Patented Dec. 1, 1953

2,661,287

UNITED STATES PATENT OFFICE

2,661,287

AQUEOUS ASBESTOS DISPERSION AND PROCESS FOR PRODUCING SAME

Glen D. Barbaras, Cleveland, Ohio, assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application November 15, 1949, Serial No. 127,529

15 Claims. (Cl. 92—1)

1

This invention relates to asbestos compositions and processes for producing them and is more particularly directed to aqueous dispersions having a pH of from 3 to 6 and comprising up to about 5% by weight of discrete, Crystallite, chrysotile asbestos fibers from 20 to 40 millimicrons in diameter and, as a dispersing agent, a dissolved metal salt having a monovalent anion and a cation containing a polyvalent metal, the amount of dispersing agent being not more than enough to give 3 milligram moles of dissociated anion per gram of asbestos, is further directed to processes for producing such dispersions in which oriented chrysotile asbestos is disoriented by mechanical action in an aqueous solution of the dispersing agent at a pH of from 3 to 6, and is still further directed to dry products obtainable by drying the products of such processes, said products consisting essentially of discrete Crystallite fibers of chrysotile asbestos about 20 to 40 millimicrons in diameter and, in intimate admixture therewith, a metal salt having a monovalent anion and a cation containing a polyvalent metal.

Chrysotile asbestos, as it occurs in nature, is made up of a mass of oriented fibers of a complex magnesium silicate. Masses of asbestos can quite readily be broken up by ordinary mechanical methods into relatively coarse fibers which consist of bundles of fibrils. By specialized techniques such as those described in British Patent 562,161, these relatively large fibers can be broken down into ultimate fibers estimated as having a diameter of the order of 300 Ångstroms. However, in aqueous suspension as well as when dried, these ultimate fibrils are associated in discrete groups or flocs easily observable by the unaided eye, and because of this flocculation the system becomes nonhomogeneous and has properties characteristic of the flocs. Therefore, it has not hitherto been possible to work with or on homogeneously dispersed discrete individual fibrils hence their usefulness has been greatly impaired.

Now according to the present invention it has been found that if the disorientation of chrysotile asbestos by mechanical action is carried out at a pH of from 3 to 6 in an aqueous solution containing as a dispersing agent a metal salt having a monovalent anion and a cation containing a polyvalent metal, the amount of such metal salt being not more than enough to give 3 milligram moles of dissociated anion per gram of asbestos, a homogeneous dispersion is obtained in which the individual asbestos particles are not flocculated. Such aqueous dispersions have a pH of from 3 to 6 and comprise up to about 5% by weight of discrete, Crystallite, chrysotile asbestos fibers from 20 to 40 millimicrons in diameter and, of

2

course, the dispersing agent. They may be dried, the dry products, consisting essentially of the discrete Crystallite fibers and the dispersing agent, being readily redispersible in water to obtain the non-flocculated dispersions.

The asbestos employed in the processes and products of this invention is known as chrysotile. This is a fibrous form of asbestos and the most common form. It may be mined from naturally occurring deposits and should be cleaned of rocks and dirt before use. It preferably should be broken up in a preliminary way, as in a chopping mill, such preliminary treatment being of a character to break up very long fibers and fiber bundles which might otherwise interfere with the mechanical action means subsequently to be employed. Preliminary breaking up may be done in the dry way, as is the case in a chopping mill.

Following preliminary chopping the chrysotile is further broken down by mechanical action in aqueous dispersion. The oriented chrysotile becomes disoriented into its ultimate, Crystallite fibrils by a combination of mechanical action and chemical treatment under such conditions that adverse chemical change of the fiber does not occur.

The mechanical action employed to effect disorientation must be of a character which tends to separate the individual fibrils from each other but which does not provide a high degree of attrition or grinding such as would break the fibrils into very short pieces. A discussion of various means applicable to this purpose is found in British Patent 562,161 and any of the methods there disclosed for mechanical treatment of the fibers in the presence of water may be used. As is there pointed out, the fibrous material is subjected to a bending and squeezing action under such conditions that the fibrous body has freedom to expand at substantially right angles to the direction of the applied force to spread out and liberate individual fibers as they are released from the pencil or bundle and that excessive breaking or cutting up of the individual fibers is substantially avoided. A ball mill may be used for this purpose and the mass thus produced may be broken up by stirring, vibration of the mass of liquid and asbestos, by spraying through a nozzle or by blowing with air or steam or by explosive heat shattering treatment using steam, air or the like. Various types of beater mills may be used and the mass may be subjected to ultrasonic treatment. A laboratory mill of the Waring Blendor type, in which high shearing forces are produced when propeller-shaped knives are revolved at very high speed, has been found to give excellent disorientation in a minimum of time with minimum reduction in fiber length.

