The present invention relates to the manufacture of sized paper by the beater-addition process, wherein an aqueous cationic dispersion of a hydrophobic ketene dimer is added to an aqueous suspension of cellulosic fibers and the ketene dimer is substantially adsorbed thereon. The invention includes the papermaking processes involved, the cationic ketene dimer dispersions employed, and the methods by which the dispersions are prepared.

Hereinafter in the specification and claims the term "dispersion" will be replaced by the term "emulsion" to designate as is customary both dispersions of the solid-in-liquid and liquid-in-liquid types.

Osberg U.S. Patent No. 2,785,067 discloses that sized paper can be made by forming an aqueous non-ionic or anionic suspension of cellulose papermaking fibers, adjusting the pH of the suspension to within the range of 5 to 9, adding thereto a non-ionic or anionic emulsion of a hydrophobic ketene dimer, sheething the suspension, and curing the sheets at an elevated temperature. According to the patent, deposition of ketene dimer from emulsion upon the fibers results from the pH adjustment described.

The hydrophobic ketene dimers have the theoretical formula

\[ R-C\equiv C-O \]

wherein the R's represent the same or different hydrophobic radicals, and cure by reaction with the cellulose; cf. Technical Association of the Pulp and Paper Industry (TAPPI) 39, 21-23 (1956).

The discovery has now been made that paper of substantially and often phenomenally improved sizing can be produced by replacing the non-ionic or anionic ketene dimer emulsion in the above process with a cationic emulsion. In other words, I have found that paper possessing outstanding sizing can be made by forming an aqueous suspension of papermaking fibers, adding thereto a small but effective amount as sizing agent of a cationic emulsion of a hydrophobic ketene dimer, sheething the suspension, and developing the sizing properties of the dimer by curing the sheets at an elevated temperature.

The ketene dimer in the emulsion is self-substantive and is rapidly adsorbed by the fibers, an effective amount, usually being adsorbed while the emulsion is being distributed therethrough. I have regularly found it possible by use of cationic emulsions on the one hand to make a substantial decrease in the amount of ketene dimer needed to produce a given level of sizing, and on the other hand, to produce a paper having a water-repellence which has rarely, if ever, been exceeded by paper made according to the beater-addition process.

The process of the present invention does not depend upon the pre-adjustment of the pH of the pulp to any particular value. Better results, however, are generally obtained when the pH of the suspension is maintained at a value less than 5 or in excess of 9, depending upon the adsorption characteristics of the particular agent added.

The present invention does not primarily depend upon the particular amount of cationic ketene dimer added. The scope of the invention includes the addition of emulsified ketene dimer in effective amount between 0.1% and 3% of the dry weight of the fibers.

Best sizing per increment of ketene dimer added occurs in the range of 1/4%-3/4% (ketene dimer on the dry weight of the fibers). This is an unusually low preferred range and evidently results from two factors associated with the cationic nature of the emulsion. The first is that the adsorption of the ketene dimer is apparently substantially more uniform with decreased aggregation of the emulsion particles so that a larger fiber area is initially protected. The second is that adsorption is more complete. The evidence is that at least 50% of the ketene dimer in preferred emulsions is deposited on the fibers.

The cationic dispersing agents referred to may be monomeric or high molecular weight hydrophilic or water-soluble basic nitrogenous surface-active agents. In general, I have found that better sizing is obtained where the dispersing agent in the final cured sheet has a high molecular weight, in excess of 2,000. Evidently the low molecular weight agents are not irreversibly adsorbed by the fibers and thus act to some extent as re-wetting agents, whereas the high molecular weight agents and the agents which are converted to high molecular form on the fibers are irreversibly adsorbed so that their re-wetting properties are suppressed.

