UNION CARBIDE

INTERNAL CORRESPONDENCE

PLAINTIFF'S EXHIBIT UC-715

METALS DIVISION

P. O. BOX 579 · 4625 ROYAL AVE., NIAGARA FALLS, NEW YORK 14

To (Name) Mr. R. E. Byrne, Jr.
Division UCC-Metals Division
Location Niagara Falls, NY

Date May 7, 1979

Originating Dept. "Calidria" Asbestos

Answering letter date

Copy to Messrs. F. J. McCarthy
J. L. Myers
File

Subject Possible Montello Patent on Oil-Wetted Asbestos

Attached is the patent information from Montello. I don't see anything in the three patents listed that bears closely on the Montello invention. The question in my mind is not so much specific prior patent art, but whether a person with a reasonable technical knowledge of chemistry and drilling mud technology, i.e. skilled in the art, could have assembled the elements described.

The invention has four limitations imposed in the choice of the oil plus the use of a surfactant. On this basis it seems to me that a reasonable application could be written for a patent based on a combination of five ingredients particularly if very critical ranges can be defined for several or all of them. Such a patent would obviously be quite narrow in scope. In this connection, it must be remembered that a patent covering only "Calidria" asbestos has a far more limited commercial scope than one covering all short-fiber chrysotile, regardless of source.

H. B. Rhodes

H. B. Rhodes

HBR:dal
Attachment

Montello
6106 EAST 32ND PLACE
TULSA, OKLAHOMA 74135
(918) 665-1170 / TWX 910-845-2396

RECEIVED
APR 27 1979
UCC-CALIDRIA
NIAGARA FALLS, N. Y.

April 24, 1979

Dr. Harry Rhodes
Union Carbide Corporation
Metals Division
P. O. Box 579
Niagara Falls, New York 14302

Dear Harry:

Sorry for the delay in getting these off to you. Frankly, it slipped my mind until my talk with Bob Byrne earlier today.

We are moving rapidly toward our first manufacturing run of any size on the oil wet product. Should have 2,500 to 3,000 bags ready by mid-May. All tests so far leave us optimistic about the possiblity of generating some very low TWA's.

Of course if there is any way of securing some kind of proprietary coverage for the product, this should be done. We'll look forward to having your thoughts.

Best regards,

MONTELLO, INC.

Kenneth N. Campbell

KNC/jd

Enc. (5)

cc: Harry Wyatt
Allen Johnson

To Whom It May Concern:

Asbestos has long been known to be an effective viscosifier in aqueous drilling fluids. It is also known to be more effective than other viscosfiers in aqueous systems containing salt and/or other contaminants. Modified forms of asbestos are also used as viscosifiers in oil base and invert systems.

The problem in the recent past has been the adoption of regulations governing the use of asbestos where any airborne fibers are emitted. This regulation has prevented many companies from using asbestos, although it is generally agreed that asbestos is the most economical viscosifier in aqueous systems, especially those containing salt and/or other contaminants.

In order to eliminate this problem, a number of different approaches have been taken, including different forms of the asbestos. These forms have included plain ground, pellets, cracked pellets, and water-wet. The above forms have not eliminated the problem of airborne fiber emissions.

The approach taken here was to coat the granular pellet with an oil like substance thereby reducing the possiblity of any airborne fiber emissions. The oil used must have the following characteristics:

1. Non-fluorescing
2. Bio-degradability
3. Low KB number
4. Must not adversely affect the yield of the asbestos

Along with the oil, a surfactant is added in very small quanities. The purpose of the surfactant in the oil is:

1. To increase the penetration of the oil into the pellets.

LAW OFFICES
HEAD, JOHNSON & CHAFIN, P. A.

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212 BEACON BLDG.
TULSA, OKLAHOMA 74103
(918) 584-4187

May 18, 1978

Montello
6106 East 32nd Place
Tulsa, OK 74105

Attention: Mr. Harry Wyatt, Vice-President

Re: Aqueous Viscosifier - Our File 78-140

Dear Mr. Wyatt:

Pursuant to your request, we have conducted a preliminary patentability search in the United States Patent & Trademark Office relating to an asbestos viscosifier which is specifically designed to eliminate the problems of air borne fiber emissions and the following patents were found as a result of that search:

Otouma et al	3,967,043	(1976)
Heron	3,660,148	(1972)
Xanthos et al	3,965,284	(1976)

Very briefly, the patent to Otouma et al teaches a dust proof asbestos which is coated with a water soluable film and is further impregnated by a water-insoluable compound.

