

UNITED STATES PATENT OFFICE

2,567,558

ASBESTOS SHEET MATERIAL AND METHOD OF MANUFACTURE

Harold W. Greider and Marion F. Smith, Wyoming, Ohio, assignors to The Philip Carey Manufacturing Company, a corporation of Ohio

No Drawing. Application December 29, 1944,
Serial No. 570,477

15 Claims. (Cl. 117—126)

1

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 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 fibers are waterlaid in felted relation by a paper making operation, a multicylinder paper making machine generally being used for the purpose.

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 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

2

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 clots 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.

In addition to the starch, other organic binder materials have had limited use in connection with asbestos paper, such as rubber latex and various synthetic rubber-like materials which are generally referred to as elastomers. Ordinary organic binders such as casein, soya protein, glue, rosin and the like have not been found to be suitable for use in the manufacture of asbestos paper. Synthetic resins of various types may be used as a binder for asbestos fibers but their cost is extremely high and for this reason their use for most purposes is not practical.

The use in asbestos paper or other asbestos-containing products of an organic binder material such as starch is objectionable for several reasons. The most serious objection is due to the fact that an organic binder material lacks the high resistance to heat which is possessed by asbestiform mineral fibers and which constitutes the main reason for use of such fibers instead of the much less expensive organic fibers. Asbestos fiber is capable of withstanding sustained temperatures of about 900° F. to 1000° F. without excessive deterioration. Moreover asbestos fiber, being inorganic, is non-combustible, and can be exposed directly to a flame without burning or smoking. Other advantages of asbestos fiber which make its use desirable result from the fact that asbestos fiber is unaffected by water and is not subject to rotting or other gradual deteriora-

tion due to moisture. Moreover, asbestos fiber is not subject to attack by organisms which result in mildew, mold, fungus growths or the like and is not attractive to, or destroyed by, vermin.

When an organic binder is used in conjunction with asbestos fiber, its presence as a binder is disadvantageous since an organic binder lacks virtually all of the desirable properties of the asbestos fiber. An organic binder, if present in an asbestos paper, will start to decompose gradually at temperatures as low as 250° F. during period of prolonged exposure. Temperatures of 300° F. are actively destructive to organic binder materials contained in asbestos paper, while at temperatures of 350° F. an organic binder will char in a matter of a few hours time. At temperatures of 400° F. and higher an organic binder will smoke and char immediately. When the organic binder in an asbestos paper or other product is disintegrated due to temperature conditions such as those above mentioned, it loses its effectiveness as a binder with the result that the asbestos product becomes lacking in strength to an excessive degree and goes to pieces. As a result of this fact, the use of asbestos paper containing starch or other organic binder material for heat insulation purposes has been limited to conditions such that only relatively mild temperatures are encountered, namely, temperatures under about 300° F. As far as the asbestos fiber itself is concerned, it could be used at considerably higher temperatures, namely, temperatures up to about 900° F. to 1000° F. and would have wide commercial utility for use at such temperatures, but no binder has heretofore been found which is suitable as a binder for asbestos paper and which will not disintegrate excessively at temperatures above about 300° F.

The extent to which an organic binder is objectionable because of its lack of resistance to heat depends in part upon the amount of binder that is used. If the amount of binder is relatively low, such as of the order of about 5% or less by weight of the asbestos paper, the binder will not burn so as to produce a flame but it will discolor and also will char and smoke in a manner that is objectionable. If additional organic binder is used, e. g. 10 to 15% by weight, the binder in the asbestos paper may actually burn with a free flame. Regardless of the amount of binder that is used, any organic binder, such as starch, rubber, glue, resin or the like, tends to give off suffocating fumes when heated, such fumes being a hazard to life and objected to by Underwriters' Laboratories, Inc., and by the National Board of Fire Underwriters as dangerous to public safety. Moreover, some gases which are given off are combustible and may even be explosive and present a further hazard for this reason. The more gradual deterioration and disintegration of organic binder material, as a result of prolonged exposures to elevated temperatures will, of course, take place regardless of amount of binder that is employed.

Other objections to use of organic binder are lack of resistance to water and moisture, rotting, molding, and attractiveness to vermin.

