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METHOD OF CONTROLLING DRAINAGE TIME OF BEATER SATURATED SLURRIES

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This invention relates generally to improved control in the processing of fiber slurries which have been beater saturated with rubber. More particularly, the invention relates to a method of controlling the drainage time of beater saturated slurries while yielding a sheet product having an improved hand.

In the various methods of beater saturating papermaking fibers, high levels of rubber normally produce a slow-draining slurry during the water removal step of making sheets or other products from the rubber-coated papermaking fibers. Such slow-draining slurries consume undue time in sheet formation, require the slowing down of the papermaking wire, and allow the formation of a sheet which is stiff and has a paper-like feel. This is particularly true where the beater saturation process has been carried out using the alum-ammonia process described in U.S. Patent No. 2,375,245—Pretzel, or using a corresponding alum-caustic process. Although it is known that faster-draining slurries may be produced by pretreating the fibers with decreased quantities of alum, usually as a solution of papermakers' alum, this type of control has not been as efficient as desirable in the production of sheets. The use of low quantities of alum for a given quantity of latex results in undue formation of clumps of rubber on the fibers and in the water. Accordingly, there is a need for a means of controlling the processing characteristics of beater saturated slurries to allow short precipitation times, uniform distribution of rubber on the fibers as well as control of the drainage characteristics of the slurry so that resulting sheets will be well formed.

It is the primary object of the present invention to supply such a method. It is another object of the present invention to describe a method of readily and inexpensively controlling the drainage characteristics of beater saturated slurries in order to produce a product having particularly good properties.

These objects are accomplished in a surprisingly straightforward and effective manner. The invention contemplates certain steps to be incorporated into any of the known beater saturating processes involving forming a slurry of papermaking fibers in water, precipitating a binder on the fibers to form coated fibers, and forming a product from the coated fibers. The present invention contemplates adding to the slurry of coated fibers a water-soluble salt of a metal in Groups I, II, IV, VII, or VIII of the Periodic Table. The salt will be dissolved in the slurry. There is then added to the salt-treated slurry sufficient alkali to achieve a pH in the range of 8.5–11.5 to form an insoluble hydroxide with the metal ion from the salt. A product is then formed from the resulting slurry.

The papermaking fibers contemplated by the present invention are known papermaking fibers such as asbestos fibers, glass fibers, mineral wool fibers, animal hair, and leather fibers. In addition, the cellulosic fibers may be used such as kraft, rag stocks, soda, semi-chemical, ground-wood, sulfite stock, alpha pulp, cotton linters either hydrated or unhydrated, as well as such fibers as jute, hemp, sisal, strings, chopped canvas, and other such fibers, which may be bleached, semi-bleached, or unbleached.

The fibers will be formed into a papermaking slurry

by known processes of beating and refining, usually in an aqueous medium. The fibers may then be beater saturated by any of the known methods of accomplishing the deposition of the rubber content of a rubber latex onto the surfaces of the papermaking fibers. Such prior processes include pretreatment of the papermaking fibers with such pretreating agents as cationic melamine-formaldehyde resin, polyvinyl pyrrolidone, alum, and any other pretreating agents to place the fibers in condition for the deposition thereon of the solids content of a rubber latex and provided the pretreating agent is soluble at pH greater than 8.5. Preferably there will be used the above-mentioned process of U.S. 2,375,245—Pretzel, or the modification of that process using caustic instead of ammonium hydroxide. The caustic contemplated will be potassium hydroxide, sodium hydroxide, or mixtures thereof. Thus the fibers preferably will be pretreated with alum, preferably added in the form of a water solution, normally in an amount in the range of 1 to 6 parts by weight alum per 1 part by dry weight of the fibers to be treated. The alum solution is added with agitation. Sufficient caustic in the form of a solution of ammonium hydroxide, or more preferably sodium hydroxide or potassium hydroxide will then be added to bring the pH of the fibrous slurry to a range of 6–8, preferably about 7. The rubber latex will then be added to the neutralized slurry, with agitation, whereupon the solids content of the rubber latex precipitates. The described preferred process of precipitating the rubber is particularly apt in the case where unusually large amounts of rubber are desired.

