Patented Sept. 10, 1946

2,407,581

UNITED STATES PATENT OFFICE

2,407,581

ASBESTOS SHEET MATERIAL

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No Drawing. Application February 9, 1945, Serial No. 577,162

9 Claims. (Cl. 117—118)

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This invention relates to asbestos products and relates especially to products which comprise fibrous material containing asbestiform mineral fibers disposed in intimately contacting relation as by felting or other operation adapted to form a sheet or sheet-like body.

The asbestos products which find most extensive commercial use are asbestos sheet materials that are usually produced by water laying and that are generally referred to as asbestos paper or asbestos "millboard," which is referred to herein generally as "paper." The bulk of the asbestiform mineral fiber that is used in asbestos paper usually runs from about $\frac{1}{16}$'' to $\frac{1}{4}$'' in length, although the fiber that is supplied for paper making generally contains a considerable quantity of shorter fibers of varying lengths and may contain a portion of longer fibers. The most generally accepted system of classification of asbestos fibers is that of the Quebec Asbestos Producers Association. The asbestos fibers which are most commonly used for the manufacture of asbestos paper are those which range from the group 5 or paper classification to the group 7 or shorts classification of the Quebec Asbestos Producers Association, or mixtures thereof.

In the manufacture of asbestos paper from asbestos fibers of the character aforesaid, the water-laying of the fibers to produce the felt is somewhat more difficult than the water-laying of ordinary paper or felts from cellulosic fibers due to the fact that the asbestos fiber forms a pulp which is "slow," namely, a pulp from which water does not drain readily. Consequently, asbestos paper is usually prepared on the multi-cylinder machine, each cylinder picking up a thin layer of the felted asbestos fibers from the water suspension in the cylinder vat and these layers being plied together on the machine to produce paper products of the desired thickness. The plying of a plurality of thin layers of asbestos fibers also tends to afford somewhat greater strength than otherwise would be the case if a single thick layer of corresponding weight were produced. Usually asbestos paper contains from three to six plies of the relatively thin water-laid asbestos fiber web produced on the individual paper forming cylinders of a multi-cylinder machine.

An asbestos paper of the character aforesaid has very little strength in the absence of a binder. Hydration by "beating," as employed for the development of strength in cellulosic papers, is ineffective with the inorganic asbestos fiber and merely results in the shortening of the fiber with

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consequent actual loss of strength of the resulting asbestos paper. The strength of the asbestos paper can be somewhat increased by the employment of asbestos fibers which are longer than the asbestos fibers usually used in the manufacture of asbestos paper. There are, however, objections to the use of long asbestos fibers in the manufacture of asbestos paper. In the first place, long asbestos fibers are of much higher cost and are usually reserved for spinning purposes. Asbestos fibers of intermediate length, namely, between the long spinning fibers and the relatively short fibers used for making asbestos paper, are generally used for reinforcement purposes, e. g., as a reinforcement in the manufacture of heat insulation materials and the like which consist in major proportion of finely-divided non-fibrous heat-resistant material that is reinforced by the asbestos fibers. Another reason why the long fibers are not used in the manufacture of asbestos paper is the fact that long fibers are difficult to form into uniform sheets from the aqueous suspension in a paper-making operation. The long fibers tend to form into clumps which result in the formed paper in slots of fiber with thin or open spaces deficient in fiber therebetween. Moreover, only a slight increase in strength is afforded by the employment of long asbestos fibers in the manufacture of asbestos paper. This invention is of particular utility in the manufacture of products from the more common and less expensive fibers of the paper-making grades mentioned above.

It has heretofore been standard practice in the manufacture of asbestos paper to use starch as the binder material for imparting strength to the paper, since starch has been found to be the most effective and economical binder for webs comprising asbestos fibers. The starch may be used in varying amounts depending upon the strength to be imparted to the asbestos paper and depending upon the purpose for which the asbestos paper is intended.

When starch is used as a binder for asbestos paper, the resulting product has the serious drawback of having virtually no resistance to water. Thus, when a piece of starch-bonded asbestos paper is placed in water, the fibers are liberated and become dissociated into a pulpy mass in only a few seconds time. It is a matter of not infrequent occurrence for an installation utilizing asbestos paper to become moistened by water as a result of accidental exposure to the weather or the breaking or leaking of a water or steam line. Starch-bonded paper has such extremely low wa-

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ter resistance that serious damage may result from such casual contacts with water. Starch-bonded paper is likewise adversely affected by humid atmosphere and when subjected to humid atmosphere becomes greatly weakened with resultant sagging and likelihood of permanent damage. It is because of poor resistance to humid atmosphere that starch-bonded asbestos paper is not recommended for use below grade, e. g., in basements, tunnels, underground conduits, etc.