Summarizing the foregoing, the use in paper or other products of asbestiform mineral fibers is highly advantageous due to the resistance of asbestiform mineral fibers to heat, to water, to rotting and other deteriorating influences. However, when organic binders are employed, the organic binders are lacking in the characteristic properties which make the use of asbestos fibers desirable and the uses to which the asbestos prod-

uct can be put become limited due to the undesirable properties and limitations of the binder material used.

It is possible to use certain inorganic binders with asbestos fibers, but the products which result from the use of inorganic binder materials have been limited to rigid and boardy products which are cementitious in character.

It is the principal purpose of this invention to bond together the fibers of an asbestos product without the use of an organic binder and without rendering the product stiff and boardy as is the case when substances such as Portland cement or soluble silicates are used as binder materials. It is a further purpose of this invention to afford asbestos products such as asbestos paper, sheets or the like having high resistance to heat, moisture, rot and other destructive influences. It is a further object of this invention to provide novel heat insulation material, board-like products, and other products fabricated from sheets of felted asbestos fibers that have been interbonded according to this invention.

We have discovered that asbestiform mineral fibers which have been produced in the form of a felted sheet-like body can be bonded together by the interaction of the asbestiform mineral fiber with a solution of a water-soluble inorganic compound containing a sulphate anion to form a coherent body that is flexible and porous, but that has much more strength than an untreated sheet of felted asbestiform mineral fibers. The interaction that occurs between the solution of the compound and the asbestiform mineral fiber is not definitely understood, but appears to be specific between the substance of the asbestiform mineral fibers and water-soluble inorganic compounds forming a sulphate anion in water solution. Numerous other inorganic compounds do not have such effect and may even decrease rather than increase the strength of the felted sheet material. While there appears to be some action of the compound on the surface of the asbestiform mineral fiber which affords a bonding material that bonds the asbestiform mineral fibers together where they come into contact when the fibers are subsequently dried en masse, the asbestiform mineral fibers retain their characteristic fibrous character and the resulting felted sheet after treatment has the desired bibulous and flexible character of asbestos paper.

The manufacture of a strong and coherent asbestos paper without the employment of any organic binder according to this invention may be illustrated as follows. Asbestos fiber, 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 formed 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 sulphuric acid, for example, applied thereto by any suitable applying means which may be in the form of a transfer roll contacting one or both sides of the sheet, spray application, tube sizing or the like. The extent to which the paper is dried before the acid is applied may be merely sufficient to enable the acid to penetrate into the paper. Preferably,

5

however, the paper is substantially completely dried (so that it will contain less than about 5% by weight of moisture) before the acid is applied, since by so doing the absorption of the acid into the paper is more complete and is more uniform. After the acid has been applied the paper is again dried as by passing it over the drying rolls which may be heated to conventional drying temperatures such as 200° to 300° F. although the degree of heating is in no way material and does not contribute to the successful manufacture of the new product. If desired, the product may be dried at ordinary atmospheric temperature. 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 is ordinarily 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 acid to the asbestos paper at an intermediate stage during the passage of the paper over the drying rolls of a conventional machine for the manufacture of asbestos paper products.

The concentration of the acid that is applied to the asbestos paper is not critical. Usually, the acid as applied is diluted with water so as to be of about 2% to about 25% concentration. The strength of the asbestos paper product is increased somewhat upon increasing the concentration of the acid that is applied thereto up to a concentration of about 25%, but the amount of strength imparted in interbonding the asbestos fibers is not proportional to the concentration of the acid employed and the concentration of the acid employed does not appear to be critical.

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 one hundred 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 across the sheet. Upon applying sulphuric acid of about 10% concentration to the sheet material so that the sheet material will take up about seventy pounds of the diluted acid 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 sixteen pounds per linear inch of width and about eight pounds per linear inch 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 D 202-41T using a Scott tensile testing machine, the test specimens of paper having been conditioned at 45% relative humidity and 77° F. for four hours before testing.

In addition to sulphuric acid other water-soluble compounds producing a sulphate anion in solution are effective in the practice of this invention to afford a bonded asbestos sheet material and the like. The compounds falling within the defined class differ somewhat in effectiveness. Those compounds, in addition to sulphuric acid, which normally are regarded as preferable in the practice of this invention are ammonium sulphate, ammonium bisulphate, sodium ammo-

6

nium sulphate, ammonium aluminum sulphate, ammonium zinc sulphate, lithium sulphate, magnesium acid sulphate, manganese sulphate, potassium sulphate, sodium sulphate, ferric sulphate, ferrous sulphate, potassium bisulphate and magnesium ammonium sulphate.

