June 14, 1960 D. A. FEIGLEY, JR., ET AL 2,940,892

ASBESTOS FIBER TREATMENT

Filed Sept. 3, 1957

Fig. 1

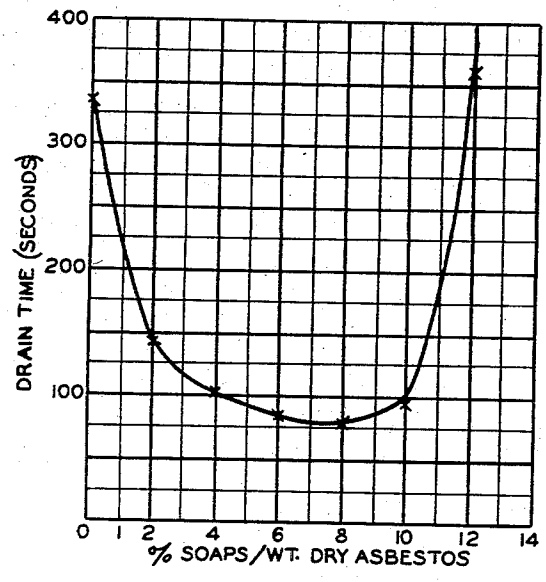
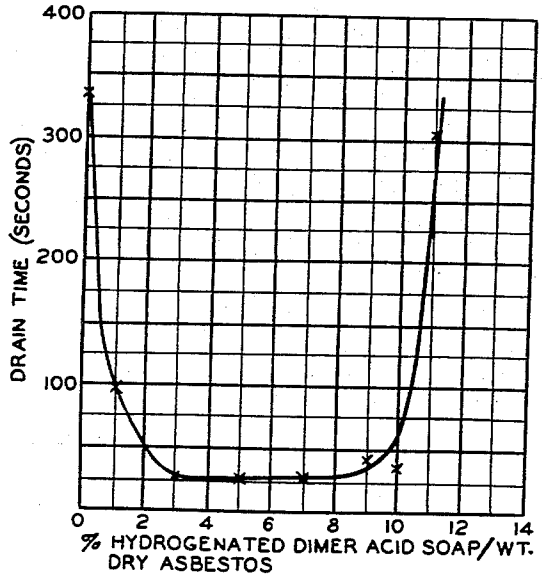


Fig. 2



INVENTOR
DAVID A. FEIGLEY, JR
LEONARD N. RAY, JR.
by
Theodore L. Thomas
ATTORNEY

Published by AsbestosClaims.Law
asbestosclaims.law/library/21805/1

United States Patent Office

2,940,892

Patented June 14, 1960

2,940,892

ASBESTOS FIBER TREATMENT

David A. Feigley, Jr., and Leonard N. Ray, Jr., Lancaster, Pa., assignors to Armstrong Cork Company, Lancaster, Pa., a corporation of Pennsylvania

Filed Sept. 3, 1957, Ser. No. 681,860

23 Claims. (Cl. 162—145)

This invention relates generally to fibrous sheets and more particularly to water-laid fibrous sheets. Still more particularly, the invention relates to fast-draining fibrous sheets containing chrysotile asbestos fibers, and to a process of making them.

In the past it has been very difficult to form asbestos sheets of substantial thickness on typical papermaking machines such as Fourdriniers and ordinary cylinder machines. This has been true in view of the very slow drainage characteristics of asbestos slurries. Such characteristics may be improved by deposition on the asbestos fibers of sufficient amounts of various kinds of rubber. However, where an asbestos sheet is desired with a very small amount of binder or without any binder at all on the fibers, the problem of slow drainage has been an insurmountable one. Additionally, it is often desirable to form sheets of mixtures of asbestos fibers with wood pulp, cotton linters, rag furnish, glass fibers, mineral wool fibers, and the like. Although the fibers to be mixed with the asbestos fibers might themselves possess excellent drainage characteristics, the mixture which includes asbestos fibers in a significant amount will have the poor drainage rates characteristic of asbestos fibers alone. Where the slurry is slow-draining, the resulting sheet after drainage is so wet and weak that wet pressing is very difficult; special equipment is needed to run at all. Hence, there is a definite need for a teaching relating to the improvement of the drainage characteristics of water-laid sheets comprising chrysotile asbestos fibers.

