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OPENING UP ASBESTOS WITH DIMETHYLSULFOXIDE

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The invention relates to the processing of asbestos. It aims to provide a simple, inexpensive yet completely novel method for: (1) opening up aggregates of fibers of ordinary asbestos, releasing a large proportion of the constituent long fibrils of very small diameter (of the order of several hundred angstroms), and making possible a more homogeneous and highly dispersed slurry of asbestos fibrils and fibril aggregates whereby the use of asbestos may be facilitated and enhanced, particularly in the formation of papers of high purity, uniform texture, and increased absorbency properties, and (2) to reduce substantially the energy requirements for the conversion of asbestos, chemically pretreated by the method disclosed in my co-pending U.S. application Ser. No. 436,304, into stable colloidal gels and dispersions containing a significant proportion of particles less than one micron in maximum dimensions.

Ordinarily, asbestos is recovered from veins of rock such as deposits of serpentine by mechanical crushing and screen classification procedures. The resulting commercial fibrous asbestos consists largely of bundles of fibers, including tightly bound clusters of fibers called "pencils" because of their rigidity; these are the components in ordinary asbestos which give it a coarse "hand." The fibers in turn consist of fibrils having diameters of the order of 200–300 A., thousands going into each fiber. It is possible to break up pencils into fibers by further severe mechanical action approaching that of carding textile yarns, but only a very small percentage, if any, of the thousands of fibrils that make up a single asbestos fiber can be freed in this manner.

An alternative route to dispersing asbestos fibers into fibrils is disclosed by Novak in U..S Patent 2,626,213, issued Jan. 20, 1953, wherein asbestos fibers are treated with a surfactant which becomes highly absorbed on the surfaces of the fibrils, and affect a gradual dispersion of the fibers into individual fibrils in large proportion, with relatively small amounts of energy such as is obtained in a paper beating operation.

There are several difficulties encountered when surfactants are used to disperse asbestos; they are absorbed tenaciously and are very difficult to remove quantitatively; they lead to the formation of large amounts of foam and attendant handling problems during manufacture, and the retention of organic material by the asbestos imposes limitations on its performance for high operating temperatures. Furthermore, even ultra thin films of surfactants on the surfaces of the asbestos fibers or fibrils are undesirable in finished articles, as in certain electrical and insulating papers.

Of particular importance in the present instance, a surfactant coating on asbestos fibers makes them unreceptive to special chemical pretreatment prior to mechanical disintegration to produce truly colloidal dispersions of microcrystalline asbestos as by the method disclosed in my copending U.S. application Ser. No. 436,304.

I have discovered a method of treating commercial asbestos of any degree of "mechanical" openness whereby the fiber bundles, "pencils," and individual fibers can be dispersed effectively and with relatively mild mechanical action into particles and individual fibrils have diameters ranging from less than a micron to 200–300 angstroms, without changing the lengths of the constituent

fibrils significantly, and without the use of an organic surfactant, thereby precluding the formation of an organic coating on the surface of the fibrils. This same novel method may be applied with equal dispersing effectiveness to chemically pretreated asbestos fibers, as by the method in my copending U.S. application Ser. No. 436,304, to lead directly and with relatively mild mechanical action, to stable colloidal dispersions and gels of microcrystalline asbestos in which a large proportion of the particles are under one micron in maximum dimension.

In accordance with my invention, regular or highly opened (mechanically) asbestos fibers, or the chemically pretreated asbestos fibers described above, are soaked in dimethylsulfoxide (DMSO) and slurried to permit uniform wetting out of the fibers by the dimethylsulfoxide; dispersion of the slurry with the attendant release of individual fibrils or fibril fragments, respectively, may be aided by treatment of the DMSO slurry in a simple pulping device such as a beater or a Bauer refiner to provide the appropriate mild mechanical action desired. After the mechanical treatment, the excess DMSO is separated from the opened-up asbestos as by centrifuge, filter, or squeeze rolls, and asbestos washed free of DMSO, dried, and packaged ready for use.

There are several features which distinguish this invention over prior art: magnetite as well as other non-asbestos inorganic impurities including clays are readily removable after the DMSO soaking or slurrying treatment, leading to a whiter, much purer product free of any superimposed surfactant. The DMSO being infinitely soluble in water washes out rapidly, completely, and without any foaming whatsoever, leaving a product that is chemically identical with the product made without the use of DMSO—whether the starting material be ordinary asbestos, or the chemically pretreated asbestos respectively.