The patent to Heron teaches the coating of asbestos cloth and other materials with polymeric coating, again for the purpose of reducing airborne fibers and dust content.

The patent to Xanthos et al teaches the encapsulating of chrysotile asbestos.

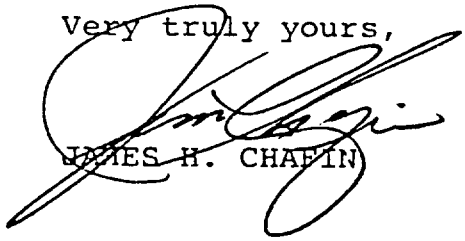
The above three patents were the closest art found in six subclasses of four separate classes of the search.

Although we are usually able to uncover the most pertinent prior art, you should be advised that a preliminary patentability search of this nature is not by any means an exhaustive search. Further, pertinent and prior art may not have been uncovered for various reasons including patents missing from the search room files and actual mis-classification of patents. The cost of the search often renders it impractical to cover foreign art and publications which could prevent the issuance of a United States patent. Similarly, by law, we are unable to look at pending applications which could ultimately prevent the issuance of a patent.

Although we did not find a specific oil and surfactant coating for asbestos material, I feel that you should study the enclosed patents before making a decision as to whether or not to incur the expense of filing and prosecuting a patent application on your invention. After you have had an opportunity to make your decision, if you wish a patent application prepared I feel we should probably get together and discuss the process used to manufacture the viscosifier product.

In the meantime, if you have any questions, feel free to contact me at your convenience.

Very truly yours,



JAMES H. CHAFFIN

JHC:ms
Enclosures

United States Patent [19]

Otouma et al.

[11] 3,967,043

[45] June 29, 1976

[54] **ASBESTOS ARTICLES HAVING DUSTPROOF PROPERTIES**

[75] Inventors: Takashi Otouma, Yokohama; Michio Nakamura, Odawara, both of Japan

[73] Assignee: Nippon Asbestos Company, Ltd., Tokyo, Japan

[22] Filed: Jan. 3, 1974

[21] Appl. No.: 430,590

[30] **Foreign Application Priority Data**

Mar. 26, 1973 Japan 48-34299

[52] U.S. Cl. 428/443; 428/524

[51] Int. Cl.² B32B 19/02

[58] Field of Search ..... 117/126 AB, 62.2, DIG. 3, 117/126 AQ; 428/443, 271, 290, 375; 427/340, 341, 342; 260/14

[56] **References Cited**

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2,190,672	2/1940	Meharg	117/DIG. 3
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3,415,674	12/1968	Voisinet	117/126 AB X
3,542,706	11/1970	Columbus et al.	260/14
3,660,148	5/1972	Heron	117/126 AB

Primary Examiner—Ronald H. Smith
Assistant Examiner—Evan K. Lawrence
Attorney, Agent, or Firm—Browdy and Neimark

[57] **ABSTRACT**

A method of preparing asbestos articles to exhibit dustproof effects in secondary processing without degradation of the inherent properties of the asbestos articles comprises the step of immersing the asbestos article in a treating agent comprising formaldehyde, a water-soluble organic compound capable of reacting with formaldehyde to form a water-insoluble compound under weakly alkaline conditions in an atmosphere maintained at a high temperature and a high humidity, a plasticizer, and a water-soluble macromolecular substance having film forming properties, and the steps of infusing the asbestos article with a weakly alkaline solution and first reacting the asbestos article in an atmosphere maintained at a high temperature and high humidity, and subsequently heat treating the resulting product to obtain the final product. The final product is impregnated in the interior substrate thereof by 0.5 to 10 wt.% of the water-insoluble compound, has a surface layer of 0.04 to 0.09 wt.% of a film of the water-soluble micromolecular substance, and has 1.5-30 wt.% of a polyhydric alcohol plasticizer.

