METHOD OF IMPROVING THE DRAINAGE OF CELLULOSE FIBER SUSPENSIONS WITH POLYMERS OF N-VINYL-N-METHYLFORMAMIDE

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5 Claims

ABSTRACT OF THE DISCLOSURE

Dewatering of aqueous cellulose fiber suspension in the formation of paper is improved by adding to the suspension from 0.05 to 4% of a water soluble polymer consisting essentially of units derived from N-vinyl-N-methylformamide, such as N-vinyl-N-methyl formamide, having 60-100% of the formic acid radicals of the polymer split off by acid hydrolysis.

The present invention relates to an improved method for dewatering cellulose fiber suspensions suitable for the manufacture of paper.

In the production of paper, card board and similar water-scooped paper webs—hereinafter called “paper”—cellulose fiber suspension which may contain more or less resin size and mineral constituents (fillers) depending on the product desired, is drained on a continuously moving wire cloth. In this process, the free water passes and drops off the paper web whereas the rest of it is removed by suction and subsequent drying, for example, on drying rollers. A substantial factor in the production of paper is the rate at which the water can pass through the paper web or can be sucked off. The drainage rate of the cellulose fiber suspensions depend, to a large extent, on the composition of the suspension, on how finely beaten the fibers are (degree of fineness) and on the mesh width of the wire cloth. By adding certain chemical substances dewatering can be accelerated without increasing the amount of fibers that drop through the wire cloth. Quick dewatering means either low drying costs or increase in production.

It is especially interesting to aid draining agents of the chemical type in the processing of waste-paper or highly beaten cellulose (parchment substitute) since, in this case, dewatering is considerably reduced by major proportions of finest fibers and slurry material.

It is known that cellulose suspensions can be dewatered better and more quickly by adding bivalent metal ions, especially calcium chloride (c.f. J. C. MacGugan, Paper Trade Journal, January 1962, p. 22). According to W. C. Cohen, et al., Proc. Amstr. Pulp Paper Ind. Techn. Assoc. 3 (1949), p. 72, this phenomenon resides in the neutralisation of the anionic group of the fibers by positive metal ions. This leads to the formation of fiber agglomerates that permit an easier removal of water from the fibrous material suspension.

Unfortunately, the water hardness plays an important part in this process. Thus, it appeared that the draining effect decreases if the water hardness increases. However, since the paper producer is, in most cases, dependent on river or pond water or on underground water of medium or high hardness, the use of calcium chloride is limited to a few cases where soft water is actually available.

The draining effect of calcium chloride is, moreover, adversely affected by the presence of resin size and aluminiaceous sulfate so that its use is only economical with unsized papers. In addition, water containing calcium chloride promotes the corrosion of steel and brass slightly more than does usual water for industrial use. Furthermore, it discloses that polymerisation products based on ethylene imine, for example polyethylenimine, are suitable for accelerating dewatering of cellulose suspensions. These products have, in addition to other effects, a retarding effect and thereby reduce the amount of solid materials in the slurry water (cf. H. Wilflinger, Das Papier 2, (1948), p. 265). A lower waste-water content generally involves a better clarification of the sewage water and thus the paper producer is in a better position to meet the requirements imposed by the law as to the introduction of waste water into effluent channels.

The above-cited draining agents based on polyethylene imine, however, exhibit a series of drawbacks. For example, it appears that papers that have been made from those suspensions treated with polyethylene imine have an increased tendency to yellowing. Moreover, pure polyalkylene imines are sensitive to sulfate-ions in an acid medium, i.e. their effectiveness decreases with increasing amounts of aluminum sulfate in an aqueous solution. H. Wilflinger, in Das Papier 2 (1948), p. 265, explains this phenomenon with the formation of salt-like sparingly soluble precipitates of polyalkylene imines in the presence of aluminum sulfate. In numerous cases, however, the paper producer depends on the use of aluminum sulfate since it is an inexpensive flocculating agent and thus proved especially suitable in the clarification of sewage water. As a precipitating and mordanting agent to be used for glues and dyestuffs it can hardly be replaced by other products showing similar economical advantages. Furthermore, aluminum sulfate serves in many cases, to control the absorptive power of papers.