The sulphates which include an ammonium cation, and magnesium acid sulphate, have been found to be particularly effective. Other water-soluble inorganic sulphates which are likewise effective, but to a somewhat lesser degree are sodium bisulphate, aluminum sulphate, magnesium sulphate, and zinc sulphate.

The foregoing substances, including sulphuric acid, are illustrative of the water-soluble inorganic compounds containing a sulphate (SO_4) anion which we have found to be effective in the practice of this invention. The concentration of the solution that is appropriate for the different substances in the class varies but, generally speaking, is of the order that has been mentioned in connection with the employment of sulphuric acid. After the treating step the residual dried binder material resulting from the treatment will desirably constitute less than 20% by weight of the asbestiform mineral fiber. For the preparation of flexible fibulose asbestos paper it is ordinarily desirable that the paper contain less than 15% by weight of material other than the fiber and any finely-divided filler that may be contained therein.

According to this invention asbestos paper can be readily manufactured which has ample strength for the purposes to which asbestos papers are generally intended. Such paper can be readily handled and subjected to various treatments and will withstand deformation as in the manufacture of thermal insulation materials comprising one or more layers of asbestos paper which has been corrugated or indented or has otherwise been deformed. When asbestos paper is prepared without any binder its tensile strength in the machine direction is quite low, usually of the order of one to two pounds per linear inch of width. An increase in strength which doubles the strength of the paper containing no binder constitutes a considerable practical improvement although a tensile strength of at least five pounds per linear inch is ordinarily desirable. As pointed out above, considerably higher strengths can readily be attained according to this invention.

Asbestos sheet material can be made according to this invention which is notable not only for its strength but also for the fact that it remains flexible and fibulose. Thus, asbestos sheet material can be made according to this invention which takes up water or other liquid material as rapidly as asbestos paper which has been bonded with, for example, five to ten per cent of starch. 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. The flexibility of paper and other sheet materials made according to this invention is also important in enabling the paper to be fabricated into articles. In referring to sheet material 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 of 1.5 inches 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 of the asbestos

sheet material made according to this invention can, if desired, be further increased by calendaring or other manipulative treatment of the sheet after it has been dried.

When the asbestos paper is treated with an acidic compound containing a sulphate anion, such as sulphuric acid or an acid salt thereof, such treatment to which the asbestos paper is subjected according to this invention does not result in objectionable acidity of the product. Asbestos fibers are normally slightly alkaline and the alkalinity of the asbestos fibers eventually neutralizes any acidity which is imparted to the paper by the applied acid or acid salt so that the ultimate product is either neutral or of the slight alkalinity which is characteristic of any asbestos sheet consisting essentially of asbestos fibers.

It is apparent from the foregoing that a sheet, or other body of interbonded asbestos fibers, may be produced according to this invention which has substantial strength and which has the heat resistance and other properties characteristic of a product made essentially of asbestos. In other words, an asbestos product can be produced according to this invention which is essentially free of organic binder or other organic material and which is free from the objections that are incident to the presence of organic material in the product. The material may be subjected to sustained temperatures of 900° to 1000° F. without deterioration. Moreover, at such temperatures, or even higher temperatures such as flame temperatures, there is no charring, discoloration, or production of objectionable smoke or fumes. Moreover, the material is not subject to attack by organisms or vermin.

One of the uses to which the product of this invention is particularly adapted is use as or in heat insulation materials of various kinds. Thus the new asbestos paper by itself may be used as a protective covering for pipes, furnace walls and the like and may be used even though temperatures as high as 900° to 1000° F. may be encountered. The new asbestos paper may also be used in the fabrication of composite insulation products. In such products, the new asbestos paper may, for example, be used as a surface layer. The new paper of this invention may also be utilized as the body portion of the heat insulation material.

In addition to the above, the new asbestos paper and sheet material of this invention may likewise be used in the manufacture of board-like materials other than those especially designed for heat insulation purposes.