Although the preferred treatment for soaking or slurrying is to use the DMSO undiluted, dilution with water or any miscible solvent is operable. The DMSO, either undiluted or diluted may be also reused for the steeping and/or slurrying treatments inasmuch as there is no evidence that it is significantly changed chemically during the soaking or slurry steps.

By using elevated temperatures, the rate of dispersing the fibrils may be enhanced, although operating temperatures of the order of 100 degrees centigrade or less are preferred. Soak or slurry times of only 15 minutes are usually adequate, although much longer times may be desirable in some instances depending on the natural compactness of the fibril aggregations. Inasmuch as time and temperature are not critical, they can be varied to suit the convenience of the operator.

Attempts were made to evaluate other reactants in lieu of DMSO which had chemical structures, high dielectric constants, or unique ion-dipole interactions similar to DMSO. For example, bis-2-hydroxyethylsulfoxide had a much milder dispersing action than DMSO, as did dimethyl formamide. Acetone and amine oxides were substantially without any effect.

DMSO has been found also to be uniquely effective in the chemical pretreatment and modification of asbestos to produce microcrystalline asbestos, as disclosed in my copending application Ser. No. 436,304, wherein asbestos is treated with dilute acid to affect the appropriate chemical modification which makes the asbestos receptive to mechanical disintegration and conversion to true colloidal particles. For example, digestion of fibrous asbestos at 10% solids in a mixture of 0.4 M HCl containing 10% DMSO results in a product that is directly and more easily reduced to stable dispersions containing a build-up of submicron particles than is the case when the same starting material is digested in an identical manner with 0.4 M HCl alone.

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The raw material may be commercial asbestos as normally received, or it may be highly opened asbestos that has been further treated to loosen the "pencils" and fiber bundles by mechanical means such as by a hammer mill or the like.

In the case of a raw material comprising ordinary mechanically open asbestos, it may be added to a beater or other vessel equipped with appropriate stirring facilities and possessing a heating jacket to control temperature; preferably the vessel may be an autoclave or a digester, closed at the top to prevent contamination. After the soaking and/or slurrying treatment, the slurry may be passed through a disintegrator such as Bauer refiner or treated in a Cowles dissolver to affect a still further dispersion of the fibers into individual fibrils. The bulk of the DMSO is then separated mechanically from the opened-up asbestos, and recovered for re-use. The DMSO remaining on the asbestos is washed from it with water (other solvents for DMSO may be used), and the DMSO recovered from the wash liquors, by steam distillation or other means. Removal of impurities from the raw asbestos after the DMSO soak and/or slurry to produce a final product of outstanding purity may be done by flotation, or by electromagnetic separation, or sedimentation using an appropriately diluted slurry prior to final filtration, drying and packaging.

Products produced in the foregoing manner are especially advantageous for the manufacture of asbestos papers, and self-supporting asbestos films having remarkable softness and flexilibity because of the high proportion of fibrils in the "paper" web, yet the dimensional stability of the inherent asbestos composition is maintained. For the same reason, the absorbency of such papers for impregnation with plastic prepolymers for the manufacture of decorative laminates or laminated plastic structures is improved. Asbestos highly opened in this manner also is particularly useful as a viscosity builder for polar liquids such as glycerine, ethylene glycol, etc.

When the invention is applied to chemically modified microcrystalline asbestos, as disclosed in my copending U.S. application Ser. No. 435,304, and soaked or slurried in accordance with the sequence of steps described above for conventional asbestos, the DMSO treatment makes possible the formation of smooth, stable colloidal dispersions and gels, free of any "ropiness" due to the presence of the long fibrils because the combination of chemical pretreatment and mechanical disintegration produces much shorter fibril fragments, a large percentage of them being under one micron in maximum dimension; by contrast the fibrils freed using ordinary, untreated asbestos may be 50 microns or much more in length on the average, even though their diameters may be of the order of 200–300 angstroms.

The following specific examples are given by way of illustration, and not as limiting of the invention, which is defined in the claims.