Attempts have been made to overcome the sensitivity of polyalkylene imines to sulfate-ions by using, instead of pure polyalkylene imines, condensation products of urea and 1,2-alkylene imines as auxiliaries.

It has now been found that dewatering of aqueous cellulose fiber suspensions to form paper on a paper machine wire cloth can be improved by incorporating into the cellulose fiber suspensions water-soluble homo- or copolymers of N-vinyl-N-methylcarboxylic acid amides of the formula

\[\text{CH}_2=\text{CH-N(CH}_3)_2-\text{CO-R}\]

in which \(R\) stands for hydrogen or the methyl or ethyl radical, the carboxylic acid radicals of the polymers being eliminated entirely or partially by acid hydrolysis.

A substantial advantage of the auxiliaries of the invention is the fact that their effectiveness in an acid medium is considerably less affected than that of, for example, polyethylene imine. This advantageous property of the polymers used according to the invention is obviously due to their substantially weaker tendency to form sparingly soluble salts with sulfate-ions in an acid medium. An influence of the water hardness on the draining effect, as observed with calcium chloride, can also not be established with the polymers used according to the invention. The draining effect of the polymers is also hardly influenced by the presence of resin size and aluminum sulfate.

Compared with the condensation products of urea and 1,2-alkylene imines the polymers used according to the invention, moreover, exhibit in a neutral medium a superior draining effect on the cellulose fiber suspension. It is, therefore, possible to use the polymers of the invention for dewatering cellulose fiber suspensions within a wide range of effectiveness and independently of the water hardness and of the presence of aluminum sulfate or resin size.
Another advantage of the polymers of the invention, especially established in practice, is the fact that, in despite their nitrogen content surprisingly, they do not bring about yellowing of the paper. Owing to their excellent drainage effect, the products of the invention are advantageously suitable for accelerating dewatering of slimy-beaten cellulose fiber suspensions or even of suspensions having a high proportion of finest fibers or slimy material due to their origin, for example, from waste paper. 

However, the invention can also be used in suspensions that contain highly bleached cellulose fibers and, hence, would not permit the use of compounds on the basis of polyalkylene imines owing to the tendency to yellowing. The presence of products of the invention influences the effect of optical brighteners much less than do those compounds on the basis of polyalkylene imines.

Still another advantage of the products to be used according to the invention is their very favorable effect of retaining filling and fibrous materials on the wire cloth during the sheet formation. Because of this advantageous retention valuable starting materials are, indeed, retained in the paper sheet to a large extent and the pulp slurries are markedly deposited thus permitting a better and easier clarification of the sewage water. It is, moreover, essential that the additives of the invention do not deteriorate the absorptive power nor the surface smoothness of the final product.

The products to be used according to the present invention are water-soluble polymers of N-vinyl-N-methyl carboxylic acid amides or copolymers of these vinyl compounds with radically polymerizable comonomers, the carboxylic acid radicals of which have been eliminated at least partially by hydrolysis with a strong mineral acid, for example hydrochloric acid, nitric acid, hydrobromic acid, sulfuric acid or phosphoric acid, at an elevated temperature. The polymers and copolymers are prepared especially from N-vinyl-N-methyl carboxylic acid amides of lower alkane-carboxylic acids having 1 to 3 carbon atoms, especially N-vinyl-N-methyl formamide, N-vinylacetamide, N-vinylcarboxylic acid amides, N-vinyl-N-methylformamide or mixtures of these monomers. Preferred is N-vinyl-N-methylformamide since the hydrolysis of the corresponding homo- and copolymers can be carried out in an especially easy and technically simple manner at relatively low temperatures of from about 50° to about 120° C. About 60 to 100%, preferably 70 to 95%, of the acyl radicals of the homo- and copolymers are advantageously split off by hydrolysis, these values indicating the mol-percentage of nitrogen present in the form of free secondary amino groups. The degree of hydrolysis is, conveniently, established by determining the content of basic nitrogen in the polymer. At the degrees of hydrolysis mentioned, the homopolymers have a content of basic nitrogen of from about 15% to 24% by weight, preferably 17 to 22.5% by weight. The carboxylic acid split off by hydrolysis and the mineral acid may, if desired, be removed from the reaction mixture by evaporation, dialysis or by means of ion exchangers. The acids may, however, also be left, in many cases, in the mixture without noticeably affecting the effect of the polymers. The molecular weights of the partially or entirely hydrolyzed homo- or copolymers to be used according to the invention are advantageously within the range of from about 20,000 to 5,000,000, preferably from about 100,000 to 2,500,000.