According to the present invention it has been ound that mechanical means alone are insuffi-ient to give a deflocculated dispersion of chryso-ile. Rather, it has been found that control of he pH during dispersion and also the presence f a dispersing agent is essential in order to ob-ain complete disorientation and avoid floccula-ion.

The dispersing agents in a process of this in-ention are dissolved metal salts having a mon-ovalent anion and a cation containing a poly-alent metal. Such salts are not ordinarily hought of as being dispersing agents. Alumi-um chloride, for example, has been described n the prior art as having the opposite effect on hrysotile asbestos; (N. N. Serb-Serbina and K. V. Shumikhina J. Applied Chem. (U. S. S. R.) 6, 273–9 (1943)). However, under the conditions f the present invention these salts have been ound to have dispersing action on chrysotile. The salts employed must be sufficiently soluble n water to have the desired action, but it will be nderstood that even sparing solubility may be ufficient for this purpose. Thus, plumbous chlo-ide, $PbCl_2$, is sufficiently soluble to have a dis-ersing action.

The anion of the dispersing agent must be nonovalent. It has been found that even traces f polyvalent anions cause flocculation of the fi-ers and their presence must be avoided. If pres-nt as impurities in the raw materials they may e removed by the addition of a small amount f a precipitant, as for example, barium acetate o remove sulfate ions. It is also preferred not o use the monovalent anion, fluoride, because his anion has a pronounced tendency to form omplex, polyvalent anions. Representative an-ons which may be used, in the order of their ef-ectiveness are the following radicals: formate, cetate, chloride, nitrate, bromide.

The polyvalent cation of the dispersing agent nay be a cation which contains only the poly-alent metal or may be one which contains a olyvalent metal in combination with another lement such as oxygen. Representative of the netals which may be present in the cation are luminum, iron, chromium, zirconium, titanium, eryllium, lead, copper, tin, indium, magnesium, arium and zinc. Representative cations con-aining another element in addition to the poly-alent metal include zirconyl, titanyl and basic luminum cations.

It is particularly preferred to employ as a dis-ersing agent a salt having a cation containing luminum, iron, chromium, zirconium or titan-um, and of these the aluminum salt is out-tanding.

The amount of dispersing agent used is criti-al. The minimum amount is, of course, that ecessary to effect dispersion. As little as 0.1 nilligram molecular weights of a suitable salt er gram of asbestos has been found to give ef-ective dispersion. The maximum amount of dis-ersing agent must be carefully controlled. The ermissable maximum is related to the character f the anion formed when the metal salt is dis-olved in water. When this anion does not trongly associate with the hydrogen ion present n the dispersion, the maximum amount of dis-ersing agent that can be added is less than when he anion associates with the hydrogen ion to orm a poorly dissociated acid. For instance, hen a chloride is used, the chloride ion formed pon dissolution does not strongly associate ith ydrogen ion, whereas when the dispersing

agent is an acetate, the acetate ion does associate with the hydrogen ion to form acetic acid which, being poorly ionized, ties up the acetate ion and reduces the effective amount present. The maximum amount of any salt used must be not more than enough to give three milligram moles of dissociated anion per gram of asbestos. Since the anions of strong acids such as hydrochloric, hydrobromic, and nitric acids are, at this dilution, practically 100% dissociated, it will be apparent that one milligram molecular weight of a trivalent metal chloride such as aluminum chloride or 1.5 milligram molecular weights of a chloride of a divalent metal such as beryllium is the maximum which can be tolerated. On the other hand, when the acetate or formate of a polyvalent metal is used, the amount of dispersing agent can be larger because the anion is poorly dissociated. The number of milligram moles of a salt which will give a particular concentration of anions in the dispersion may readily be calculated by reference to the dissociation constant of the acid corresponding to the anion, at the dilution and pH used.