More in detail, the papermaking process of the present invention is applicable to any type of hydrated cellulose fiber at any convenient consistency of the fibrous suspension. The preferred consistency is that at which permits rapid and uniform distribution of the sizing emulsion to take place and is usually 0.5%-6%, based on the dry weight of the fibers. The pH of the suspension need not be pre-adjusted. The emulsion is added at any convenient point in the papermaking system ahead of the wire, and if desired, the pH may be adjusted to any predetermined optimum value, the thermosetting amino-triazine-formaldehyde acid colloids for example being generally best adsorbed at pH 4.5 and the macropolyalkylpolymethyleneimines being best adsorbed at about pH 10. Preferably, the fibrous suspension should be gently stirred for a few moments to distribute the emulsion uniformly through the suspension and allow adsorption to go to substantial equilibrium. In preferred instances, as much as 75%-80% of the dimer is adsorbed by the fibers. The suspension is then sheeted and the resulting web is dried according to normal practice. Adsorption of the ketene dimer is substantially irreversible, so that the pH of the web during formation can be adjusted to any desired value. However, reaction of the ketene dimer with cellulose is favored by acid and alkali, so that we prefer to sheet the suspension at a pH in the range of 5-6 or 8-9.

The web is dried at normal temperatures which are generally sufficient to develop a substantial part of the sizing properties of the ketene dimer. It is preferred to complete the reaction of the ketene dimer with the cellulose by forming the paper into rolls having a temperature in the range of 175°-250° C. or thereabouts so as to prolong curing conditions until reaction of the ketene dimer with the cellulose fiber has gone to substantial completion.

The emulsions of the present invention essentially consist of a cationic emulsion of a hydrophobic organic ketene dimer in aqueous medium, the ketene dimer thus being the dispersed phase and the aqueous medium being the continuous phase.

The emulsions may be prepared in any convenient way and the invention does not depend upon the particular method selected. The ketene dimer may be directly emulsified in water containing a water-soluble cationic organic dispersing agent. If desired, the ketene dimer may be emulsified first in water and the dispersing agent added separately during the operation, and in certain instances the emulsifying agent may be pre-dispersed in the ketene dimer.

The ketene dimers are generally solids melting below
100° C. and may be liquids as in the case of the ketene dimer prepared from tall oil fatty acids (chiefly a mixture of linoleic and oleic acids). The liquid ketene dimers may be emulsified directly with water containing the emulsifying agent and the normally solid dimers are generally best emulsified in molten form or in benzene, etc. solution. Unnecessary heating should be avoided to minimize decomposition. The emulsions are advantageously homogenized hot to decrease particle size and improve stability and then cooled so as to form a solid-in-liquid dispersion. The emulsions may be prepared at any convenient solids content. Before use they are advantageously diluted to 1%–5% solids by weight so as to favor rapid and uniform distribution throughout the fibrous suspension.

Use of the hydrophilic organic cationic dispersing agent renders at least part of the emulsified ketene dimer auto-substantive when added to an aqueous suspension of papermaking cellulosic fibers. In practice somewhat more is added. The precise amount of dispersing agent needed varies from instance to instance depending chiefly on the surface characteristics of the ketene dimer and the dispersing agent and the optimum amount is hence most easily determined by laboratory trial.

The dispersing agent may be any surface-active hydrophilic cationic nitrogen base material, and may be monomeric or polymeric.

As monomeric agents there may be used monomeric nitrogen bases containing at least one hydrophilic organic aliphatic salt. Among such bases are the aliphatic ammonium salts, e.g., octadecyltrimethyl ammonium chloride and 9,10-decadienyl dimethyl-2-hydroxyethyl ammonium chloride; the higher aliphatic amide quaternaries, e.g., octadecanamido propyl dimethyl-2-hydroxyethyl ammonium chloride; aliphatic amines, e.g., the reaction product of one mol of octadecylamine with 2 moles of ethylene oxide; the higher aliphatic amido amines such as the reaction product of 2.5 moles of octadecyl chloride or oleoyl chloride with one mol of triethylenetetramine; higher amido-amino soaps, e.g., the product obtained by heating 1.8 moles of stearic acid with diethylenetriamine at 200° C. until 1.5 moles has reacted by way of amimation (leaving 0.3 mol of stearic acid in soap form); the higher aliphatic substituted heterocyclic amines such as N-octadecyl piperazine and N-octadecyl piperidine; the higher aliphatic substituted cyclic quaternaries including 1-cyclohexyl-1,4,4-trimethyl piperazinilium dichloride; aryl quaternaries, e.g., N-hexadecyl pyridinium chloride; and sulfonium compounds such as hexadecyl dimethyl sulfonium bromide.

