This invention relates to asbestos products and relates especially to products which comprise fibrous material containing asbestosform 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 "mill board," which is referred to herein generally as "paper." The bulk of the asbestos form mineral fiber that is used in asbestos paper usually runs from about 1/4" to 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 fibers are water-laid in felted relation by a paper making operation, a multitylinder 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 "heating," as employed for the development of strength in cellulosic papers, is ineffectual 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 asbestos fibers, 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 formation of fiber of 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 commonly 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 that is possessed by asbestosform mineral fibers and that 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 desirability result from the fact that asbestos fiber is unaffected by water and is not subject to rotting or other gradual...
deterioration 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 a lower temperature than asbestos as low as 250° F. during periods 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 temperature 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 800° 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 temperature 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 objectionable to Underwriters' Laboratories, Inc., and 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 exposure to elevated temperatures will, of course, take place regardless of amount of binder that is employed.

Other objections to use of organic binders are lack of resistance to water and moisture, rotting, mildew, and unnatural appearance.

Summarizing the foregoing, the use in paper or other products of asbestos mineral fibers is highly advantageous due to the resistance of asbestos 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 product 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 cemntitious in character.

It has also been proposed to impregnate asbestos paper with soluble silicates, such as commercial silicate solution, and then dry the resultant sheet, the silicate, upon drying, becoming of a hardened glass-like character so that the dried product is rigid, boardy and brittle, and cracks readily when flexed.

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 as asbestos paper and the heat-insulation material, lumber-like products, and other products fabricated from sheets of felted asbestos fibers that have been interbonded according to this invention.

We have discovered that asbestos mineral fibers which have been produced in the form of a felted sheet-like body can be bonded together by the interaction of the asbestos mineral fiber with a solution of a water-soluble inorganic phosphate to form a coherent body that is flexible and porous but that has much more strength than an untreated sheet of felted asbestos mineral fibers. The interaction that occurs between the solution of the water-soluble inorganic phosphate and the asbestos mineral fiber is not definitely understood, but appears to be specific between the substance of the asbestos mineral fibers and water-soluble inorganic phosphate. Numerous other inorganic compounds do not have such effect and may even decrease rather than increase the strength of the felted sheet material. While 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 objectionable to Underwriters' Laboratories, Inc., and 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 exposure to elevated temperatures will, of course, take place regardless of amount of binder that is employed.

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 art. Deviation from the usual stage is that 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 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 ortho-phosphoric acid, H₃PO₄, 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, tub 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, 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 30% 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 30%, 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 effective water content 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 across the sheet. Upon applying phosphoric acid of about 1% concentration to the sheet material so that the sheet material will take up about seventy percent 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 14 pounds per linear inch of width and about 4 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.

Asbestos-paper or other felted sheet-like body wherein the asbestiform mineral fibers have been bonded together by the action of water consists between the asbestiform mineral fibers and the phosphoric acid, has the advantage of retaining 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 fibers together, the fibers being liberated to form a pulpy mass. When subjected to the boiling water test, the paper, wherein the fibers had been bonded together by the action of phosphoric acid, successfully withstand 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. The high resistance to water that is afforded by the bonding together of the asbestiform mineral fiber by the action of phosphoric acid thereon is of great practical advantage in that asbestos paper having good wet strength can be readily produced. By comparison, ordinary asbestos paper which has been bonded by means of starch has virtually no resistance to water and even when moistened with cold water immediately loses its strength and becomes reduced to a plastic pulp-like mass. While a water-insoluble binder such as rubber may be used in asbestos paper in order to afford improved water-resistance, the higher cost of rubber is a practical disadvantage and, of course, rubber, being organic, tends to impair fire resistance and tends to give off malodorous smoke when heated.