Example 1

Chrysotile asbestos, recovered by the mechanical disintegration of serpentine rock, and further opened by mechanical crushing and sieving techniques such as to have a surface area of about 30 square meters per gram was slurried in a pulp beater as follows: 180 pounds was added to 820 pounds of dimethylsulfoxide in the beating vessel, and agitated at 100 r.p.m., for 15 minutes at room temperture (25 degrees centigrate). The resulting slurry was centrifuged, and the effluent diverted to the DMSO recovery unit along with the water used to wash the product free of DMSO. The asbestos "cake" recovered from the centrifuge contained a large proportion of free asbestos fibrils having diameters in the 200–300 angstrom range, and lengths averaging several millimeters in length. The "cake" was then redispersed at low consistency—only 0.2%—with water in a paper beater, and paper made from this product on a conventional Fourdrinier machine,

and dried in the conventional manner. A binder was not added. The resulting paper possessed an unusual soft texture, smooth surface, and absorbed a solution of melamine formaldehyde prepolymer rapidly.

Example 2.—Microcrystalline asbestos

A highly opened form of conventional chrysolite asbestos was pretreated with hydrochloric acid as described in Example 1 of my U.S. application Ser. No. 435,304, except that it was pretreated in a 10% slurry comprising 0.4 M hydrochloric acid and 10% DMSO for 30 minutes, and agitated during the digestion by means of an anchor-type paddle at 100 r.p.m. The product was recovered and dried to produce a yield of 87.5%, and a SiO_2/MgO ratio of 1.2 to 1.0 by weight. The resulting product was soaked in 50% DMSO-water for 25 minutes at 80 degrees centigrade. The excess DMSO-water was squeezed out to produce a paste of 30% solids, and this paste was passed through a Bauer refiner at ½ mm. clearance. The attrited paste was slurried in water, filtered, and the wash water was retained to permit DMSO recovery. The filtered product was oven dried and packaged as a low-density flour, or powder. The final product produced stable aqueous dispersions upon mixing in water at 4% solids from which continuous, self-supporting films of asbestos could be cast; when added to glycerine or ethylene glycol, clear, very highly viscosity thixotropic greases resulted at only 2% solids; when added to organic phosphates, silicone oils, esters, and alcohols, they were converted into very thick but clear smooth products having a grease-like appearance and consistency.

As indicated in my U.S. patent application Ser. No. 436,304, the chemical modification useful to produce microcrystalline material involves an increase in the silica to magnesia ratio so that the ratio is between about 1.05:1 and 1.30:1 by weight. This range of ratio is obtained by proper selection of acid concentration and time. The necessary acid concentration varies with the concentration of asbestos in the slurry increasing slightly as the concentration is increased. This is due to the fact that the asbestos has some material alkalinity which absorbs a portion of the acid before it can work chemically on the fiber itself.

Example 3.—Treatment of low grade asbestos fines

Thirty-five pounds of Coalinga chrysotile asbestos were charged with 65 pounds of DMSO into a soaking kettle, and held 60 minutes at 80 degrees centigrade, with mild agitation. The mass was centrifuged, put through a Bauer refiner at ½ mil clearance, washed free of DMSO, spray dried and packaged. The product was completely open, and contained a large proportion of the constituent platelet having a diameter of about 200–400 angstrom units. This ultra-fine form of asbestos was effective as a flocullant for sewage densification.

Example 4.—Microcrystalline asbestos

A long fiber premium grade chrysotile was pretreated with 0.4 M hydrochloric acid at 10% solids for 25 minutes at 100 degrees centigrade, and the product was washed and dried. The dried product was fed through a hammer mill to open it up mechanically, then added to a soaking kettle where water and DMSO were added to form a 10% paste of the asbestos in 50:50 water-DMSO. The material was agitated at 100 r.p.m. for 60 minutes at room temperature after which the excess DMSO was squeezed out, washed free of DMSO in a washing tank and fed at 30% solids through a Rietz extractor during which intense mechanical working of the asbestos occurred as evidenced by the asbestos becoming very hot. The attrited paste was reduced to a 2% slurry in a mixing tank and put through an electromagnetic separator to remove the iron oxide and dried in a drum drier. The product contained at least 15 percent of particles under one micron in size, and made excellent thixotropic dispersions in water and organic phosphates, silicone oils, esters and alcohols.