For reasons already stated, I have discovered it advantageous to use as emulsifying agents hydrophilic cationic organic basic nitrogenous compounds having molecular weights in excess of 2,000 and more particularly in excess of 10,000. I have found three types of these higher molecular weight materials to be particularly useful.

The first type embraces the high molecular weight water-soluble cationic non-thermosetting polyalkylene-polymamines or which polyethylenimine is typical. Such polyethylenimines are well adsorbed at alkaline pH values and thus permit the manufacture of well-sized paper having no metal or formaldehyde content. Similar materials may be made by condensation of lower polyethylene polylamines with 1,3-dichloropropene, by condensation of ammonia or lower polyalkylene polylamines with epichlorhydrin or by condensation of methylenebisacrylamide with ethylenediamine.

The second type embraces the water-soluble non-thermosetting high molecular weight linear carbon polymer carrying sufficient cationic groups to render the molecule as a whole cationic. Advantageously, such polymer may carry a sufficient number of amide groups as are customary for the production of paper of improved dry strength. Preferably the ratio of quaternary groups to amide groups is between about 20:80 and 5:95 and the ratio of the total number of quaternary groups and amide groups to the carbon atoms of the chain is between about 1/3:1 and 3/8:1. Linear resins of this type have the advantage of usefulness over a broad pH spectrum and have the property of producing paper of substantial dry strength without concomitant wet strength.

Particularly effective resins may be formed by copolymerizing 1 mol of p-(chloromethyl) styrene with 9 moles of acrylamide and reacting the product with trimethylamino to convert the chloromethyl groups to quaternary ammonium groups.

The third type are amido-aldehyde condensates in partially polymerized hydrophilic cationic form. Such materials may be prepared by reacting an amido compound, for example melamin, guanamine, or formoguanamine or a triguanamine with formaldehyde preferably in the presence of a small amount of a watersoluble polyalkylene-polymamine) first under alkaline conditions and then under acid conditions until a substantial viscosity has been achieved, after which the solution may be neutralized for stabilization purposes. There may also be used the water-soluble resins formed by reacting urea and formaldehyde in the presence of a minor amount of glycidyl dimethyl 3-ureidopropyl ammonium chloride; or the water-soluble thermosetting condensation products of a nonionic or cationic linear non-thermosetting carbon chain polymer carrying unsubstituted amide groups with an equal weight of one or more of the foregoing cationic thermosetting polymers. Resins of these types are cellulose-substantive and a number are widely used in the manufacture of wet-strength paper. As prepared, they typically have molecular weights in the range 3000–15000 but grow to a molecular weight far in excess of 10,000 on curing.

As stated, the amount of cationic dispersing agent, regardless of molecular weight, should be at least sufficient to render the emulsified ketene dimer substantive to cellulosic fibers in aqueous suspension. In such minimal amount the material has no significant effect upon the properties of the paper the amount of cationic agent being roughly 5%–20% of the weight of the ketene dimer. It is a feature of the invention that very much more of the cationic dispersing agent may be present and, if desired, the amount may be increased so that the wet or dry strength of the paper is significantly improved. For this purpose the amount of cationic agent may be increased so that it is between 100% and 1,000% the weight of the ketene dimer or more. Such resins, when of the curing type, develop their strengthening properties ahead of the time needed to develop the sizing properties of the ketene dimer.

The invention will be more particularly described with reference to the examples. The examples constitute embodiments of the invention and are not to be construed as limitations thereon.

Example I

The following illustrates the preparation of a stable cationic emulsion of a ketene dimer size using a typical monomeric cationic dispersing agent as emulsifier.