In addition to phosphoric acid, other water-soluble inorganic phosphates are effective in the practice of this invention to afford a bonded asbestos sheet or the like. Those water-soluble inorganic phosphates which, like phosphoric acid, provide a product having high resistance to water, and which are preferably employed in the practice of this invention are selected from the group consisting of phosphoric acid, sodium acid phosphosphate, potassium acid pyrophosphate, sodium pyrophosphate, sodium phosphate (monobasic), sodium phosphate (tribasic), ammonium phosphate (monobasic), ammonium phosphate (tribasic), potassium phosphate (monobasic), barium orthophosphate, magnesium hydrogen phosphate, chromium phosphate, aluminum acid phosphate, and magnesium biphosphate. Among these foregoing substances, the phosphates of ammonium and the pyrophosphate of sodium are especially effective. The magnesium hydrogen phosphate, above mentioned, constitutes an abbreviated designation for magnesium phosphate, which is normally insoluble, but which has been dissolved in the presence of about two molar equivalents of phosphoric acid. Other examples of water-soluble inorganic phosphates which provide a bonded sheet-like body comprising asbestiform mineral fibers according to this invention are aluminum acid phosphate, potassium pyrophosphate, potassium superphosphate (dibasic), potassium phosphate (tribasic), sodium ammonium phosphate, sodium phosphate (dibasic), sodium meta-phosphate, sodium hexametaphosphate, potas-
sium metaphosphate, monofluorphosphoric acid, and difluorphosphoric acid.

The foregoing substances are illustrative of those compounds which are referred to herein and in the claims as “water soluble inorganic phosphates,” namely, the hydrates of phosphorus pentoxide and the water-soluble inorganic salts of the hydrates of phosphorus pentoxide. The term “hydrates of phosphorus pentoxide” includes the several forms of phosphoric acid of which the most common are the ortho-, meta- and pyrophosphoric acids and the term “water soluble inorganic phosphates” includes the water soluble inorganic salts of the above named acids. The term “phosphoric acid” as used herein and in the claims refers to any of the hydrates of phosphoric acid. The lower hydrates of phosphoric acid such as the meta- and pyro-phosphates tend to hydrolyze when in water solution to the ortho phosphate form. The substances monofluorphosphoric acid and difluorphosphoric acid have been included in this category since these substances in water solution hydrolyze to form an equilibrium mixture containing phosphoric acid and hydrofluoric acid and, therefore, belong with the group of substances which is effective because of the special action of the hydrates of phosphoric pentoxide.

The water-soluble inorganic phosphates listed above differ somewhat in effectiveness and for this reason 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 phosphoric acid.

After the treating step the residual dried binder material resulting from the treatment will desirably constitute less than 20% by weight of the asbestos mineral fiber. For the preparation of flexible fibulous 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. The finished paper can be readily handled and subjected to various treatments and will withstand deformation as in the manufacture of thermal insulation sheet 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 without any binder constitutes a considerable 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 bibulous. Thus, asbestos sheet material can be made according to this invention which takes up water or other liquid material as readily as asbestos sheet bonded with, for example, five to ten per cent of starch. Typical embodiments of this invention will take up 30% 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 the 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 therefore suitable for molding into a 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 phosphate, such as phosphoric 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 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 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 objection which is incident to the presence of organic material in the product. The material may, for example, 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 which is prepared according to this invention 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 particular, the new asbestos paper for example, can 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 can be made 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 build-up roofings which are commonly prepared using a plu-
rality 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 fibers to form a asbestos-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 phosphate compound for reaction with the fibers to cause bond to deposit is not limited, as disclosed in the felted relationship are in contact with the treating substances as contained in an aqueous solution and the felted fibers are permitted to dry en masse so that the bonding material occurring at the surfaces of the asbestos 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 and other commercial varieties of asbestos, namely, anthophyllite, actinolite, tremolite, crocidolite, amosite, various amphibole fibers and Canadian piercuite. 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 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 phosphate-treating step according to this invention and such treatment will result in the interbonding of the asbestos fibers in the sheet. However, if high 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, more friable and more expensive 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 as ordinarily made up for the market does not contain 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 fibers are not exposed to high temperature, may discolar 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, show little or no decomposition 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 or-
ganic material or other non-heat resistant material.  Since the product of the invention can be made 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 temperature, 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 a paper 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 8% by weight of organic material can be tolerated in this sheet while still maintaining 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. 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 felled relation in said sheet-like body with a water-soluble inorganic phosphate.