In making a chrysotile dispersion by a process of this invention the pH of the aqueous medium is maintained in the range from 3 to 6. The ordinary pH of chrysotile dispersions is in the range from 8 to 10, and until the pH is lowered to 6 no substantial amount of chemical dispersing action occurs. On the other hand if the pH is lowered below about 3, acid attack of the individual fibers occurs and deterioration of the fiber results. This deterioration would occur at a higher pH than 3 in the absence of the dispersing agent. The pH range is critical and the considerations pertaining to it herein referred to have apparently not been recognized in the prior art.

The novel chrysotile dispersions of this invention therefore are aqueous dispersions having a pH of from 3 to 6. They comprise up to about 5 per cent by weight of chrysotile fibers, and the fibers are in the form of non-flocculated, discrete Crystallites from 20 to 40 millimicrons in diameter. The length of the fibers should be several times their diameter, and preferably as long as possible, provided adequate dispersion can be maintained. The dispersions also contain the dissolved dispersing agent as described above.

The novel, dry products of this invention are prepared by drying the aqueous dispersions. They consist of an intimate admixture of the discrete Crystallite chrysotile fibers and the dispersing agent. They are readily redispersible in water to form the aqueous dispersions above described.

The aqueous asbestos dispersions of this invention are useful in the manufacture of formed asbestos products such as asbestos sheets. The dried products provide a particularly useful form in which the dispersible material may be transported and stored with maximum economy.

A particularly useful type of sheet may be produced by filtering relatively long fibers from their dispersions. Such dried sheets are unusual in their high tensile and tear strength, and flex resistance. Their water resistance may be improved by treatment with reagents commonly employed for such purpose, for example, alkyl silicon chlorides, stearato chromic chloride and the like.

This invention will be better understood by reference to the following illustrative examples.

Example I

Crude, chrysotile asbestos from Quebec, Canada, was hand cobbed, picked free from adhering rock impurities, and put through a Wiley chopping mill to reduce the average fiber length to about ¼ inch. Three parts by weight of this fiber were suspended in 297 parts of water, and the resulting 1% fiber suspension was mixed in the Waring Blendor at full speed (approximately 12,000 R. P. M.) for 3 minutes to disorient the fiber bundles. The resulting thick, viscous, opaque aqueous suspension of asbestos fibers was continuously mixed for at least 3 minutes more while a one tenth molar solution of one of the metal salts listed below was added dropwise until an excellent dispersion of the fibers was obtained, and no marked improvement resulted on further addition of the metal salt solution. The dispersions rated excellent were thin, fluid, translucent dispersions in which no agglomerates or fiber flocs were visible to the unaided eye and in which individual fibers were not even visible under the crossed Nicols of the light microscope. The electron microscope revealed that the fibers had diameters of 20 to 40 millimicrons and an average length in excess of 30 microns, too long to be measured with the electron microscope. The amounts of various salt solutions added to yield excellent dispersions are listed in the following table:

Salt	Ccs. M/10 soln. per gm. asbestos	Mg. moles dispersing agent per gm. asbestos	pH	Calculated mg. moles dissociated anion per gm. asbestos
Aluminum formate	1	0.1	4.8	0.28
Basic aluminum formate	1	0.1	5.3	0.2
Aluminum acetate	1.5	0.15	4.4	0.14
Aluminum chloride	2	0.2	4	0.6
Zirconyl acetate	2	0.2	5	0.26
Zirconyl chloride	6	0.6	5	1.2
Aluminum nitrate	8	0.8	4	2.4

Example II

Crude chrysotile asbestos was chopped, mechanically fibrillated and treated with dispersing agents in the Waring Blendor in a manner similar to that described in Example I. In this case, good dispersions were obtained which were not quite as thin or translucent as the excellent dispersions obtained in Example I. The color of dispersion was characteristic of the metal salt used.

Salt	Ccs. M/10 soln. per gm. asbestos	Mg. moles dispersing agent per gm. asbestos	pH	Calculated mg. moles dissociated anion per gm. asbestos
Ferric chloride	10	1	3.1	3.0
Chromic chloride	10	1	4.9	3.0
Beryllium acetate	10	1	5.5	1.7
Titanyl chloride	10	1	4.0	2.0
Magnesium acetate (15 cc. of M/10 acetic acid added to reduce pH)	10	1	4.8	1.9
Copper acetate	10	1	5.7	1.8

Example III

Crude chrysotile asbestos was chopped, fibrillated and treated with dispersing agents in the Waring Blendor as in Examples I and II, but in this case, only a fair dispersion was obtained.