It is also apparent that the new product of this invention, when made without employment of organic material contained therein, is superior to ordinary asbestos felt used in the manufacture of roofings such, for example, as built-up roofings which are commonly prepared using a plurality of plies of asbestos paper saturated with asphalt and bonded together with a suitable mopping asphalt. Since the asbestos paper may be made according to this invention which is without any combustible material contained therein and which remains coherent notwithstanding the fact that the asbestos paper is subjected to very high temperature, it is obvious that improved fire resistance can be afforded by using as a base for roofing the new asbestos sheet material of this invention either dry or impregnated with a waterproofing material such as a bituminous material.

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 and the application of the treating compound thereto. 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 airborne 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. The moment of application of the compound for reaction with the fibers is not important so long as the fibers as disposed in felted relation are in contact with the treating substance as contained in an aqueous solution and the felted fibers are permitted to dry en masse so that the bonding material occurring at the surface of the asbestiform mineral fiber will harden and serve to interbond the asbestiform mineral fibers at the points of contact between the fibers. If desired, a plurality of thin sheets of asbestos paper or the like to which the treating compound has been applied and which is still in a wet state may be plied together so as to form a product consisting of a plurality of plies, the plies being bonded together when dried by the product of interaction between the asbestiform mineral fibers and the treating compound.

In the ordinary case, according to this invention, the usual asbestos fiber of commerce may be used, namely, chrysotile asbestos fiber. According to this invention and as used in the claims, the term asbestos is intended to include, in addition to chrysotile asbestos, other commercial varieties of asbestos, namely, anthophyllite, actinolite, tremolite, crocidolite, amosite, various amphibole fibers and Canadian picrolite.

While it is a principal advantage of this invention that an asbestos product can be produced which is essentially free of organic material which is used either as a binder or as part of the fibrous content of the product, the advantages of this invention may be availed of even though some organic material may be present in the product. For example, an asbestos paper containing a minor amount of organic fiber such as ordinary cellulosic paper fiber may be subjected to the sulfate-treating step according to this invention and such treatment will result in the interbonding of the asbestos fibers in the sheet. However, for most purposes where high fire resistance is desired, less than 5% by weight of the fiber should be organic fiber. It is possible to include in the asbestos paper other 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. However, in any event, the content of asbestos fiber should be sufficient so that the asbestos fibers in the fibrous product come into intimate association, thereby permitting the asbestos fibers to become bonded together at a multiplicity of points of contact between the asbestos fibers for the creation of a bond between the asbestos fibers which imparts coherency and strength to the product as a whole. As a general rule the product produced according to this invention should consist in major proportion by weight of asbestiform mineral fibers.

The new fibrous product of this invention ordinarily made up for the market does not con-

tain any organic binder. However, an organic binder may be applied depending upon the intended use of the product. Thus, while it is an advantage of this invention that the usual binder that is used in the manufacture of asbestos paper, namely, starch, may be omitted altogether, it is not without the scope of this invention to employ the special treating compounds in conjunction with starch. However, even in such case, it is normally desirable to take advantage of this invention by reducing the quantity of starch below that which is ordinarily used. Thus, for example, the asbestos paper may contain 1% or less by weight of starch without detracting materially from the heat resistance of the paper for in such case the paper, when exposed to high temperature, may discolor to some extent but will not give off flame or an undue amount of smoke, and the paper will retain its bond notwithstanding the carbonization of the starch. These comments are equally applicable to other organic binders. It is ordinarily desirable that the asbestos paper or the like be made up employing less than 2% of organic binder. As mentioned above, an asbestos paper according to this invention may, for example, be impregnated with a bituminous saturant for various purposes. Other types of binder, which may or may not be organic, may be applied to the sheet material as in the manufacture of gasket material, brake linings and the like. Moreover, the product of this invention may be impregnated with other types of bonding material such as soluble silicates which become hardened when dried and which may, if desired, be insolubilized by such expedients as the use of suitable insolubilizing agents or by heat curing.