It is the primary object of the present invention to present such an improvement. It is the further object of the present invention to present a fibrous product which includes chrysotile asbestos fibers therein, which product possesses those characteristics necessary to render it fast-draining. It is a further object of the present invention to supply a method by means of which strong, water-laid, fibrous sheets of fibers comprising asbestos fibers may be readily prepared at high speed on standard papermaking equipment.

These objects are accomplished in a surprisingly effective and straightforward manner. The invention contemplates a sheet which has been made by forming in water a slurry comprising chrysotile asbestos fibers. To the slurry is added in critical amounts a water-soluble, aliphatic, organic compound having at least 10 carbon atoms therein. The compound must contain at least one carboxylic acid salt group. The compound may also have other reactive centers therein other than the carboxylic acid salt groups, and preferably contains olefinic groups, i.e., carbon-to-carbon double bonded unsaturation. The resulting treated slurry will be found to be fast-draining and suitable for the formation of a strong wet sheet. A sheet is then formed from the thus treated slurry in the usual manner.

It is known to treat bundles of asbestos fibers, particularly in rock form, with detergents and fatty acid soaps. Such treatment is set forth in U.S. 2,626,213—Novak, issued January 20, 1953, and U.S. 2,652,325—Novak,

issued September 15, 1953. These two patents teach the treatment of bundles of asbestos fibers with massive quantities of detergents and soaps for the purpose of separating the minute fibers one from the other. The patents disclose the enormous increase in drainage time when asbestos fibers are treated according to the teachings of the patents.

It remains to the present description, however, to point out that certain compounds, and—most important of all—critical quantities of those compounds yield an effect precisely opposite from that taught by the above-described patents.

The role played by use of critical amounts of the additives utilized by the present invention is best illustrated by reference to the drawings in which:

Fig. 1 illustrates the change in drainage rate of asbestos slurries of fixed consistency treated with increasing amounts of a monobasic carboxylic acid soap; and

Fig. 2 illustrates the change in drainage rate of asbestos slurries of fixed consistency treated with increasing amounts of a soluble hydrogenated dimerized carboxylic fatty acid soap.

Both figures illustrate the completely unobvious and unexpected discovery that asbestos fiber slurries treated as taught by the present invention undergo initially a sharply decreasing drainage time, passing through an early optimum drainage time, and swiftly rising to a value worse than that possessed by the untreated slurry.

It can readily be seen that the drainage times contemplated by the present description are so different in order of magnitude from those contemplated by the above-described patents that the difference is one of kind. This is emphasized by the fact that the change in drainage rate contemplated by the present invention is also in a direction opposite to that contemplated by the above-described patents.

The material contemplated for treatment in accordance with the present invention is chrysotile asbestos in the form of fibers and minute particles. These fibers may be used alone, or as mixtures with other papermaking fibers, or as mixtures of asbestos fibers with cement such as Portland cement. The chrysotile asbestos fibers must always be present since the present invention is directed at improving the drainage characteristics of asbestos fibers whether they be alone or in admixture with other fibers or with cement.

The amount of asbestos fibers present in a mixture of dissimilar fibers will range from 100% by weight chrysotile asbestos fibers on down to about 3% by weight asbestos fibers, based on the total dry weight of fibers present. The beneficial effects obtained from the use of asbestos fibers in mixtures of other fibers generally becomes insignificant when the amount of asbestos fibers to be used falls below about 3% by weight asbestos fibers based on the total weight of the fibers used. Less than 3% by weight asbestos fibers produces a mixture in which the effect of the asbestos is generally lost. Thus, the present invention contemplates sheets containing between about 3% and 100% by weight chrysotile asbestos fibers. Where fibers other than asbestos are to be incorporated into the sheet, the characteristics of those other fibers are relatively insignificant when contrasted with the drainage characteristics of the asbestos fibers in the mixture. Cellulosic fibers such as wood pulp, cotton linters, rag furnish, or noncellulosic fibers such as glass fibers, mineral wool, and any of the other papermaking fibers will all have their drainage times drastically increased when admixed with more than about 3% by weight asbestos fibers based on the total weight of the fibers. The present invention is particularly concerned in one modification with the preparation of specialty papers which contain chrysotile asbestos and sulfite pulp wherein the as-

Published by AsbestosClaims.Law
asbestosclaims.law/library/21805/2

bestos is present in the range of about 3–15% by weight based on the total weight of the fibers.

Where the asbestos fibers are to be mixed with a cement, the asbestos fibers will be present in an amount of 10–90% by weight of the asbestos-cement mixture. Within this range the amounts will vary according to the particular asbestos-cement product desired.