As auxiliaries to be used according to the invention there are preferably mentioned the at least partially hydrolyzed products of homopolymers of N-vinyl-N-methyl carboxylic acid amides. As far as hydrolyzed products of copolymers of N-vinyl-N-methyl carboxylic acid amides are used, the proportion of the comonomers may be up to about 50%, preferably up to 30%, calculated on the weight of the copolymer.

For preparing the copolymers any radically polymerizable compound may be used as comonomer of the N-vinyl-N-methyl carboxylic acid amides, for example vinyl alcohol, vinyl esters such as vinyl acetate, other open-chain N-vinyl carboxylic acid amides, N-vinyl-lactams and, in particular vinyl sulfonic acid, acrylic acid, methacrylic acid and the acrylic and methacrylic acid amides. The entirely or partially hydrolyzed homo- or copolymers to be used according to the invention may be prepared by the process disclosed in U.S. application Ser. No. 766,942 filed Oct. 11, 1968 by Beermann, Schnabel and Ulmschneider, said application corresponding to German application P 53,845 (renumbered P 17 20 737.3) filed Oct. 20, 1967.

The at least partially hydrolyzed homo- or copolymers are introduced into the fiber suspension, advantageously, at a moment between the last beating operation or the last thickening and the dewatering on the wire cloth of the paper machine. Too heavy a shearing stress of the suspension, as caused by pumps and the like, should be avoided after the incorporation of the auxiliaries. The amount of the herein disclosed polymeric auxiliaries to be incorporated into aqueous cellulose fiber suspensions is within the range of from about 0.05 to about 4%, calculated on the weight of the dry cellulose fibers. In most cases, however, amounts of from 0.05 to 0.3% by weight are sufficient.

The auxiliaries to be used according to the invention may be incorporated into fiber suspensions that have been obtained either from fresh cellulose or from waste paper. The filling materials to be introduced into the fiber suspensions may be the mineral substances containing silicates or sulfates as usually employed in the paper industry, such as kaolin, China clay, talcum and heavy spar, as well as titanium dioxide.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

**Example 1**

Varying amounts of a poly-N-vinyl-N-methylformamide hydrolyzed to an extent such that the basic nitrogen content amounts to 21% by weight (88 mol-percent of nitrogen present in the form of free secondary amino groups) and the viscosity is 380 cp in a 13.1% aqueous solution, are introduced into 1% aqueous fiber suspensions obtained by beating up newspaper print paper and showing a degree of fineness of about 65° SR. The pH value of the suspension is about 7. About 2 g. of atiro fibers are taken from the suspension and placed into a Schopper-Riegler apparatus and the dewatering time is determined with the lower outlet pipe closed.

Suspended, the pH-values of which are adjusted to 5 by means of aluminum sulfate, are treated in the same manner.

In both cases the discharge time is also measured without adding a product and compared with polyethylene imine. The values obtained are compiled in Table I.