Salt	Ccs. M/10 soln. per gm. asbestos	Mg. moles dispersing agent per gm. asbestos	pH	Calculated mg. moles dissociated anion per gm. asbestos
Barium chloride	10	1	3.8	2.0
Stannic chloride	10	1	6	4.0
Indium nitrate	4	0.4	4.5	1.2
Stannous chloride	10	1	3	2.0
Aluminum bromide	8	0.8	4	2.4

Example IV

Chrysotile asbestos from Quebec, Canada, No. 3 grade was not chopped but was directly fibrillated and treated with dispersing agents in the Waring Blendor as in Examples I, II, and III with substantially the same results.

Example V

Chrysotile asbestos from Quebec, Canada, No. 5 grade, obtained already milled, was fibrillated and treated with dispersing agents in the Waring Blendor as in Examples I, III, and III with substantially the same results but differing in that No. 5 grade fibers are shorter and contain pulverized mineral impurities which readily settle out of the suspensions and can be removed by decantation.

Example VI

Crude chrysotile asbestos from Quebec, Canada, was hand cobbed, picked free from adhering rock impurities and put through a Wiley chopping mill to reduce the average fiber length to approximately ¼ inch. A suspension of 2.5 grams of this fiber in 250 cc. of distilled water was charged into a one quart porcelain ball mill along with 1.5 lbs. of glass beads $\frac{5}{16}$ inches in diameter. Two cubic centimeters of a one molar solution of aluminum chloride were added and the mixture was milled for 36 hours. An excellent thin translucent dispersion of ultimate asbestos fibrils resulted.

Example VII

Five hundred grams of a 1% dispersion of chrysotile asbestos was prepared according to the procedure of Example I and contained 0.15 millimoles of aluminum acetate per gram of asbestos or a total of 0.153 gram of aluminum acetate for the 5 grams of asbestos. The suspension was dried at room temperature by evaporation. The dry product was broken up into a fine voluminous fluff in a hammer mill. Two grams of this product were readily redispersed by mixing for two minutes in 198 grams of water in the Waring Blendor.

Example VIII

Three hundred grams of a ½% dispersion of #2 grade chysotile asbestos was prepared according to the procedure of Example II and contained 0.28 millimole of aluminum acetate per gram of asbestos or a total of 0.0857 gram of aluminum acetate for 1.5 grams of asbestos. The dispersion was filtered through a finely porous ceramic block 8 inches in diameter. The asbestos film remaining on the filter was allowed to dry at room temperature. It was a soft, very flexible film but remarkably strong as indicated by a tensile strength of 700 lbs. per square inch measured on the Scott Horizontal Tensile Tester and a tear strength of 43 grams per cm. as measured by the Elmendorff Tear Tester.

I claim:

1. An aqueous dispersion having a pH of from 3 to 6 and comprising up to about 5% by weight of discrete, Crystallite, chrysotile asbestos fibers

rom 20 to 40 millimicrons in diameter and, as a lispersing agent, a dissolved metal salt having a nonovalent anion and a cation containing a polyalent metal, the amount of dispersing agent being enough to give from 0.1 milligram moles of he salt to 3 milligram moles of dissociated anion per gram of asbestos.

2. An aqueous dispersion having a pH of from to 6 and comprising up to about 5% by weight f discrete, Crystallite, chrysotile asbestos fibers rom 20 to 40 millimicrons in diameter and a disolved aluminum acetate in an amount enough o give from 0.1 milligram moles of the salt to 3 nilligram moles of dissociated acetate ion per ;ram of asbestos.

3. An aqueous dispersion having a pH of from to 6 and comprising up to about 5% by weight f discrete, Crystallite, chrysotile asbestos fibers rom 20 to 40 millimicrons in diameter and a disolved aluminum formate in an amount enough o give from 0.1 milligram moles of the salt to 3 nilligram moles of dissociated formate ion per ;ram of asbestos.

4. An aqueous dispersion having a pH of from to 6 and comprising up to about 5% by weight f discrete, Crystallite, chrysotile asbestos fibers rom 20 to 40 millimicrons in diameter and a disolved zirconyl acetate in an amount enough to ;ive from 0.1 milligram moles of the salt to 3 miligram moles of dissociated acetate ion per gram f asbestos.