Although asbestos-cement compositions may vary widely in the relative quantities of asbestos and cement present, many of the compositions contain 40% by weight asbestos fiber and 60% by weight cement. This will be particularly true of those asbestos-cement compositions used as building boards. Such boards may be fabricated by laminating thin sheets followed by cure or by the formation of a sufficiently thick sheet in the first place. Where a thick sheet is to be formed, it is customary to use a hydraulic press to aid in removing the water from the asbestos-cement slurry. By means of the present invention, the time for the removal of such water is greatly reduced.

The asbestos-cement sheets and boards may be cured in any known manner. For example they may be cured for one month at room temperature, generally under moist conditions. Alternatively, they may be cured for a shorter period, for example, 24 hours at room temperature, followed by autoclaving at elevated temperatures for eight hours as is known in the art. Certain asbestos-cement products are manufactured wherein a portion of the cement is replaced with other materials such as quartz sand. Such replacement does not affect the present invention since the present invention is concerned with the treatment of the asbestos fibers in order to reduce the drainage rate of all aqueous slurries which contain the normally slow-draining asbestos fibers.

The forming of the slurry of fibers is accomplished by methods known in the art. The asbestos fibers and other fibers, if any, are taken up in water generally to a consistency in the range of about 0.5–5%. The slurry will generally be mechanically refined as in a beater, Jordan engine, disc refiner, and the like. Since asbestos fibers will always be present in the final slurry, it is often desirable to refine separately the asbestos fibers and any cellulosic fibers used; asbestos fibers may cause undue wear and erosion on certain of the tackle in the mechanical refiners. The slurries may be combined into a single slurry once the desired degree of refinement has been carried out. The consistency will be adjusted to that desired in order to produce a sheet having the desired properties. Thus, the consistency will usually vary between about 0.5–2% depending on machine speed, caliper of paper or felt to be produced, and the like. With the final slurry refined to the desired degree, there may then be carried out the step of adding to the slurry those compounds of the present invention which will control the drainage characteristics of the entire slurry.

These compounds may generally be defined as aliphatic, water-soluble salts of organic, carboxylic acids. As a further limitation, the compounds must contain at least 10 carbon atoms in the carbon chain of the acid. The compounds must contain at least 10 carbon atoms in the chain, since as will be shown, if the carboxylic acid chain contains less than 10 carbon atoms, the compound will not substantially improve the drainage rate of the asbestos fibers.

The compounds to be added are water-soluble salts of organic carboxylic acids of at least 10 carbon atoms. More than one carboxylic acid group may be present on the molecule. The compounds may be di-, tri-, or tetracarboxylic acids so long as they contain at least 10 carbon atoms. Aromatic organic carboxylic acids are inoperable; the acids must be aliphatic. However, the aliphatic chain may be aromatic-substituted, as in phenyl stearic acid. The carbon chain in the compound may possess other reactive groups, including unsaturated carbon-to-carbon bonds.

Water-soluble organic acid salts having large numbers of carbon atoms are especially suitable in the present invention. Such acids are best illustrated by the dimerized and trimerized fatty acids which are readily available in commerce. These acids are prepared by the thermal polymerization of drying oil acids carried out in a pressure vessel in the presence of water in the form of steam. The resulting compositions generally contain on the average about 3% monomer, 75% dimer, and 22% trimer. Such a product is known as dimerized fatty acids and will have an iodine value of approximately 90, and an acid number of approximately 190. The dimerized acid itself is essentially a 36-carbon dicarboxylic acid obtained by dimerization of the linoleic acid of soya, cottonseed, corn, and linseed oils of commerce. The product is frequently referred to as dilinoleic acid. This dimerized acid product may be purchased under the name "Empol 1022." It is apparent that the dimerized acids and the trimerized acids resulting from the above-described pressurized process may be separated or further concentrated as desired. Thus, the trimer acid may be purchased as such. The trimer acid is a 54-carbon acid and contains a plurality of carboxylic acid groups. As a further variation on the dimer and trimer acids, any residual unsaturation in the carbon chain may be eliminated by hydrogenation. The hydrogenated dimer acid may be purchased under the name "Emery 3020–S"; the predominantly straight trimer acid may be purchased under the name "Emery 3055–S." These polymerized fatty acids described above are pre-eminently suitable in the present invention and constitute a preferred embodiment thereof, particularly in unsaturated form.