<table>
<thead>
<tr>
<th>Auxiliary</th>
<th>Amount used referred to atro cellulose, percent by wt.</th>
<th>pH- value</th>
<th>Dewatering time, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene imine</td>
<td>0.1</td>
<td>7</td>
<td>118</td>
</tr>
<tr>
<td>Hydrolised poly-N-vinyl-N-methylformamide</td>
<td>0.1</td>
<td>6</td>
<td>60</td>
</tr>
<tr>
<td>Polyethylene imine</td>
<td>0.1</td>
<td>5</td>
<td>139</td>
</tr>
<tr>
<td>Poly-N-vinyl-N-methylformamide</td>
<td>0.1</td>
<td>5</td>
<td>139</td>
</tr>
</tbody>
</table>

**Example 2**

Varying amounts of a partially hydrolyzed poly-N-vinyl-N-methylformamide having a basic nitrogen content of about 16.6% by weight (69 mol-percent of nitrogen present in the form of free secondary amino groups) are
introduced into the cellulose suspensions described in Example 1 which have been adjusted to pH 5.0 by means of aluminum sulfate. The reduction of the fineness degree of the suspensions is measured in a Schopper-Riegler apparatus. For comparison's sake, varying amounts of a condensation product of urea and ethylene imine are examined under the same conditions. The results are compiled in Table II and indicate a median value obtained from 5 separate measurements.

**TABLE II**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount used referred to atro cellulose, percent by wt.</th>
<th>pH value</th>
<th>Degree of fineness, according to SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensation product of urea and ethylene imine</td>
<td>0.2</td>
<td>6.8</td>
<td>64.8</td>
</tr>
<tr>
<td>Partially hydrolized poly-N-vinyl-N-methylformamide</td>
<td>0.3</td>
<td>6.0</td>
<td>64.3</td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

A 1% aqueous fiber suspension is prepared from unbleached sulfite cellulose and unbleached wood pulp (60:40). The degree of fineness is 70.5° SR and, after acidification with aluminum sulfate to a pH of 5.0, it is 73° SR. Varying amounts of a poly-N-vinyl-N-methylformamide hydrolyzed to an extent such that the basic nitrogen content amounts to 22.2% by weight (93 mol percent of nitrogen present in the form of free secondary amino groups), are introduced into samples of these suspensions and the dewatering time is measured as disclosed in Example 1 and compared with that of polyethylene imine and that of a condensation product of urea and ethylene imine (Table III).

**TABLE III**

<table>
<thead>
<tr>
<th>Auxiliary</th>
<th>Amount used referred to atro cellulose, percent by wt.</th>
<th>pH value</th>
<th>Dewatering time, secs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene imine</td>
<td>0.3</td>
<td>6.0</td>
<td>220</td>
</tr>
<tr>
<td>Condensation product of urea and ethylene imine</td>
<td>0.5</td>
<td>6.0</td>
<td>230</td>
</tr>
</tbody>
</table>

We claim:

1. In a process for dewatering an aqueous cellulose fiber suspension to form paper on a paper machine wire, the improvement of which comprises incorporating into the cellulose fiber suspension from about 0.05 to about 4%, referred to the weight of the dry cellulose fiber portion of the suspension, of a water soluble polymer consisting essentially of units derived from N-vinyl-N-methylformamide, having from 60 to 100% of the formic acid radicals of the polymer split off by acid hydrolysis.

2. The process of claim 1 wherein from 70 to 93% of the formic acid radicals of the polymer are split off by acid hydrolysis.

3. The process of claim 1 wherein in said suspension is incorporated at least a partially hydrolyzed polymer consisting of a polymer having at least 70% of its recurring units derived from N-vinyl-N-methylformamide.

4. The process of claim 1 wherein in said suspension is incorporated at least a partially hydrolyzed polymer consisting of a polymer having at least 70% of its recurring units derived from N-vinyl-N-methylformamide and up to 30% of its recurring units derived from vinylsulfonic acid.

5. The process of claim 1 wherein in said suspension is incorporated at least a partially hydrolyzed polymer consisting essentially of recurring units derived from N-vinyl-N-methylformamide which has a molecular weight of about 20,000 to 5,000,000.

**REFERENCES CITED**

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