2 Claims, 1 Drawing Figure

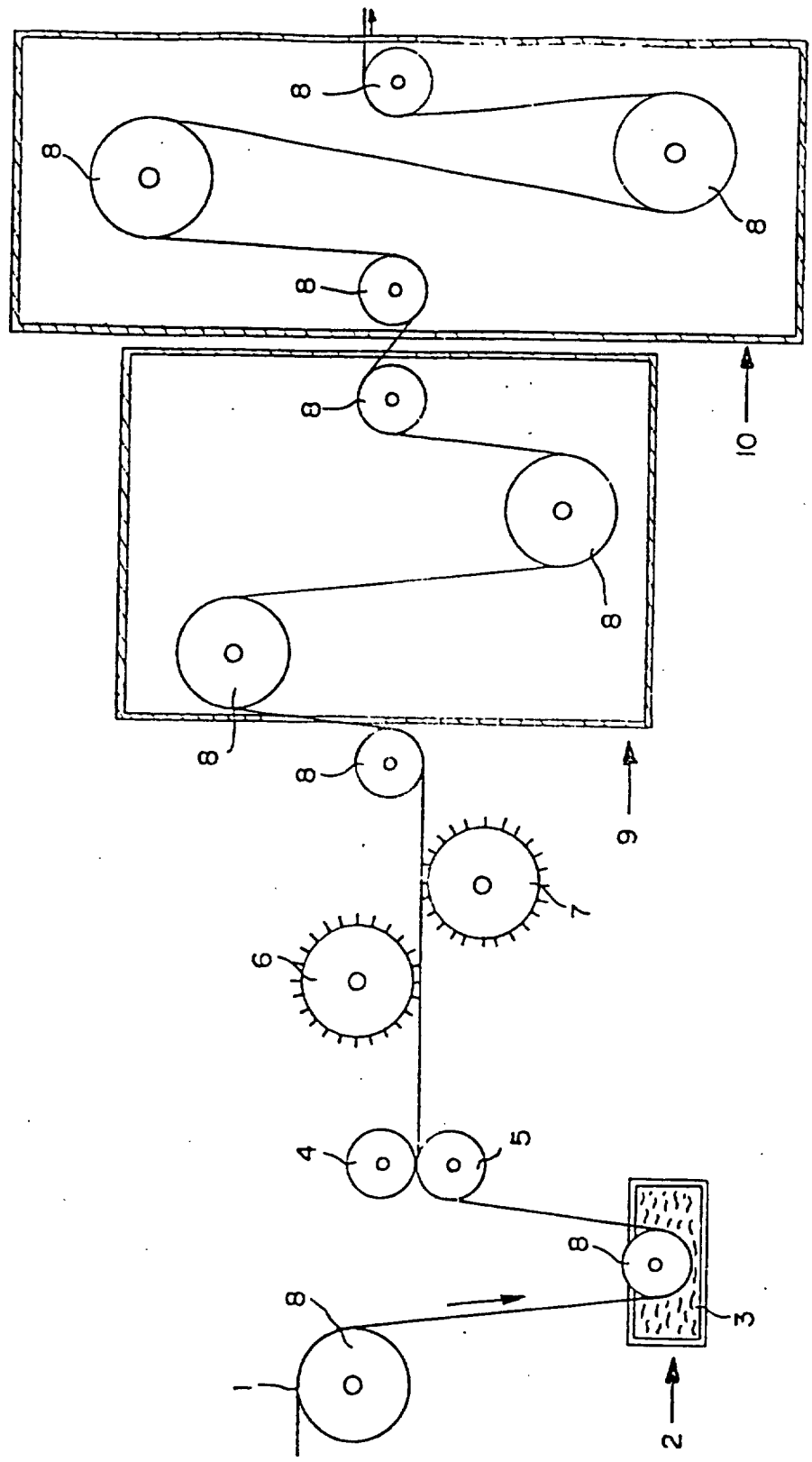


FIG. 1

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asbestosclaims.law/library/15947/7

ASBESTOS ARTICLES HAVING DUSTPROOF PROPERTIES

FIELD OF THE INVENTION

The present invention relates to a method of preparing and treating asbestos articles to exhibit dustproof properties in secondary processing, particularly spun and woven asbestos articles, by treating such articles with a treating agent without degradation of the inherent asbestos properties of the articles.

BACKGROUND OF THE INVENTION

Emulsions, dispersions or solutions containing macromolecular substances have heretofore been used for imparting dustproof properties to asbestos articles. According to conventional techniques, such treating agents are impregnated into the interior substrate and/or onto the surface portions of an asbestos article and then the dispersion medium or solvent is removed by drying, thereby leaving a film of the macromolecular substance contained in the treating agent. Since in the secondary processing of asbestos articles they are subjected to cutting and other processing operations, it is essential that the dustproof properties be imparted uniformly to not only the surface portions but also the interior substrate of asbestos articles. However, in conventional techniques, the dispersed substance or solute tends to gather on the surface portions of an asbestos article at the drying step, thus the distribution density is frequently lower in the interior substrate portion of the article. Consequently, optimal dustproof effects cannot be obtained using conventional techniques.