In addition to the fiber and bonding components of the products produced according to this invention, the product may include a minor quantity of a finely-divided 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. Another filler which affords considerable porosity is fine pumice. Moreover, other fillers such as clay, talc, pigments to impart suitable color, etc. may be employed. When the product of this invention is designed to be resistant to high temperatures, the filler material should be heat resistant, namely, should not decompose and char when exposed to temperatures of the order of 900° F. Ordinarily, if the filler material is heat resistant, an inorganic filler is employed. Ordinarily, the major proportion by weight of the fiber plus the filler contained in the product should consist of asbestiform mineral fibers and, for providing resistance to heat, the fiber plus any filler, should contain less than 10% of organic material or other non-heat resistant material.

Since the product of the invention can be made up so as to consist substantially of asbestos fiber, or asbestos fiber together with other heat resistant fiber or filler, the product can be exposed to temperatures such as 900° F. to 1000° F. without injury. This is of considerable advantage in enabling asbestos paper products which have been impregnated with a soluble silicate to be heat cured at temperatures of the order mentioned to insolubilize the silicate. If ordinary asbestos paper containing an organic binder were to be

subjected to such heat curing temperatures, the paper would become discolored, charred and weakened and an unsatisfactory product would result.

For most purposes where resistance to exposure to high temperatures is desired, it is desirable to produce the product of this invention so as to be substantially free of any organic material. This is also desirable in order to afford high resistance to rotting, mildew, etc. However, about 6% by weight of organic material can be tolerated in the product while still affording these attributes in an unusually high degree.

While this invention has been described in connection with certain typical examples of the practice thereof it is to be understood that this has been done merely for purposes of illustration and that the scope of this invention is to be defined by the language of the following claims.

We claim:

1. As an article of manufacture a flexible coherent bibulous felted-fiber sheet-like body, said fibers comprising asbestos fibers which are interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said sheet-like body with a water-soluble inorganic compound which produces a sulphate anion in water solution.

2. As an article of manufacture a flexible coherent bibulous felted-fiber sheet-like body according to claim 1 wherein said sheet-like body contains less than 2% by weight of organic binder.

3. A flexible coherent bibulous felted-fiber sheet-like body which consists in major proportion by weight of asbestos fibers and which contains less than about 6% by weight of organic material, said asbestos fibers being interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said sheet-like body with a water-soluble inorganic compound which produces a sulphate anion in water solution, and said sheet-like body containing less than 15% by weight of material other than fiber plus any finely-divided filler contained therein and having a tensile strength of at least about 5 pounds per linear inch of width.

4. As an article of manufacture a flexible bibulous felted-fiber asbestos paper wherein asbestos fibers constitute the major proportion by weight of the fiber plus any filler contained in said paper, said asbestos fibers being interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said felted-fiber asbestos paper with a water-soluble inorganic compound which produces a sulphate anion in water solution to provide a tensile strength of at least 5 pounds per linear inch of width for the said flexible and bibulous asbestos paper which for sheet thicknesses up to 0.05 inch is bendable 180° around a 1.5 inch diameter mandrel in 2 seconds at 77° F. without rupture or breaking at the surface.

5. As an article of manufacture a flexible bibulous asbestos paper according to claim 4 wherein any organic fiber plus any organic filler constitutes less than 10% by weight of the fibers plus any filler contained in said paper.

6. As an article of manufacture a flexible bibulous asbestos paper according to claim 4 which contains less than 6% by weight of organic material.

7. As an article of manufacture a flexible

11

bibulous asbestos paper according to claim 4 which is substantially free of organic material.

8. A product comprising felted fibers disposed in a sheet-like body, a major proportion by weight of the fiber plus any filler contained in said sheet-like body consisting of asbestos fibers, said asbestos fibers being interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said sheet-like body with a water-soluble inorganic compound which produces a sulphate anion in water solution, said sheet-like body being impregnated with a bituminous waterproofing material.

9. A product according to claim 8 wherein any organic material other than said bituminous waterproofing material constitutes less than 10% by weight of the fiber plus any filler contained in said sheet-like body.

10. As an article of manufacture a flexible coherent bibulous felted-fiber sheet-like body, the fibers plus any filler contained in said sheet-like body consisting in major proportion by weight of asbestos fibers and comprising less than 10% by weight of organic material, said asbestos fibers being interbonded in situ in said sheet-like body by the interaction of said asbestos fibers in situ as disposed in felted relation in said sheet-like body with a solution of a water-soluble inorganic compound which produces a sulphate anion in water solution, and which is selected from the group consisting of sulphuric acid, ammonium sulphate, ammonium bisulphate, sodium ammonium sulphate, ammonium aluminum sulphate, ammonium zinc sulphate, lithium sulphate, magnesium acid sulphate, magnesium ammonium sulphate, manganese sulphate, potassium sulphate, sodium sulphate, ferric sulphate, ferrous sulphate, and potassium bisulphate, and said sheet-like body having a tensile strength of at least 5 pounds per linear inch of width.