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Example 5

Commercial chrysotile asbestos of intermediate fiber length was fed into a soaking kettle with water and DMSO to produce a 15% paste in a 75% DMSO-25% water mixture. The mixture was agitated at 200 r.p.m. for 120 minutes at room temperature, filtered, washed free of DMSO in a washing tank and purified in a flotation tank after which it was made up into a 2% slurry in a beater. When made into paper, the product was exceptionally white, and performed most effectively as base paper of high dimensional stability and ideal absorbency for water color paintings.

Example 6

A low grade highly mechanically opened commercial chrysotile was fed into a soaking kettle along with DMSO, water and hydrochloric acid to produce a 10% paste in a 25% DMSO-75% water mixture containing sufficient acid to produce a 0.4 molar solution. It should be noted that there is sufficient alkalinity in the asbestos to neutralize a portion of this hydrochloric acid so that the effective amount of acid is lowered to produce about the same activity as 0.2 molar acid on a 5% basis. The mixture was agitated at 100 r.p.m. for 50 minutes at 100 degrees centigrade after which it was centrifuged, washed free of DMSO in a slurry washing tank and oven dried. Despite the lack of attrition the product contained substantial percentages of microcrystalline asbestos under one micron in particle size. Apparently, the mechanical action in the centrifuge and in the slurrying tank in the presence of DMSO was sufficient to break up the product sufficiently so that a sufficient amount of sub-micron particles was formed to produce a stable colloidal dispersion in water.

Example 7.—Microcrystalline asbestos

A long fiber chrysotile was dry fluffed in a large Waring Blendor and was soaked in DMSO, water and hydrochloric acid to product a 10% paste in a 30% DMSO-70% water mixture containing sufficient acid to yield a 0.4 M solution. It was heated at 100 degrees centigrade at 150 r.p.m. for 30 minutes after which the product was filtered, washed free of water and dried in a drum dryer. Here again there was sufficient mechanical action in the handling of the product after acid treatment to give a product containing substantial quantities of microcrystalline material under one micron in size so that the product gave thixotropic dispersions in water and grease-like products of high viscosity in tricresyl phosphate and glycols.

This product like the product of the last example and the other acid treated products of Examples 2 and 4 were obtained in yields of about 85–90% based on the original asbestos and contained a ratio of SiO_2 to MgO higher than that in original asbestos.

Example 8

Commercial chrysotile of an intermediate grade was dry fluffed in a Reitz distintegrator and soaked at 12% concentration with an 80% DMSO-20% water mixture. Agitation was at 150 r.p.m. and continued for 90 minutes at 50 degrees centigrade. The material was put into squeeze rollers, washed with DMSO, put into a tank and spray dried. The resultant product contained a large proportion of fibrils in the 150 A. diameter range.

It is obvious that the products disclosed are useful wherever asbestos is ueful and have the advantage of being very well opened up and free of contaminants.

I claim:

1. The method of opening up asbestos which comprises submitting it to mechanical action in a slurry with dimethylsulfoxide for a time sufficient to allow the dimethylsulfoxide to penetrate through the asbestos mass and for the mechanical action to largely separate the asbestos into fibrils with a diameter of the order of a few hundred angstrom units, and thereafter washing the asbestos free of dimethylsulfoxide.

2. The method of claim **1** in which the dimethylsulfoxide is used in undiluted form.

3. The method of claim **1** in which the dimethylsulfoxide is used diluted with water.

4. The method of producing microcrystalline asbestos having a large proportion of particles under one micron in largest dimension, which comprises treating asbestos with dilute acid to increase the ratio of silica to magnesia to between about 1.05:1 and 1.30:1 by weight, and submitting it to mechanical action in a slurry with dimethylsulfoxide for a time sufficient to allow the dimethylsulfoxide to penetrate through the asbestos whereby the product is opened up and largely converted to a material of submicron particle size, and thereafter washing the asbestos free of dimethylsulfoxide.

5. The method of claim **4** in which the acid treatment and the dimethylsulfoxide treatment are simultaneous.

6. The method of opening up asbestos which comprises submitting said asbestos soaked in dimethylsulfoxide in an amount sufficient to aid in the opening of said asbestos to mechanical action, continuing the mechanical action to obtain asbestos particles and fibrils ranging from less than a micron to a few hundred angstrom units in their largest dimension, and then washing the asbestos free of dimethylsulfoxide.

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