Another class of acids which meets the definition of organic acids given earlier are those found in the various grades of wood rosin. Wood rosin contains as its primary ingredient abietic acid. The next most common organic acid in wood rosin is neoabietic acid. Smaller amounts of dihydroabietic acid, tetrahydroabietic acid, and d-pimaric acid are present, along with a minor amount of dihydroabietic acid. The various grades of wood rosins also contain small amounts of hydrocarbons and sterols which play no role in controlling the drainage characteristics of chrysotile asbestos fibers but which do no harm when wood rosin is used in soluble form.

Many commercially available fatty acids and fatty acid soaps meet the earlier described definition of those compounds which control the drainage characteristics of asbestos fibers. These soaps may be in solid or liquid form. As a general rule, liquid soaps are characteristic of the unsaturated higher fatty acids, and solid soaps are characteristic of the saturated higher fatty acids. As an example of such acids, there may be given "Neo-Fat 4212" which is a liquid and is a fatty acid mixture of 46% by weight oleic acid, 39% linoleic acid, 3% linolinic acid, the balance being a natural resin. As an example of the soaps, there is "P&G Soap" which is a mixture of the sodium soaps of stearic, oleic, and palmitic acids; this is a solid soap.

A further class of compounds useful in controlling the drainage characteristics of asbestos fibers are the maleic acid or maleic anhydride adducts (Diels-Alder reaction) of any of the unsaturated acids described above as for example, linoleic acid, oleic acid, dilinoleic acid, and the various rosin and polymerized rosin acids.

It will be appreciated that all of the above-described compounds meet the stated definition of aliphatic organic compound having at least 10 carbon atoms, said compound containing at least one carboxylic acid salt group.

As stated earlier, the compounds useful in the present invention must be converted to their water-soluble form. In view of the size of most of the molecules, the compounds are not generally per se soluble. They are, however, easily rendered soluble by reaction with an alkaline material such as ammonia, sodium hydroxide, potassium hydroxide, carbonates of ammonia, sodium, and po-

Published by AsbestosClaims.Law
asbestosclaims.law/library/21805/3

tassium, and even to some extent with alkaline earth metal compounds and organic amines. It must be emphasized that the compounds used in the present invention need not be very soluble to be operable. They are used in amounts much less than 0.1% by weight of the water, so easy solubility is not necessary. In the present specification and claims, it is contemplated that the defined organic carboxylic acids are rendered water-soluble where necessary by reaction of the acid with a solubilizing alkaline ingredient to form a salt. Thus, the compound to be used will be selected from the group consisting of water-soluble acids, water-soluble acid salts, and mixtures thereof.

The actual step of adding the organic acid salt to the asbestos-containing aqueous slurry is readily accomplished by simply physically adding the salt to the slurry. Preferably the salt will first be taken up in water to form an aqueous solution or suspension and the salt will be added in the form of that solution or suspension. Use of a solution aids in quick dispersion of the water-soluble acid throughout the slurry and hastens the reaction that takes place between the organic acid and the surface of the asbestos fiber.

The amount of organic acid to be used in the present invention is critical within a narrow range. It has been found that the addition of amounts of the organic acid greater than about 11% by weight based on the dry weight of the asbestos fibers causes a reversal of the dramatic improvement in drainage rate which is the essence of the present invention. Hence, as a practical matter, the amount of acid to be used—no matter what particular acid—will always be less than about 11% by weight based on the dry weight of the asbestos fibers. The precise amount less than this practical maximum will be determined to some extent by the particular organic acid salt used. Relative hardness of the water can cause some variation in the amount. As described earlier, those organic acid salts within the definition of those which control the drainage characteristics of asbestos fibers and which possess more than one carboxylic acid group on very long carbon chains have a more pronounced effect for the purpose intended than the monocarboxylic acid salts. Within these two extremes, varying degrees of activity will be encountered, depending on the precise number of carboxylic acid groups. The minimum amount of the salts to be added will run about 0.2% by weight based on the dry weight of the asbestos fibers; this is the amount at which the improved drainage rate becomes consistently noticeable. The preferred amount of the salt will generally be in the range of 3–8% by weight acid based on the dry weight of the fiber .

Once the organic acid has been added in the desired amount to the aqueous slurry comprising asbestos fibers, agitation will be carried out for a sufficient length of time to disperse the acid thoroughly throughout the slurry. This time generally runs about one to ten minutes. The temperature of the water, efficiency of agitation, consistency of the slurry, and like factors will control the agitation time. As stated earlier, the water-soluble organic acid salt reacts with the surface of the asbestos fiber and, since the reaction is fairly rapid, agitation need not be prolonged. This will be particularly true where the organic acid is added in the form of a water solution so that no time need be wasted waiting for the acid to dissolve in the water of the slurry.