An emulsification medium was prepared by adding 7.3 cc. of a 35% by weight solution of octadecanamido propyl dimethyl 2-hydroxyethyl ammonium dihydrogen phosphate in aqueous isopropanol to 250 cc. of water at 65° C. (equivalent to 10% of dispersing agent based on the weight of ketene dimer). Into this with rapid agitation was slowly poured 25 gm. of molten hexadecyl ketene dimer at 60°. The resulting emulsion was homogenized hot and a nearly white emulsion was obtained. The emulsion was rapidly cooled to room temperature to preserve particle size, and a creamy suspension was obtained. The suspension separated slightly after 24 hours, but became uniform with slight agitation.
Example 2

The procedure of Example 1 was repeated except that 3.6 ml. of a 35% aqueous N-octadecylpyridinium chloride solution was used as the dispersing agent (equivalent to 5% based on the dry weight of the ketene dimer). A similar emulsion was obtained.

Example 3

The procedure of Example 1 was repeated except that 2.5 gm. of the zwitserfom form of powdered octadecanamidopropyl dimethyl 2-carboxymethyl ammonium chloride (de betaine) in place of the emulsifying agent therein used. A similar suspension was obtained.

Example 4

The following illustrates the preparation of a ketene dimer sizing dispersion of a cationic thermosetting paper wet strength resin as dispersing agent. A large excess of the resin is used so that the emulsion is useful for the production of well-sized paper of good wet strength.

The procedure of Example 1 was repeated except that the amount of ketene dimer was decreased to 5 gm., the amount of water was decreased by 100 gm., and the quaternary ammonium solution was replaced by 100 gm. of a 12% by volume aqueous solution of a melamine-formaldehyde acid colloid prepared by acidifying trimethylolmelamine solution according to U.S. Patent No. 2,345,543 using hydrochloric acid as the acid.

Example 5

A ketene dimer sizing dispersion was prepared by the method of Example 1 replacing the emulsifying agent solution used therein with an equal amount of a 35% by weight solution of the non-colloidal water-soluble cationic wet-strength melamine-formaldehyde-iminobispropylamine-glycol resin prepared according to the general method of copending Wooding et al. U.S. application Serial No. 629,774, filed on December 21, 1956, now U.S. Patent No. 2,856,314.

Example 6

The following illustrates the preparation of a ketene dimer sizing dispersion by use of a small amount of a cationic linear carbon chain polymer carrying amide and quaternary ammonium groups.

The procedure of Example 1 was repeated except that the solution of quaternary ammonium dispersing agent was replaced by 7.2 gm. of a 35% (solids basis) solution of the non-polymer formed by copolymerizing 95 mol of acrylamide with 5 mol of diallyl dimethyl ammonium chloride. During polymerization only one of the allyl groups reacted, so that the product was essentially a linear carbon chain polymer carrying amide at quaternary ammonium groups.

The polymer was a material known to act as a dry strength agent for paper. If desired, the amount of polymer may be greatly increased so as to form an emulsion effective in producing paper of improved dry strength as well as sizing.

Example 7

The following illustrates the preparation of a size b the method of Example 6 wherein the amide groups are replaced by phenyl groups.

The procedure of Example 6 was repeated except that the polymer was prepared by copolymerizing 1 mol of 2 methyl-5- Vinylpyridine with 5 mol of styrene and quaternizing the product with 1 mol of allyl bromide.

Example 8

The procedure of Example 1 was repeated except that a 33% solids aqueous solution of high molecular weigh polyethyleneimine (Gardner-Holdt viscosity of K at 25°C.) was used as sole emulsifying agent. A very good alkaline emulsion was obtained.

Example 9

The following illustrates the manufacture of sized paper using typical cationic ketene dimer sizes according to the present invention.

The pulp was a bleached sulfite-bleached hardwood kraft (50/50 ratio) pulp (selected because of its difficulty to size). The pulp has been beaten to a Green freeness of 440 ml. and was used at a consistency of 0.6% based on the dry weight of the fibers.