2. 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. An article of manufacture a flexible coherent bibulous felted-fiber sheet-like body according to claim 1 wherein the water-soluble inorganic phosphate is selected from the group consisting of phosphoric acid, sodium acid pyrophosphate, potassium acid pyrophosphate, sodium pyrophosphate, ammonium phosphate (monobasic), ammonium phosphate (dibasic), potassium phosphate (monobasic), barium orthophosphosphate, magnesium hydrogen phosphate, chromium phosphate, aluminum acid phosphate, and magnesium biphosphate.

4. 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 mineral fibers in situ as disposed in felled relation in said sheet-like body with a water-soluble inorganic phosphate, and said sheet-like body contains less than 15% by weight of material other than fiber plus any finely-divided filler container therein.

5. A flexible coherent bibulous felted-fiber sheet-like body according to claim 4 wherein the water-soluble inorganic phosphate is selected from the group consisting of phosphoric acid, sodium acid pyrophosphate, potassium acid pyrophosphate, sodium pyrophosphate, ammonium phosphate (monobasic), ammonium phosphate (dibasic), potassium phosphate (monobasic), barium orthophosphosphate, magnesium hydrogen phosphate, chromium phosphate, aluminum acid phosphate, and magnesium biphosphate.

6. 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 felled relation in said felted-fiber asbestos paper with a water-soluble inorganic phosphate to provide a tensile strength of at least about 5 pounds per linear inch 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.

7. As an article of manufacture a flexible bibulous asbestos paper according to claim 6 wherein any organic fiber plus any organic binder constitutes less than 10% by weight of the fibers plus any finely divided filler contained in said paper and which contains less than 15% by weight of material other than fiber plus any finely-divided filler contained in said paper.

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

9. As an article of manufacture a flexible bibulous asbestos paper according to claim 6 which is substantially free of organic material.

10. 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 felled relation in said felted-fiber asbestos paper with a water-soluble inorganic phosphate selected from the group consisting of phosphoric acid, sodium acid pyrophosphate, potassium acid pyrophosphate, sodium pyrophosphate, ammonium phosphate (monobasic), sodium phosphate (trisodium), ammonium phosphate (monobasic), ammonium phosphate (dibasic), potassium phosphate (trisodium), barium orthophosphosphate, magnesium hydrogen phosphate, chromium phosphate, aluminum acid phosphate, and magnesium biphosphate to provide a tensile strength of at least about 5 pounds per linear inch of width for 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.

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

12. As an article of manufacture a flexible bibulous asbestos paper according to claim 10 which contains less than 6% by weight of organic material.

13. As an article of manufacture a flexible bibulous asbestos paper according to claim 10 which contains less than 6% by weight of organic material.

14. As an article of manufacture a flexible bibulous asbestos paper according to claim 10 which contains less than 6% by weight of organic material.
ulous asbestos paper according to claim 10 which is substantially free of organic material.

14. 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 phosphate, said sheet-like body being impregnated with a bituminous waterproofing material.

15. A product according to claim 14 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.

16. 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 phosphoric 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.

17. 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 phosphate 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.

18. 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 pyrophosphate of sodium, 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.

19. 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 phosphate, said asbestos fibers being initially contacted with said aqueous solution of a water-soluble inorganic phosphate 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 water-soluble inorganic phosphate, said solution of said water-soluble inorganic phosphate being applied at such concentration that said sheet-like body after drying is flexible and bibulous.

20. 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 19 wherein said water-soluble inorganic phosphate is selected from the group consisting of phosphoric acid, sodium pyrophosphate, potassium pyrophosphate, sodium pyrophosphate, sodium metaphosphate (monobasic), sodium phosphate (tribasic), ammonium phosphate (monobasic), ammonium phosphate (dibasic), ammonium phosphate (tribasic), potassium phosphate (monobasic), barium orthophosphate, magnesium hydrogen phosphate, aluminium phosphate, and magnesium dibasic phosphate.

HAROLD W. GREIDER.
MARION F. SMITH.

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