BRIEF SUMMARY OF THE INVENTION

This invention provides a method which overcomes the above mentioned defects in conventional techniques by imparting dustproof properties uniformly to not only the surface portions but also the interior substrate portion of an asbestos article without the degradation of its inherent asbestos properties. The treating agent used in this invention is one prepared by forming a mixture of formaldehyde with a water-soluble organic compound capable of both being aged under weakly alkaline conditions in an atmosphere maintained at a high temperature and a high humidity and reacting with formaldehyde to form a water-insoluble compound, adding a plasticizer such as a polyhydric alcohol or any other liquid alcohol having a high molecular weight, and finally incorporating a water-soluble macromolecular substance having film-forming properties into the resulting mixture. An asbestos article to be treated, hereinafter referred to as a "starting article," such as a spun or woven article of asbestos in the form of cloth, tape, rope or the like, is immersed in this treating agent in order to impregnate the starting article with the treating agent. Then the resulting product is first aged with a weakly alkaline substance in an atmosphere maintained at a high temperature and a high humidity, and subsequently subjected to heat treatment and dried.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic diagram of an apparatus employed in carrying out the method of this invention.

DETAILED DESCRIPTION

The product formed in accordance with the method of this invention is hereinafter referred to as the "complete product." Because the treating agent used in the present invention is impregnated through the entire starting asbestos article and close adhesion and bonding among asbestos fibers in the asbestos article is obtained in the aging and heat treatment steps, the amounts of each ingredient in the treating agent is defined based on the weight of the dried complete product.

The complete product comprises 1.5 to 30 wt.% of said polyhydric alcohol or other high-molecular-weight alcohol, 0.04 to 0.09 wt.% of the water-soluble macromolecular substance having film-forming properties which is uniformly distributed through the surface layer, and 0.5 to 10 wt.% of the water-insoluble compound formed during the heat treatment and aging steps which is distributed through the interior of the complete product. The treating agent to be used in this invention may further comprise methanol as a stabilizer for an aqueous solution of formaldehyde. If the amount of polyhydric alcohol or other high-molecular-weight alcohol, the plasticizer, is less than 1.5 wt.%, plasticizing effects in the asbestos article cannot be obtained, and if the amount of the plasticizer exceeds 30 wt.%, the plasticizer, a liquid substance, will ooze out when the asbestos article is pressed by fingers or the like. If the amount of the water-soluble macromolecular substance to be used as the film-forming substance is less than 0.04 wt.%, the resulting dust-proof effects are too low, and if the amount of this substance exceeds 0.09 wt.%, the surface layer of the asbestos article becomes too readily combustible. In this invention, the content of the water-insoluble substance formed by the reaction between the water soluble organic compound and formaldehyde is limited to a range of from 0.5 to 10 wt.% because at a content below 0.05 wt.% the dustproof effects are too low and at a content exceeding 10 wt.% the complete product becomes too hard to work in the subsequent secondary processing.

Some examples of treating agents employed in the method of this invention are set forth below:

Example 1	
Melamine (15% aqueous solution)	50 parts
Formaldehyde (20% aqueous solution)	50 parts
Glycerin plasticizer	3 parts
Polyethyleneoxide water-soluble macromolecular substance (0.5% aqueous solution)	10 parts
Methanol	1 part
Total	114 parts
Example 2	
Urea (10% aqueous solution)	50 parts
Formaldehyde (20% aqueous solution)	50 parts
Ethylene glycol plasticizer	5 parts
Polyvinyl alcohol water-soluble macromolecular substance (0.5% aqueous solution)	10 parts
Methanol	2 parts
Total	117 parts
Example 3	
Urea (25% aqueous solution)	50 parts
Formaldehyde (38% aqueous solution)	50 parts
Glycerin plasticizer	5 parts
Polyethyleneoxide water soluble macromolecular substance (0.5% aqueous solution)	10 parts
Methanol	4 parts
Total	119 parts
Example 4	
Phenol (10% aqueous solution)	40 parts

Union Carbide trial exhibit UC-715: H. B. Rhodes to R. E. Byrne, Jr. on a Possible Montello Patent on Oil-Wetted As... Published by AsbestosClaims.Law
ACL Doc 15947 · Page 8 of 26 asbestosclaims.law/library/15947/8

-continued

Formaldehyde (20% aqueous solution)	40 parts
Glycerin plasticizer	40 parts
Methyl cellulose water-soluble macromolecular plasticizer (1% aqueous solution)	10 parts
Methanol	2 parts
Total	132 parts

Example 5

Aqueous solution of phenol prepolymer (average molecular weight — 200; concentration — 60%	1 part
Formaldehyde (5% aqueous solution	1 part
Glycerin plasticizer	3 parts
Polyethyleneoxide water-soluble macromolecular substance (0.5% aqueous solution)	10 parts
Water	85 parts
Total	100 parts