After the reaction of the organic acid with the surface of the asbestos fiber, the slurry is formed into a sheet of paper or felt or board on standard papermaking equipment as, for example, a Fourdrinier wire or cylinder machine.

Drainage time of the slurry will be found to have been drastically reduced by treatment with the organic acid salt. Depending on the particular acid chosen, drainage time may be reduced to as little as one tenth of that of the untreated asbestos fibers. As mentioned earlier, the drainage time may be controlled by selection of the particular acid within the class of compounds defined which will produce the best drainage time in the formation of a particular sheet. Since the drainage time is reduced, the sheet formed is dryer and stronger and thus may be handled through wet presses on the machine in accordance with usual technics.

It is apparent that the usual sizing agents such as starch, casein, and cellulose gums may be used in conjunction with the sheetmaking processes described herein. Sizing and other processing variables may be carried out after the fibers have been treated and before the treated slurry is passed to the wire, or once the sheet has been formed on the wire. Hence, papers and felts made by the present process find a wide range of utility as writing and wrapping papers, as backing for floor and wall coverings, as gasketing materials, and the like.

For certain purposes it may be desirable to precipitate synthetic rubber binder onto the asbestos fibers, or mixture of fibers, to strengthen the sheet. Small amounts, generally 1–5% by weight rubber based on the weight of the fibers, will usually suffice for this purpose. Mere addition of the latex to the treated slurry followed by agitation will cause precipitation of this small amount of rubber onto the fibers. Where larger amounts of rubber are to be added, addition of a precipitating agent such as a solution of papermaker's alum will speed and complete the precipitation. The synthetic rubbers which can be used are those used in beater saturation processes and include butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, polychloroprene, and the like.

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

Example I

Chrysotile asbestos (5D) was refined for 15 minutes at 1.5% consistency in a Valley beater. When 40 parts of this refined asbestos was dispersed in 12,000 parts of water and formed into a sheet in a 12" x 12" Noble and Wood forming mold, the drainage time was 390 seconds. The resulting sheet after drainage was so weak and wet that wet pressing was extremely difficult.

The run was repeated save that various acids were added to the 40 parts of chrysotile asbestos fibers dispersed in the 12,000 parts of water prior to the forming of the 12" x 12" sheet. Each acid was added as a 16% solution in water to which sufficient potassium hydroxide had been added to render the solution slightly alkaline.

The following table illustrates the results:

Run No.	Organic Acid	Amount of Organic Acid Salt, Parts	Drain Time in Seconds
1	None	None	390
2	Neo-Fat 4212	3	110
3	P & G Soap	2	240
4	FF Rosin	3	98
5	FF Rosin	1.5	86
6	Stearic Acid	3	110
7	Myristic Acid	3	265
8	Decanoic Acid	3	305
9	Octanoic Acid	3	380
10	Empol 1022 (dimer acid)	3	37
11	Brassidic Acid	3	165
12	Emery 3020-S (hydrogenated dimer acid).	3	35
13	Emery 3055-S (trimer acid)	1.5	39
14	Phenyl Stearic Acid (mixture of 9- and 10-substituted).	3	47

Neo-Fat 4212 is a mixture of oleic acid, 46%; linoleic acid, 39%; linolinic acid, 3%; and a resin, 12%. P & G Soap is a mixture of the sodium salts of stearic, oleic, and palmitic acids; it was added as such in water solution. In all runs except run 3 the water-soluble acid solution was prepared by dissolving 100 parts of the

acid, 25.5 parts KOH, in 495.5 parts water. Sufficient of this solution was used to give the amount of acids shown in the above table.

It can be seen that run 9 which used octanoic acid, an 8-carbon acid, gave substantially no improvement over the control which used nothing. However, run 8, which used decanoic acid, a 10-carbon acid, produced better than a 20% decrease in drainage time.

Example II

Into 12,000 parts of water was dispersed 40 parts sulfite pulp. The drainage time of this slurry under the conditions of Example I was 29 seconds; the Canadian 3-gram freeness was 320 seconds. Portions of the sulfite pulp were replaced with asbestos fibers to determine drainage rates of the mixture. Following are the results:

Sulfite Pulp, Parts	Asbestos Fibers, 5D Parts	Canadian Freeness	Drain Time in Seconds
40	None	320	29
38	2	260	41
36	4	200	55
34	6	170	72

When the mixture of 34 parts sulfite pulp and 6 parts asbestos fibers in water was treated with 0.44 part of Neo-Fat 4212 solubilized as in Example I, the drainage time was 26 seconds and the Canadian freeness was 360.

