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METHOD OF MAKING BEATER-SATURATED WATER-LAID PRODUCT CONTAINING PAPER-MAKING AND TEXTILE STAPLE FIBERS

William A. Moggio and John M. Lesniak, Millersville, Pa., assignors to Armstrong Cork Company, Lancaster, Pa., a corporation of Pennsylvania

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This invention relates generally to the production of a beater saturated fiber sheet product which resembles a woven textile. More particularly, the invention relates to a beater saturated product which has the hand, drape, and feel of a textile product as opposed to the normal harsh and brittle feel of a paper-like product.

In copending application Ser. No. 442,482, filed Mar. 24, 1965, there is described a process of controlling the drainage characteristics of slurries of beater saturated, rubber-coated fibers. That process in general calls for the addition of a water-soluble metallic salt to the fibrous slurry containing the precipitated rubber binder, followed by the addition of alkali to achieve an elevated pH. The present process utilizes that process but includes certain additional features necessary to produce a strong, soft, textile-like sheet product.

Accordingly, the present process contemplates forming in water a slurry of papermaking fibers, and adding to the slurry an alum solution. After agitation, the alum-treated slurry is neutralized with alkali to a pH in the range of 6 to 8, preferably 7. To the neutralized slurry there is then added a rubber latex in an amount of 200%–650% by weight dry rubber solids based on the dry weight of the papermaking fibers. There is then added, in indifferent order, long staple fibers in an amount of 50%–900% by dry weight based on the dry weight of the papermaking fibers, and a water-soluble salt of a metal in Group I, II, IV, VII, or VIII of the Periodic Table. After thorough mixing of the long staple fibers and the metal salt with the rubber-coated papermaking fibers, alkali is added to achieve a pH in the range of 8.5–1 to 1.5 to form an insoluble hydroxide with the metal ion from the salt. A sheet may then be formed from the resulting slurry, and the sheet will possess textile-like characteristics.

The papermaking fibers to be used in the present process are the known papermaking fibers such as asbestos, glass, mineral wool, animal hair, leather, as well as the cellulosic fibers such as kraft, rag stock, soda, semi-chemical, ground-wood, sulfite stock, alpha pulp, cotton linters, 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 or otherwise refining the fibers in an aqueous medium.

The fibers may then be treated by the alum-ammonia process described in U.S. 2,375,245—Pretzel, or more preferably, by a modification thereof which may be referred to as the alum-caustic process. In this process, the refined fibers in water are treated with a solution of alum, preferably papermakers' alum. The solution of aluminum sulfate is simply poured into the slurry with agitation. The amount of alum to be used may be varied somewhat but will generally lie within the range of 1 to 6 parts by weight alum per 1 part by dry weight of the fiber to be treated.

After agitation, alkali will be added to the alum-treated slurry to bring the pH up to a range of 6–8, preferably 7. Although ammonium hydroxide may be used for such treatment, it is preferred to use an alkali metal hydroxide

such as potassium hydroxide, and preferably, sodium hydroxide. The addition of the alkali to achieve the stated pH will produce aluminum hydroxide, much of which deposits on the fibers themselves. Some aluminum hydroxide, may remain suspended in the water. The quantity in the water is dependent on the alum to fiber ratio. The neutralized slurry is then ready for the addition of the synthetic rubber binder.

These binders are those normally contemplated for use in the beater saturation processes. 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, although the tackiness characteristic of the lower styrene content is preferred in the binder solids. There may also be used the butadiene-acrylonitrile copolymers normally containing 50%–80% by weight butadiene, the neoprenes (polychloroprenes), the homopolymers of butadiene as well as homopolymers and/or copolymers of butadiene homologs such as isoprene all can be used as binders in the present system; the so-called butyl rubber latices are useful.

The synthetic rubber latex will simply be added to the neutralized slurry in the requisite amount. In order to form the textile substitute of the present invention, relatively huge amounts of rubber binder are necessary, based on the dry weight of the papermaking fibers. Therefore, an amount of synthetic rubber latex binder will be added to achieve a dry rubber solids content of 200%–650% by weight based on the dry weight of the papermaking fibers. Such a large amount of rubber solids has normally been avoided in the beater saturation arts in the past since it is almost unavoidable to precipitate some of the rubber solids in the water rather than on the fibers. In the present process, however, it is acceptable and even desirable when some of the rubber content of the latex precipitates on the aluminum hydroxide in the water as opposed to precipitating on the fibers themselves. It is one of the advantages of the present invention that such precipitation of rubber solids in the water actually enhances the final product. Accordingly, a notorious disadvantage is turned to an advantage in the present process. The mere addition with agitation of the synthetic rubber latex to the neutralized slurry will bring about precipitation of all the rubber solids in the latex. This precipitation normally occurs fairly rapidly and in any case will be completed within half an hour, and in most cases within 15 minutes or less.