In each instance, the sizing emulsions were diluted to 1% solids with water before use to facilitate distribution through the fiber suspension. The pH of the pulp suspension was adjusted to the values shown in the table below. The sizing emulsions were used at the pH at which they were prepared, and were added to the fibers suspensions in amounts as shown in the table below. After addition, the suspensions were gently stirred for three minutes to allow adsorption of the ketene dimer solids to go to completion, the pH of the suspensions adjusted to the values shown in the table, and handsheets made and tested according to standard laboratory practice. The sheets were formed in each instance at basis weights of 200 lb. (25" x 40"/500 ream) for the water adsorption and lactic acid tests and at 50 lb. for the remaining tests. The sheets were pressed between blotters and oven-cured for 12 hours at 100°C. The sheets were then conditioned for 24 hours at 50% relative humidity and 73°F. and tested as shown in the table. Results are as follows:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene Dimer, percent</th>
<th>Emulsifier</th>
<th>pH</th>
<th>H2O Absorption</th>
<th>Lactic Acid Penetration</th>
<th>Enk. Bay Siek</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>1.0</td>
<td>Blank</td>
<td>4.5</td>
<td>4.5</td>
<td>12.0</td>
<td>128</td>
<td>12.0</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>8.6</td>
<td>4.5</td>
<td>4.5</td>
<td>45.8</td>
<td>69.2</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>33.3</td>
<td>87.8</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>33.3</td>
<td>80.1</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>32.8</td>
<td>88.2</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>35.8</td>
<td>80.1</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>33.3</td>
<td>87.7</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>35.8</td>
<td>80.1</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>33.3</td>
<td>87.7</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>35.8</td>
<td>80.1</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>33.3</td>
<td>87.7</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
<td>4.5</td>
<td>4.5</td>
<td>35.8</td>
<td>80.1</td>
</tr>
</tbody>
</table>

1 Hexadecyl ketene dimer based on dry weight of fibers.
2 Based on weight of ketene dimer.
3 Before addition of sizing dispersion.
4 After 15-minute soak at room temperature.
5 By penetrometer.
6 Lb. per inch, adjusted to 50 lb. basis weight (25" x 40"/500 lb. ream).
I claim:
1. A process for the manufacture of sized paper of improved tensile strength which comprises forming an aqueous suspension of cellulose papermaking fibers, adding thereto an emulsion of a hydrophobic ketene dimer in an aqueous medium containing a thermosetting cationic amido-aldehyde condensation product in acid condensed yet hydrophilic stage as paper-strengthening agent, the weight of said ketene dimer being between \( \frac{1}{20}\% \) and 3% of the dry weight of the fibers and the weight of said cationic nitrogenous paper-strengthening agent being between about 14% and 3% of the dry weight of the fibers, uniformly distributing said added emulsion through said aqueous suspension whereby a substantial proportion of said added ketene dimer and paper-strengthening agent are uniformly adsorbed on the surface of said fibers, sheeting said suspension to form a water-laid web at about pH 4.5, and heating said web to dry the same and to develop at least a substantial part respectively of the sizing and wet strengthening properties of the ketene dimer and paper strengthening agent thereon.

2. Sized paper formed by heating a water-laid web having adsorbed thereon a hydrophobic organic ketene dimer and a thermosetting cationic amido-aldehyde condensation product.

3. As a new composition of matter a cationic emulsion of a hydrophobic organic ketene dimer wherein the ketene dimer is the dispersed phase in a continuous phase and the aqueous phase contains a thermosetting hydrophilic cationic melamine-formaldehyde wet-strength acid colloid as principal emulsifying agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,559,220 Maxwell et al. July 3, 1951
2,627,477 Downey Feb. 3, 1953
2,698,793 Landes et al. Jan. 4, 1955
2,762,270 Keim et al. Sept. 11, 1956
2,772,310 Morris Nov. 27, 1956
2,785,067 Osberg Mar. 12, 1957
2,865,743 Weisgerber Dec. 23, 1958