11. As an article of manufacture a flexible, bibulous felted-fiber asbestos paper consisting in major proportion by weight of asbestos fibers interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said felted-fiber asbestos paper with a solution of sulphuric acid, any organic material contained in said asbestos paper constituting less than 10% by weight of the fiber plus any filler contained in the asbestos paper.

12. As an article of manufacture a flexible, bibulous felted-fiber asbestos paper consisting in major proportion by weight of asbestos fibers interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said felted-fiber asbestos paper with a solution of a sulphate of ammonium, any organic material contained in said asbestos paper constituting less than 10% by weight of the fiber plus any filler contained in the asbestos paper.

13. As an article of manufacture a flexible, bibulous felted-fiber asbestos paper consisting in major proportion by weight of asbestos fibers interbonded in situ by the interaction of said asbestos fibers in situ as disposed in felted relation in said felted-fiber asbestos paper with a solution of magnesium acid sulphate, any organic material contained in said asbestos paper constituting less than 10% by weight of the fiber plus any filler contained in the asbestos paper.

12

14. In the manufacture of a flexible bibulous coherent sheet-like body of felted fibers consisting in major proportion by weight of asbestos fibers, the steps comprising contacting the asbestos fibers while disposed in said sheet-like body of felted fibers with an aqueous solution of a water-soluble inorganic compound containing a sulphate anion, said asbestos fibers being initially contacted with said aqueous solution of a water-soluble inorganic compound containing a sulphate anion after the fibers in said felted-fiber sheet-like body have been disposed in felted relation in said sheet-like body, and thereafter drying the sheet-like body of felted fibers, thereby bonding together the contacting asbestos fibers in said sheet-like body by interaction in situ between said asbestos fibers as disposed in felted relation in said sheet-like body and said compound, said solution of said water-soluble inorganic compound containing a sulphate anion being applied at such concentration that said sheet-like body after drying is flexible and bibulous.

15. In the manufacture of a flexible bibulous coherent sheet-like body of felted fibers consisting in major proportion by weight of asbestos fibers, the steps according to claim 14 wherein said water-soluble inorganic compound containing a sulphate anion is selected from the group consisting of sulphuric acid, ammonium sulphate, ammonium bisulphate, sodium ammonium sulphate, ammonium aluminum sulphate, ammonium zinc sulphate, lithium sulphate, magnesium acid sulphate, magnesium ammonium sulphate, manganese sulphate, potassium sulphate, sodium sulphate, ferric sulphate, ferrous sulphate, and potassium bisulphate.

HAROLD W. GREIDER.
MARION F. SMITH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
363,905	Merrill -----	May 31, 1887
703,200	Heany -----	June 24, 1902
1,233,801	O'Malley -----	July 17, 1917
1,353,622	Ashenhurst -----	Sept. 21, 1920
1,581,619	Sulzberger -----	Apr. 20, 1926
1,690,079	Seigle -----	Oct. 30, 1928
1,820,538	Kennedy -----	Aug. 25, 1931
1,876,783	Stadtfeld -----	Sept. 13, 1932
1,885,113	Jenkins -----	Nov. 1, 1932
1,962,577	Wolochow -----	June 12, 1934
1,969,156	Schuttler -----	Aug. 7, 1934
1,972,500	Toohy et al. -----	Sept. 4, 1934
2,006,392	Greider -----	July 2, 1935
2,034,522	Loetscher -----	Mar. 17, 1936
2,046,494	Rolleghem -----	July 7, 1936
2,068,219	Badollet -----	Jan. 19, 1937
2,128,097	Mains -----	Aug. 23, 1938

FOREIGN PATENTS

Number	Country	Date
1,414	Great Britain -----	1853
5,029	Sweden -----	Aug. 8, 1893
13,412	Australia -----	May 21, 1928