Once the rubber has been precipitated, the slurry is in condition to receive the staple synthetic fibers or other fibers and the water-soluble metal salt. The uncoated fibers will normally have a length in the range of ⅛ inch to 1 inch and are added to the slurry of rubber-coated papermaking fibers in an amount of 50%–900% by weight based on the dry weight of the papermaking fibers themselves. The usual agitation suffices to distribute the staple fibers throughout the slurry. These staple fibers may be synthetic fibers such as rayon, acetate, polyamide fibers, polyester fibers, poly(vinyl chloride) fibers, and other hard-to-handle fibers as far as beater saturation is concerned.

After the staple fibers have been thoroughly distributed throughout the slurry, the water-soluble salt will then be added, if it has not been added prior to the addition of the staple fibers. It makes little difference in the process if the uncoated fiber or the water-soluble salt is first added to the slurry of coated fibers. These 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

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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% of 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, and after the uncoated fibers have been added, 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 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 slurry will then be formed into a sheet in a papermaking wire or cylinder, or other device. On drying, it will be found that the sheet has an extraordinary drape for a beater saturated, water-laid product, reminiscent of a textile. The hand is soft and there is little or none of the harshness or brittleness normally associated with a paper or felt product. The product does not crease in the normal sense of the word and, in some modifications, is surprisingly difficult to tear with the fingers in thicknesses of about 0.02 inch. Hence this product may be used in place of woven cloth and has many applications such as doilies, tablecloths, and certain items of clothing.

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

Example 1

A series of runs was made in which one part by weight of a papermaking fiber was dispersed in 1,850 parts water, and the slurry was refined. There was then added 15 parts by volume of a 20% by weight aluminum sulfate solution with agitation. Sufficient 10% sodium hydroxide solution was then added in each case to obtain a pH of 7.0. A synthetic rubber latex was then added with agitation. Following precipitation of the latex there was then added 8 parts by volume of a 1.2% by weight magnesium sulfate solution, followed by the addition of uncoated staple fiber, followed by the addition of sufficient 10% by weight sodium hydroxide solution to achieve a pH of 9.5. The following table illustrates the particular ingredients in the amounts used.

Weight and Type of Papermaking Fiber	Weight and Type of Staple Fiber	Weight and Type of Binder
1, leather	4, polyamide (nylon, ¼ inch)	3, butadiene-styrene copolyme.
1, asbestos	6, polyamide (nylon, ⅜ inch)	5, butadiene-styrene copolymr.
Do	6, regenerated cellulose (rayon, ¼ inch)	3, butyl rubber. er
Do	do	2, butadiene-styrene.
1, cotton linters	4, regenerated cellulose (rayon, ½ inch)	3, butadiene-styrene.
1, bleached sulfite	12, polyester (Dacron, ¼ inch)	Do.
1, asbestos	9, acrylic (Orlon, ¼ inch)	3, neoprene.
Do	6, glass, ¼ inch	Do.
Do	6, cellulose acetate, ¼ inch	3, butadiene-styrene copoly
Do	6, cotton linters	Do. mer.

Each of the finished slurries described above was formed into a sheet measuring 0.020 inch thickness, dried at 220° F., and cooled. Each sheet was soft and flexible and possessed none of the harshness and brittleness of normal paper and felt products. Each sheet had the hand and drape of a textile product. The second sheet in the above table, the one made with 1 part asbestos, 6 parts nylon, and 5 parts binder, was exceedingly strong and difficult to tear with fingers.

Example 2

Runs were made using 2 parts asbestos fibers in 1,850 parts water, followed by the usual alum-sodium hydroxide treatment, followed by addition of 6 parts (dry basis)

butadiene-styrene copolymer binder. 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. The following table identifies the metal salt and the volume of 1% by weight solution used.

Metal salt:	parts by volume, milliters
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.

We claim:

1. The method of forming a beater saturated, nonwoven textile substitute which comprises forming in water a slurry of papermaking fibers, adding alum to said slurry, adjusting the pH of the alum-treated slurry to a range of 6–8 by adding alkali thereto, adding a synthetic rubber latex in an amount of 200%–650% by weight dry rubber solids based on the dry weight of the papermaking fibers to the neutralized slurry whereby the solids content of the binder precipitates, adding to the resulting slurry in indifferent order long, staple fibers in an amount of 50%–900% by weight based on the dry weight of the papermaking fibers and a water-soluble salt of a metal 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 containing said staple fibers 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 sheet from the resulting slurry.

2. The method according to claim **1** wherein said alkali comprises sodium hydroxide.

3. The method according to claim **1** wherein said water-soluble salt comprises magnesium sulfate.

4. The method according to claim **1** wherein the pH adjustment of the alum-treated slurry is about 7 and the pH of the salt-treated slurry is about 9.5.

5. The method according to claim **1** wherein said synthetic rubber binder is added in an amount of about 500% by weight based on the dry weight of the papermaking fibers.

6. The method according to claim **1** wherein said staple fibers are added in an amount of about 400% by weight based on the dry weight of the papermaking fibers.

7. The method according to claim **1** wherein said papermaking fibers comprise asbestos fibers.

8. The method according to claim **1** wherein said staple fibers comprise nylon fibers.

9. A product made according to the method of claim **1**.

References Cited

UNITED STATES PATENTS

2,375,245	5/1945	Pretzel	162—169
3,057,772	9/1962	Magill et al.	162—146

S. LEON BASHORE, *Primary Examiner.*