There are known binders which are water-insoluble and that have been used to a very limited extent for bonding asbestos paper. For example, rubber latex and synthetic rubber-like materials which are generally referred to as elastomers have been used. However, such materials are considerably more expensive than starch. Moreover, asbestos paper is generally used in situations where there is likelihood of exposure to high temperatures and rubber or rubber-like compounds are objectionable for such purpose, because of the malodorous vapors and smoke that are evolved when such compounds are subjected to heat. Ordinary organic binders such as casein, soya protein, glue, rosin and the like have not been found to be suitable for the manufacture of asbestos paper. There are certain types of water-resistant synthetic resins which are used to bond asbestos paper, but their cost is so great that their use is impractical for any but specialized uses.

It is a purpose of this invention to provide a binder for asbestos paper which is inexpensive, which can be readily applied, and which, after application, affords an asbestos paper or other asbestos containing fibrous body which is highly resistant to moisture and to water.

We have discovered that certain oxalates have the property of bonding asbestiform mineral fibers and that the bonded fibers resist disintegration when subjected to water so as to provide highly water-resistant asbestos products such as asbestos paper. As typical of such substances, oxalic acid has been found to possess this peculiar property of bonding asbestos fibers, and of providing a bond which is resistant to moisture. The action of the oxalic acid is not understood but appears to be specific between the substance of the asbestiform mineral fibers and the oxalic acid.

The manufacture of a strong, coherent and water-resistant asbestos paper according to this invention may be illustrated as follows: Asbestos paper, which may be any of the usual paper grades of asbestos fiber heretofore used in the manufacture of asbestos paper products, is made up into an aqueous furnish according to conventional methods used in the manufacture of asbestos paper and the furnish is made up into sheet material on a paper-making machine in the usual way until an asbestos paper is produced having the ultimate thickness and weight desired. The paper thus produced is free of any binder, and, after it has been formed, it is subjected to drying as by passing it over a plurality of drying rolls. According to this invention, the asbestos paper, which has been formed and dried, has a solution of oxalic acid applied thereto by any suitable means which may be in the form of a transfer roll for contacting one or both sides of the sheet, spray application, tub sizing or the like. The extent to which the paper is dried before the oxalic acid is applied may be merely sufficient to enable the oxalic acid to penetrate

into the paper. Preferably, however, the paper is substantially completely dried (so that it will contain less than about 5% by weight of moisture) before the oxalic acid is applied, since by so doing the absorption of the oxalic acid into the paper is more complete and is more uniform. After the oxalic acid has been applied, the paper is again dried as by passing it over drying rolls which may be heated to conventional drying temperature such as 200 to 300° F., although the heating is not material and, if desired, may be omitted. The dried paper may, for example, contain about 5% or less of retained moisture although the extent of drying is not critical. After the paper has been dried, it ordinarily is wound on a reel, trimmed to desired width and made up into rolls as is conventional in paper-making operations.

The above-described process can advantageously be carried out in a single and continuous operation by applying the oxalic acid to the asbestos paper at an intermediate stage during the passage of the asbestos paper over the drying rolls of a conventional machine for the manufacture of asbestos paper products.

The concentration of the oxalic acid that is applied to the asbestos paper is not critical. Usually, the acid is applied to the paper when diluted with water so as to be of about 10% to about 20% concentration. The strength of the asbestos paper product is increased somewhat upon increasing the concentration of the oxalic acid that is applied thereto up to a concentration of about 30%, but the amount of strength that is imparted to the asbestos paper is not proportional to the concentration of the oxalic acid that is employed.

The effectiveness of the bonding that may be afforded between the fibers of an asbestos paper may be illustrated in connection with the following example. If asbestos paper is made by a conventional paper-making operation so as to weigh about ten pounds per 100 square feet, the resulting web or sheet when dried and without having had any binder included in the furnish, has a tensile strength of only about two pounds per linear inch of width in the machine direction of the sheet and a tensile strength of only about one-half pound per linear inch of width across the sheet. Upon applying oxalic acid of about 20% concentration to the sheet material so that the sheet material will take up about seventy pounds of the dilute oxalic acid solution for each one hundred pounds of the asbestos sheet and then drying the sheet, the resulting product has a tensile strength in the machine direction of the sheet of about thirteen pounds per linear inch of width and about five pounds per linear inch of width across the sheet. The tensile strengths that are given above and elsewhere herein are as determined by the method prescribed in A. S. T. M. standard D202–41T using a Scott tensile testing machine, the test specimens of paper having been conditioned at 45% relative humidity at 77° F. for four hours before testing.