Example III

Into 3,500 parts of water was placed 40 parts asbestos fiber. The resulting slurry was beaten for 15 minutes in a Valley laboratory beater. Portland cement in the amount of 40 parts was dispersed in 500 parts water in a Waring Blendor for three minutes and then added to the asbestos slurry with agitation. The asbestos cement slurry was then poured into a 12" x 12" mold to a level of 5¾" above the screen. Drainage time was 268 seconds.

A run identical to that described above was made except that the asbestos fibers were treated with a solution containing 1.5 parts (dry basis) of the potassium salt of a hydrogenated dimerized acid (Empol 3020) prior to the addition of the cement slurry. The drainage time was 75 seconds.

We claim:

1. A water-laid sheet comprising chrysotile asbestos fibers whose surfaces are reacted with about 0.2–11% by weight based on the dry weight of the fibers of a water-soluble salt of an aliphatic organic compound having at least 10 carbon atoms, said compound being selected from the group consisting of fatty acids, polymerized fatty acids, rosin acids, polymerized rosin acids, the reaction product of an unsaturated organic acid and a compound selected from the group consisting of maleic acid and maleic anhydride, and mixtures thereof.

2. A sheet according to claim 1 wherein said compound is a polycarboxylic acid.

3. A sheet according to claim 2 wherein said polycarboxylic acid contains 36 carbon atoms.

4. A sheet according to claim 2 wherein said polycarboxylic acid contains 54 carbon atoms.

5. A sheet according to claim 1 wherein said compound is saturated.

6. A sheet according to claim 1 wherein said compound is unsaturated.

7. A sheet according to claim 1 wherein said compound is a polycarboxylic acid possessing olefinic unsaturation.

8. A sheet according to claim 1 wherein said compound is a saturated polycarboxylic acid.

9. A sheet according to claim 1 comprising a mixture of asbestos fibers and cellulose fibers, said asbestos fibers being present in an amount of 3–15% by weight of the mixture.

10. A sheet according to claim 1 comprising a mixture of asbestos fibers and cement, said asbestos fibers being present in an amount of 10–90% by weight of the mixture.

11. A sheet according to claim 10 containing about 40% by weight asbestos fibers.

12. A sheet according to claim 1 having a synthetic rubber binder deposited on the reacted surfaces of the asbestos fibers.

13. The process of making a fibrous sheet comprising chrysotile asbestos fibers which comprises forming in water a slurry comprising chrysotile asbestos fibers, adding to said slurry a water-soluble salt of an aliphatic, organic compound having at least 10 carbon atoms in an amount of about 0.2–11% by weight based on the dry weight of the asbestos fibers, said compound being selected from the group consisting of fatty acids, polymerized fatty acids, rosin acids, polymerized rosin acids, the reaction product of an unsaturated organic acid and a compound selected from the group consisting of maleic acid and maleic anhydride, and mixtures thereof, and forming a sheet from the thus treated slurry.

14. The process according to claim 13 wherein said compound comprises a polycarboxylic acid.

15. The process according to claim 13 wherein said compound is a saturated compound.

16. The process according to claim 13 wherein said compound comprises an unsaturated compound.

17. The process according to claim 13 wherein said compound comprises an unsaturated polycarboxylic acid.

18. The process according to claim 13 wherein said compound comprises a saturated polycarboxylic acid.

19. The process according to claim 13 wherein cement is added to the slurry of salt-treated fibers.

20. The process according to claim 13 wherein a synthetic rubber is deposited on the salt-treated fibers prior to the sheet-forming step.

21. The process according to claim 13 wherein said slurry comprises a mixture of asbestos fibers and cellulosic fibers, said asbestos fibers being present in an amount of at least about 3% by weight based on the total dry weight of the fibers present.

22. The process according to claim 21 wherein said added compound comprises an unsaturated polycarboxylic acid.

23. The process according to claim 21 wherein said added compound comprises an unsaturated monocarboxylic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,626,213	Novak	Jan. 20, 1953
2,652,325	Novak	Sept. 15, 1953
2,759,813	Feigley	Aug. 21, 1956
2,772,970	Feigley	Dec. 4, 1956

Published by AsbestosClaims.Law

asbestosclaims.law/library/21805/5