The binders contemplated by the present invention are those synthetic rubber binder dispersions known to be adaptable in a beater saturation process. Typical of these synthetic rubbers are the butadiene-styrene copolymers (SBR) often containing 30%–80% by weight butadiene. High styrene butadiene-styrene copolymers may also be used. The butadiene-acrylonitrile copolymers, normally containing 50%–80% by weight butadiene and the neoprenes (polychloroprenes) which are polymers of 2-chloro-butadiene-1,3 are also widely used. Homopolymers of butadiene as well as homopolymers and/or copolymers of butadiene homologs such as isoprene all can be used to form useful products; the so-called butyl rubber latices are useful. Other rubbery and elastomeric substances which can be deposited on fibers may be used in the present method.

Although prior processes sometimes state that they are adaptable to use with large amounts of rubber, usually 200%–650% by weight rubber based on the dry weight of the fibers, as a practical matter such processes are not as smooth as they might be. Such large amounts of rubber solids in the fibrous slurry compared with the amount of fibers produces more often than not precipitation of the rubber solids in the water as well as precipitation of the rubber solids on the fibers. The rubber solids are thus dispersed in small clots throughout the fibrous slurry. The resulting slurry may drain either too fast or too slow according to the exact nature of the precipitation of the large amount of rubber. As mentioned earlier, a fast-draining slurry produces a web which is not homogeneous. A slow-draining slurry produces a web which is homogeneous but, due to the fineness of the rubber precipitate, the wire may become clogged and the drainage time of the sheet will be too high. If the drainage time of the sheet is long, that is, if the Canadian 3-gram freeness is low, both the drainage time and the quality of the resulting sheet may be controlled by the present method. It is a particular advantage of the present invention that precipitation of rubber in the water as well as on the fibers does no harm to the processing characteristics of the slurry or to the sheet formed therefrom. In fact, with extraordinarily high amounts of rubber, it is a normal and expected part of

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the present method to accept precipitation of the rubber in the water and to utilize the situation to form a good sheet having an improved hand.

The present invention contemplates adding a water-soluble salt to the slurry of coated papermaking fibers which may or may not have rubber precipitated in the water. The water-soluble salts are those which result from the reaction of acetic acid or the inorganic mineral acids with the proper metallic compound. The inorganic mineral acids are typically hydrochloric acid, nitric acid, and sulfuric acid. The metallic portion—the cation—of the water-soluble salt to be added to the slurry will be any of the metals found in the groups of the periodic system mentioned earlier. Aluminum and chromium do not work in the control of processing characteristics of the slurry, probably because of the ease with which these two metals form anions with oxygen at an alkaline pH. The metals which function in the present method appear to do so by virtue of the nature of their behavior after the salt-containing slurry has been made alkaline, to be described below. Typical of the water-soluble salts which operate in the present method are lead acetate, manganous chloride, ferrous chloride, ferric chloride, calcium chloride, cobalt chloride, nickel chloride, and the corresponding nitrates and water-soluble sulfates thereof. There should also be mentioned magnesium sulfate, copper sulfate, zinc nitrate, cadmium sulfate, and beryllium sulfate, and the corresponding water-soluble chlorides thereof.

The water-soluble salts are preferably added in the form of their water solution, with agitation. The maximum amount of the salt to be added to control the drainage characteristics is determined by the weight of the cation portion of the salt. The weight of the cation portion of the salt should not exceed about 50% by weight of the uncoated fibers on a dry basis. Larger amounts of the salt are not only wasteful, but may impart a harshness of hand to the finished sheet. As to the minimum amount of salt to be added, quite small amounts are effective. Activity of the different operable water-soluble salts will differ, but a reasonable minimum may be established at about 0.1% by weight of the cation portion of the salt based on the weight of the uncoated fibers.

