier machine. The hexadecyl ketene dimer emulsion was prepared as in Example 29. In contrast to Example 29, the emulsion was added continuously to the stock just before the fan pump, additions being made with both 5 and 7 lb. of the dimer per ton of air-dried stock. The pH of the system throughout the run was about 8.4. The concentration of ketene dimer at the wire was about 10 parts per million parts of water for the one run and about 14 parts of ketene dimer per million parts of water in the other run. As compared to similar runs using rosin and alum, there was a marked reduction in foaming tendency during the period the dimer emulsion was used on the machine, but no other differences in machine operation were noted.

The ultimate sizing was developed on the machine, no appreciable increase in sizing being noted in subsequent curing. The sizing of paper prepared with the ketene dimer emulsion was compared with runs made on the same machine using rosin and alum size. Sizing was determined by noting the time for penetration of the sized sheet by a 20% aqueous solution of lactic acid. The paper sized with 5 lb. of hexadecyl ketene dimer per ton of pulp had a sizing of 893 seconds, while the paper containing 7 lb. of hexadecyl ketene dimer per ton of pulp had a sizing of over 2700 seconds. In comparison six runs of the standard rosin-sized paper containing 1% rosin size prepared on this machine had the following sizing: 333 seconds, 314 seconds, 178 seconds, 355 seconds, 300 seconds, and 393 seconds.

In the above examples definite curing cycles were used to most clearly point up the differences due to the controlled variables in the examples, such as type of ketene, type of pulp, and the pH of the pulp slurry. In commercial practice this is not necessary as can be seen from Examples 29 and 30. When the paper is dried on a heated roll, or by similar means, the heat of drying will generally be sufficient to cure the sheet. When an alternative method of drying, such as air drying, is used, simple storage of the paper at room temperature for a day or two will be sufficient to cure the sheet. However, a separate curing step may be used if desired. When a separate curing step is used, the paper will generally be heated at about 100° C. for five or ten minutes or longer.

In the process of beater sizing as the term is used in the art and in the instant application, it is understood that the ketene dimer may be added to the paper system at that point which is most convenient to the actual manufacturing needs, such as, for example, by addition of the dimer emulsion to the paper furnish at any point prior to sheet formation, such as addition at the head box, fan pump, beater engine, Jordan, or the like. Addition at any point prior to sheet formation is included in the term "beater addition" as used in the art. Furthermore, the ketene dimer emulsions used in the process of the instant invention may be used in conjunction with conventional papermaking ingredients, such as, for example, wet strength resins, fillers, dyes, pigments, and the like, to provide in all cases a paper product having the desired sizing properties.

As stated before, any of the emulsions of U. S. 2,627,477 to William Downey may be used. However, particularly preferred are those emulsions which are prepared using a nonionic emulsifier. In addition to those nonionic emulsifiers specifically used 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 trade name "Tween 85"; polyoxyethylene sorbitol hexaoleate, sold by the Atlas Powder Company under the trade name "Atlox 1086"; polyoxyethylene sorbitol laurate, sold by the Atlas Powder Company under the trade name "Atlox 1045"; polyoxyethylene sorbitol oleate-laurate, sold by the Atlas Powder Company under the trade name "Atlox 1045A";

polyethylene glycol ester of rosin, sold by the Hercules Powder Company under the trade name "Synthetics AR150"; the polyethylene glycol ester of rosin, sold by the Hercules Powder Company under the trade name "Synthetics AR200"; the polyethylene glycol ether of an alkylated phenol, sold by the Hercules Powder Company under the trade name "Synthetics AF100"; and finally, the ethylene oxide adduct of a mixture of rosin and alkylated phenol, sold by the Hercules Powder Company under the trade name "Synthetics B97." Of the anionic emulsifiers, those which are particularly preferred are the alkaryl sulfonates such as that sold by Nino Laboratories, Inc. under the trade name "Toximul 100," and the sodium salts of higher fatty alcohols, such as those sold by E. I. du Pont de Nemours and Company, Inc. under the trade name "Aquarex D."

I claim:

1. A process for the internal sizing of paper with a sizing material which does not require the use of a precipitating agent which comprises adding to an aqueous suspension of cellulosic paper stock at a point ahead of sheet formation an aqueous emulsion of a ketene dimer, 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 having at least 6 carbon atoms, aryl, aralkyl, and alkaryl groups, said aqueous suspension being at a pH of 5 to 9, inclusive, said ketene dimer being added to the said aqueous suspension to give a concentration of from about 5 parts of said ketene dimer to about 200 parts of said ketene dimer per million parts of water, forming a sheet from the said stock and drying the said sheet.

2. The process of claim 1 wherein R is an aryl radical.

3. The process of claim 2 wherein R is phenyl.

4. The process of claim 1 wherein R is an alkyl radical having 8 or more carbon atoms.

5. The process according to claim 4 wherein the alkyl radical is tetradecyl.

6. The process according to claim 4 wherein the alkyl radical is hexadecyl.

7. The process according to claim 4 wherein the alkyl radical is a mixture of hexadecyl and tetradecyl.

8. The process according to claim 4 wherein the ketene dimer is prepared from montanic acid.

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