5. In a process for producing an aqueous asestos dispersion the step comprising disorienting riented chrysotile asbestos by agitation at a pH f 3 to 6 in an aqueous solution containing as a lispersing agent a metal salt having a monoalent anion and a cation containing a polyalent metal, the amount of dispersing agent being enough to give from 0.1 milligram moles of he salt to 3 milligram moles of dissociated anion per gram of asbestos.

6. In a process for producing an aqueous asestos dispersion the step comprising disorienting oriented chrysotile asbestos by agitation at a H of 3 to 6 in an aqueous solution containing n aluminum acetate in an amount enough to ;ive from 0.1 milligram moles of the salt to 3 miligram moles of dissociated acetate ion per gram f asbestos.

7. In a process for producing an aqueous asestos dispersion the step comprising disorienting riented chrysotile asbestos by agitation at a pH f 3 to 6 in an aqueous solution containing an luminum formate in an amount enough to give rom 0.1 milligram moles of the salt to 3 milligram moles of dissociated formate ion per gram f asbestos.

8. In a process for producing an aqueous asestos dispersion the step comprising disorienting riented chrysotile asbestos by agitation at a pH f 3 to 6 in an aqueous solution containing zironyl acetate in an amount enough to give from .1 milligram moles of the salt to 3 milligram noles of dissociated acetate ion per gram of asestos.

9. A dry composition consisting essentially of liscrete Crystallite fibers of chrysotile asbestos bout 20 to 40 millimicrons in diameter and, in ntimate admixture therewith, a metal salt havng a monovalent anion and cation containing a olyvalent metal, the amount of said salt being nough to give from 0.1 milligram moles of the alt to 3 milligram moles of dissociated anion er gram of asbestos when the composition is disersed in water at a concentration of not more than 5% by weight of asbestos and the composition, when so dispersed, giving a pH of from 3 to 6.

10. A dry composition consisting essentially of discrete Crystallite fibers of chrysotile asbestos about 20 to 40 millimicrons in diameter and, in intimate mixture therewith, an aluminum acetate in an amount enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated acetate ion per gram of asbestos when the composition is dispersed in water at a concentration of not more than 5% by weight of asbestos.

11. A dry composition consisting essentially of discrete Crystallite fibers of chrysotile asbestos about 20 to 40 millimicrons in diameter and, in intimate mixture therewith, an aluminum formate in an amount enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated formate ion per gram of asbestos when the composition is dispersed in water at a concentration of not more than 5% by weight of asbestos.

12. A dry composition consisting essentially of discrete Crystallite fibers of chrysotile asbestos about 20 to 40 millimicrons in diameter and, in intimate mixture therewith, a zirconyl acetate in an amount enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated acetate ion per gram of asbestos when the composition is dispersed in water at a concentration of not more than 5% by weight of asbestos.

13. An aqueous dispersion having a pH of from 3 to 6 and comprising up to about 5% by weight of discrete, Crystallite, chrysotile asbestos fibers from 20 to 40 millimicrons in diameter and, as a dispersing agent, a dissolved metal salt selected from the group consisting of aluminum acetate, aluminum formate, and zirconyl acetate, the amount of dispersing agent being enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated anion per gram of asbestos.

14. In a process for producing an aqueous asbestos dispersion the step comprising disorienting oriented chrysotile asbestos by agitation at a pH of 3 to 6 in an aqueous solution containing as a dispersing agent a metal salt selected from the group consisting of aluminum acetate, aluminum formate, and zirconyl acetate, the amount of dispersing agent being enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated anion per gram of asbestos.

15. A dry composition consisting essentially of discrete Crystalite fibers of chrysotile asbestos about 20 to 40 millimicrons in diameter and, in intimate admixture therewith, a metal salt selected from the group consisting of aluminum acetate, aluminum formate, and zirconyl acetate, the amount of said salt being enough to give from 0.1 milligram moles of the salt to 3 milligram moles of dissociated anion per gram of asbestos when the composition is dispersed in water at a concentration of not more than 5% by weight of asbestos.

GLEN D. BARBARAS.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,907,616	Tucker	May 9, 1933

FOREIGN PATENTS

Number	Country	Date
37,900	Germany	Apr. 24, 1885
499,807	Great Britain	Jan. 30, 1939