For ease of distribution of the solution of the water-soluble salt and water throughout the slurry containing the precipitated rubber, it is preferred to use a dilute solution on the order of 1%–5% by weight of the salt in water. This solution will be added with agitation in order to distribute the water-soluble salt thoroughly throughout the slurry.

After the water-soluble salt has been thoroughly distributed throughout the slurry of coated fibers, it is necessary to add sufficient caustic to adjust the pH of the slurry to a range 8.5–11.5, and preferably to 9.5. Although ammonium hydroxide, sodium hydroxide, or potassium hydroxide may be used, ammonium hydroxide may form soluble complexes with some of the metals used in making the water-soluble metal salt. Potassium hydroxide is comparatively expensive. For these reasons, sodium hydroxide is the caustic of choice. Preferably the caustic will be added in the form of its water solution, the concentration being any convenient concentration, a 10% solution of the caustic being a good average. Sufficient of the caustic solution is added with agitation to establish a pH within the above-mentioned pH range in the slurry, the target pH being 9.5. A pH higher than about 11.5 may unduly harm or react with the ingredients in the slurry, while a pH below about 8.5 is not high enough to achieve the full desirable effects of the present method. The pH of the resultant slurry may be checked in known manner with a suitable pH meter or test paper. Once the process has become stabilized in the commercial production of any particular product, the amounts of the ingredients will be known and occasional checks may be all that is required.

The final slurry, with its pH of about 9.5, is ready for dewatering as soon as the caustic has been thoroughly admixed. A product will be formed from the resulting slurry by removing water therefrom as by introducing the agitated slurry into a mold, or more preferably, onto a papermaking or feltmaking wire or cylinder. The drainage characteristics of the particular finished slurry will be found to be controllable by the amount of water-soluble metal salt that has been added within the limits described above. Increased amounts of the water-soluble salt increase the drainage time and decrease the Canadian 3-gram freeness. In accordance with the present method then, it is possible to decide exactly the drainage characteristics desired of the slurry under preparation, and adjust the water-soluble metal salt addition accordingly.

The present method lends itself to modifications involving the use of synthetic fibers in the form of staple fibers, notoriously difficult to handle in beater saturation processes. Synthetic fibers such as polyamide fibers, polyester fibers, poly(vinyl chloride) fibers, and other hard-to-handle fibers may be added to a slurry immediately after precipitation of the rubber as described above. The use of these synthetic fibers may be particularly desirable in using the extraordinarily large amounts of rubber contemplated as a modification of the present method as described and claimed in copending application Ser. No. 442,481, filed concurrently herewith.

As emphasized above, the method of the present invention particularly operates to speed up the drainage time of a slurry which otherwise would be too slow.

The following examples illustrate several embodiments of the invention. All parts are by weight unless otherwise stated.

Example 1

Two parts of refined 6D asbestos was dispersed in 1,850 parts of water. Thirty parts by volume of a 20% aluminum sulfate solution was then added with agitation, followed by the addition of sufficient 10% sodium hydroxide solution to obtain a pH in the slurry of 7.0. To the resulting slurry was added a butadiene-styrene copolymer latex (Tylac TM563) in an amount sufficient to add 6 parts dry weight of rubber. This amount is 300% by weight rubber based on the dry weight of the fibers.

After 15 minutes of agitation, all the latex had precipitated onto both the asbestos and the precipitated aluminum hydroxide.

The resulting slurry was divided into 8 equal portions, each of about 250 parts by volume, each containing one-quarter part of the original asbestos fiber. The different portions of the slurry were treated with various amounts of a 1.2% solution of magnesium sulfate, followed by the addition of 3 parts by volume of a 10% sodium hydroxide solution to achieve a pH of 9.5. Table 1 indicates the drainage characteristics of each portion of the beater saturated asbestos slurry using different levels of magnesium sulfate.