The asbestos paper which has been bonded by the application of oxalic acid thereto is notable for its capacity to retain its structural integrity and a substantial part of its dry strength when contacted with water. A very severe accelerated test for determining the resistance of asbestos paper to water consists in immersing a small sample of the product (about 1 x 2 inches) in boiling water. Failure, if it occurs, is taken as the point at which the binder no longer acts to hold the

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fibers together, the fibers becoming liberated to form a pulpy mass. When subjected to the boiling water test, the asbestos paper, wherein the absestos fibers had been bonded together by the action of the oxalic acid, successfully withstood the boiling water test for over 90 minutes. The test was discontinued at that time because the paper had not disintegrated and there was no indication that longer exposure to boiling water would result in disintegration of the paper. Under similar conditions, a starch-bonded asbestos paper disintegrates virtually immediately.

In addition to oxalic acid, we have found that the water-soluble acid salts of oxalic acid, namely, ammonium acid oxalate, sodium acid oxalate and potassium acid oxalate are likewise effective in affording a water-resistant bonded asbestos paper or other body comprising asbestiform mineral fibers. Ammonium oxalate is likewise satisfactory. These substances differ somewhat in their effectiveness and the concentration of the solution that is applied to the asbestos paper will vary somewhat, depending upon the particular oxalate used, but the concentration is generally of the order of that above mentioned in connection with the use of oxalic acid.

Sodium oxalate and potassium oxalate also have the peculiar property of bonding asbestos paper or the like so that it will have good dry strength; but these particular oxalates do not provide a large increase in water resistance. However, since the employment of such oxalates is new and is of advantage under some circumstances, the employment of water-soluble oxalates for bonding fibrous bodies comprising asbestiform mineral fibers is to be regarded as coming within the scope of this invention in its broadest aspects. In this connection, oxalic acid is regarded as hydrogen oxalate and as being included within the term oxalate.

When oxalic acid or other oxalate is used to bond the fibers of asbestos paper, it is not essential that starch be omitted. When the oxalate is of the class aforesaid which affords high wet strength, the presence of starch does not detract from the obtainment of high wet strength and improves the dry strength. For example, asbestos paper weighing about 10 pounds per 100 square feet may be made containing about 1% of starch and, after drying, have applied thereto a 10% solution of oxalic acid. The tensile strength of such product in the machine direction of the sheet is about 12 pounds per linear inch of width, as compared with about 5 pounds per linear inch of width when the starch was not present. The effect of the starch is considerably in excess of the purely additive effects of the starch and oxalic acid, for asbestos paper containing 1% of starch only has a tensile strength of about 3 pounds per linear inch of width. In other words, there is a special coaction which results from the combination of the starch with the oxalic acid.

When this invention is practiced using starch, any amylaceous material may be employed such as cornstarch, wheat starch, potato starch, tapioca starch, rice starch, etc. Modified starches, including those that have been modified by heat treatment, oxidation, enzyme action, acid treatment or other analogous treatment may be employed and are to be regarded as embraced by the term amylaceous material.

The asbestos paper that is produced according to this invention is flexible and bibulous and is well adapted for the various uses to which asbestos paper is particularly suited. Typical embodiments of this invention will take up 30% or more of water and preferably 40% or more of water when immersed in water at 77° F. for five minutes. In referring to the sheet material produced according to this invention as being flexible, it may be mentioned as typical that sheets having a thickness up to .050 inch or less may be bent 180° around a mandrel 1.5 inches in diameter in two seconds at 77° F. without rupture or breaking at the surface and are thus of a suitable degree of flexibility for fabrication purposes. Thin sheets are, of course, more flexible than thick ones and the flexibility can, if desired, be further increased by calendering or other manipulative treatment of the sheet after it has been dried.

It is not necessary that the new product of this invention be fabricated in the manner above described, namely, by the water-laying of a felted sheet of asbestos fibers. Thus, the asbestos fibers may be brought into intimately associated felted relationship in other ways either wet or dry. In this connection, operations such as carding, garnetting and the like, which accomplish a deposition of air-borne fibers to form a sheet-like body, are to be regarded as providing "felted" fibers as the term "felted" is used herein and in the claims. More generally, all that is required is the disposition of the asbestiform mineral fibers in intimately contacting relation in a fibrous body and the application thereto of a solution of an oxalate so that the action that occurs between the asbestiform mineral fiber and the oxalate occurs in situ with resultant bonding action of the character herein described.