TABLE 1

Vol. of $MgSO_4$ solution, ml.:	Canadian standard freeness
¼	840
½	720
¾	570
1	400
1¼	310
1½	305
1¾	265
2	205

Example 2

A variety of runs was made using different binders and fibers, the binder being present in various amounts. Each run was made along the lines of the description in Example 1 in which a 20% solution of alum was added to the fibrous slurry, the pH brought to 7 with sodium hydroxide, the latex added with agitation, and sufficient

time allowed for the solids content of the latex to precipitate on the fibers and in the water. At this point in the precipitation, all the slurries except that containing 20% by weight of binder based on the weight of the fibers contained precipitated fines which passed right through the drainage wire and were lost in attempts to make sheets. The addition of caustic solution to achieve a pH of 9.5 alone without the prior addition of the water-soluble metallic salt caused the formation of large clumps from which a satisfactory sheet could not be made. However, the addition of a 1% magnesium ion based on the weight of the fibers, followed by the caustic treatment to a pH of 9.5, produced slurries that were easily handleable with no loss of fines and which formed acceptable sheets, all of the slurries then having Canadian standard freenesses in the range of 550–750.

Table 2 gives the data on the series.

TABLE 2

Run No.	Binder Type	Fiber	Percent Binder	Volume of 20% Alum Solution
1	Butadiene-nitrile	Asbestos	300	20
2	Neoprene	do	300	15
3	Butadiene-nitrile terpolymer.	do	300	15
4	Isoprene polymer	do	300	13
5	Butyl polymer	do	300	15
6	Natural rubber	do	300	15
7	Butadiene-styrene copolymer (Tylac TM563).	do	500	24
8	do	do	200	12.5
9	do	do	300	15
10	do	Cotton linters	300	12.5
11	do	Cellulose-bleached sulfide.	20	0.6
12	do	do	50	1.5
13	do	do	300	19
14	do	Leather	500	18
15	do	do	300	10
16	Butadiene-styrene copolymer (FRS-2000).	Unrefined cotton linters.	200	12.7

Example 3

Runs were made which duplicated Run 9 in Table 2, save that different metallic salts were added in different amounts to the precipitated slurry. The precipitated slurry before treatment was unsuitable for forming a sheet product due to the large amount of precipitated fines which were lost with the white water. The addition of caustic alone to a pH of 9.5 caused the formation of large clumps, again unsuitable for sheet formation. However, the addition of a 1% solution of the metal salt indicated in the amount indicated improved the sheet formation as opposed to either the untreated slurry, or the caustic treated slurry in the absence of the metal salt.

Table 3 identifies the metal salt and the volume of 1% by weight solution used.

TABLE 3

Metal salt:	Parts by vol., ml.
Lead acetate	2.5
Manganous chloride	5
Ferrous chloride	5
Ferric chloride	10
Calcium chloride	25
Cobaltous chloride	5
Nickelous chloride	2.5
Magnesium sulfate	1.5
Copper sulfate	5
Zinc nitrate	2
Cadmium sulfate	2.5
Beryllium sulfate	2.5
Barium chloride	20

The large amount of calcium chloride and barium chloride is apparently needed due to the presence of sulfate ion in the slurry.

I claim:

1. In the method of making beater saturated products by forming a slurry of fibes in water, precipitating a rubber binder on said fibers to form coated fibers, and forming a product from the coated fibers, the improved method of controlling the drainage time of the slurry of coated fibers which comprises adding to said slurry of coated fibers a water-soluble salt selected from the group consisting of metals in Groups I, II, IV, VII, and VIII of the Periodic Table, adding sufficient alkali to the salt-treated slurry to achieve a pH in the range of 8.5–11.5 to form an insoluble hydroxide with the metal ion from the salt, and forming a product from the resulting slurry.

2. A method according to claim 1 in which said rubber binder comprises a butadiene-styrene copolymer.

3. A method according to claim 1 in which said alkali comprises sodium hydroxide.

4. A method according to claim 1 in which said water-soluble salt comprises magnesium sulfate.

5. A method according to claim 1 in which said pH is 9.5.

6. A method according to claim 1 in which said fibers comprise asbestos fibers.

7. The product formed by the method of claim 1.

References Cited

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S. LEON BASHORE, *Primary Examiner.*