It is not essential that the oxalate be applied during the production of the asbestos paper. For example, if desired, asbestos paper may be first incorporated in a product, e. g., as a surfacing for a heat insulation, and thereafter may be treated with a solution of oxalic acid, an acid salt of oxalic acid, or ammonium oxalate, as by brush application. After drying, the asbestos paper will be found to be highly resistant to moisture.

It is not essential that the asbestos paper or other sheet-like body or product be composed entirely of asbestos paper. For example, asbestos paper may, and frequently does, contain a minor proportion of organic fiber such as ordinary cellulosic paper fiber. It is also possible to include in the asbestos paper mineral fibers such as rock wool, slag wool, glass fibers and the like which are heat-resistant, but such fibers have the disadvantage of being more brittle and frangible than asbestos fibers. It is normally desirable that the asbestiform mineral fibers constitute the major proportion by weight of the fibers and of the finished product.

In the ordinary case, according to this invention, the usual asbestos fiber of commerce may be used, namely, chrysotile asbestos fiber. In addition to chrysotile asbestos fiber, other asbestiform mineral fibers may be used, such as anthophyllite, actinolite, tremolite, crocidolite, amosite, various amphibole fibers, Canadian picrolite, and the like.

In addition to the fiber and the bonding components of the asbestos products produced according to this invention, the product may include a minor quantity of filler material. For example, a small quantity, e. g., of the order of 5% to 10% of the weight of the fiber, of a material such as diatomaceous earth, may be employed. A filler such as diatomaceous earth does not have an adverse effect on the porosity and absorptiveness of the paper and usually increases these properties,

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Another filler that affords considerable porosity is pumice. Moreover, other fillers such as clay, talc, pigments to impart suitable color, etc., may be employed. Ordinarily, the filler, like the asbestos, will be heat resistant, namely, will not decompose or char when exposed to temperatures of the order of 900° F. It is usually desirable that the major proportion of the fiber plus any filler contained in the product should consist of asbestiform mineral fibers and, for providing resistance to heat, the fiber plus any filler contained therein should contain less than 10% of organic material or other nonheat resistant material. For most fabrication purposes, the asbestos product should contain less than about 20% by weight of material other than the fiber plus any filler contained therein.

We claim:

1. A coherent fibrous body wherein the fibers consist in major proportion by weight of asbestiform mineral fibers, said asbestiform mineral fibers being bonded by the interaction in situ between said asbestiform mineral fibers and a water-soluble oxalate.

2. A coherent fibrous body according to claim 1 wherein said asbestiform mineral fibers are bonded by said oxalate in combination with an amylaceous material.

3. A product comprising felted fibers disposed in a sheet-like water-resistant body, said sheet-like body comprising asbestiform mineral fibers which constitute the major proportion by weight of the fiber plus any filler contained in said sheet-like body, said asbestiform mineral fibers being bonded by the interaction in situ between said asbestiform mineral fibers and oxalic acid.

4. A product comprising felted fibers disposed in a sheet-like water-resistant body, said sheet-like body comprising asbestiform mineral fibers which constitute the major proportion by weight of the fiber plus any filler contained in said sheet-like body, said asbestiform mineral fibers being bonded by the interaction in situ between said asbestiform mineral fibers and an acid salt of oxalic acid.

5. A product comprising felted fibers disposed in a sheet-like water-resistant body, said sheet-like body comprising asbestiform mineral fibers which constitute the major proportion by weight of the fiber plus any filler contained in said sheet-like body, said asbestiform mineral fibers being bonded by the interaction in situ between said asbestiform mineral fibers and ammonium oxalate.

6. A flexible coherent bibulous sheet-like body which consists in major proportion by weight of asbestiform mineral fibers, the asbestiform mineral fibers in said sheet-like body being bonded by the interaction in situ between said asbestiform mineral fibers and a water-soluble oxalate.

7. A product comprising felted fibers disposed in a sheet-like water-resistant body according to claim 3 wherein said asbestiform mineral fibers are bonded by said oxalic acid in the presence of an amylaceous material.

8. A product comprising felted fibers disposed in a sheet-like water-resistant body according to claim 4 wherein said asbestiform mineral fibers are bonded by said acid salt of oxalic acid in the presence of an amylaceous material.

9. A product comprising felted fibers disposed in a sheet-like water-resistant body according to claim 5 wherein said asbestiform mineral fibers are bonded by said ammonium oxalate in the presence of an amylaceous material.

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