The method of the present invention can be illustrated with reference to FIG. 1; guide rollers of varying diameters are connoted by reference number 8. A starting article 1 is passed through a treating bath 2 containing treating agent 3 to impregnate the starting article with the treating agent. The impregnated article is forwarded through squeeze rolls 4 and 5 where excess treating agent is removed so that the weight of the impregnated article is 2.1 to 2.2 times the weight of the starting article. Then, the impregnated article is brushed by means of brushing rolls 6 and 7 to infuse a water-soluble alkaline component through the asbestos article and into the treating agent impregnated in the starting asbestos article in order to attain the weakly alkaline conditions (pH 8~11) necessary for the reaction of the reactive substances in the treating agent. During this brushing treatment, the impregnated asbestos article is also squeezed by the brushing rolls so that the weight of the impregnated article is about 2 times the weight of the starting article. Then, the aging step is conducted for 15 to 20 minutes in an aging tank 9 filled with high humidity conditions (R.H. 20%~100%) at 70°C~100°C. The article coming from the aging tank is heat-treated and dried in a drying furnace 10 maintained at about 70°C~150°C. This results in a complete product which comprises 1.5 to 30 wt.% of the polyhydric alcohol or other high molecular-weight alcohol as the plasticizer, 0.04 to 0.09 wt.% of the water-soluble macromolecular substance having film-forming properties uniformly distributed in the surface layer and 0.05 to 10 wt.% of the water-insoluble compound distributed through the interior of the complete product and formed by the above aging and heat treatment steps. In the foregoing example the brushing treatment is adapted to attain weakly alkaline conditions, but means for attaining weakly alkaline conditions are not limited to a brushing step and it is possible to add an alkaline substance such as aqueous ammonia or a dilute solution of sodium hydroxide by some other suitable means.

The water-soluble organic substance such as melamine, urea, phenol and phenol prepolymer used in the above examples 1-5 is fixed and bonded to the surface of the asbestos fibers in the aging tank 9 and reacts with formaldehyde to form a water-insoluble resinous compound. This reaction proceeds and is completed in the drying furnace 10. The water-insoluble compound formed by this reaction acts as a dust-proofing binder bonding asbestos fibers to one another in the interior of the asbestos article. The water-soluble macromolecular substance such as polyethyleneoxide, polyvinyl alcohol or methyl cellulose forms a film on the surface layer of the starting article at the drying step and thus exhibits dust-proof effects. Furthermore, since the polyhydric or other high-molecular-weight alcohol such as glycerin or ethylene glycol is distributed through the interior of the starting article as a liquid plasticizer, despite the above-mentioned bonding activity and film-forming activity brought about in the interior and the surface layers of the asbestos article, the flexibility is not lost in the complete product.

In order to know the dustproof effects of the complete product made in accordance with this invention, tests were conducted in the following manner using products made with the treating agents of the above Examples 1 to 5. A film filter is connected to a suction pump and the sucking rate is adjusted to 200 cc/min. The sample is cut with scissors at the same height as the filter and about 30 cm from the filter. Asbestos fiber dust formed by the cutting step is collected by the filter. The collected dust particles are fixed on the filter film by use of a fixing agent, and after the filter film is made transparent by use of a chemical, the filter film is observed under a phase-contrast microscope. The number of particles having a length greater than 5 μ is counted and the number of asbestos dust particles per cc of air is calculated. Results are shown in the following Table:

Table 1

	Number of asbestos dust particles per cc of Air	Flexibility	Appearance
Untreated Article	30	good	good
Product of Example 1	1.2	good	good
Product of Example 2	1.3	good	good
Product of Example 3	0.9	slightly inferior	slightly colored
Product of Example 4	1.2	good	slightly colored
Product of Example 5	1.3	good	good

As is indicated by the results from the foregoing Table, in the complete product of this invention, surfaces of interior asbestos fibers are covered with the water-soluble resinous compound and these fibers are bonded tightly to one another by such water-insoluble resinous compound. Furthermore, a film is formed on the surface layer of the asbestos article. Accordingly, in the complete product of this invention, the dustproof effects are attained in not only the interior but also the outer portions and these effects are very high. Moreover, although the interior and outer portions of the asbestos article are in the coated state, flexibility is imparted to the complete product by the presence of the plasticizer and therefore, the inherent flexibility of the asbestos article is not lost in the complete product of this invention.

The foregoing description of this invention will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify such invention and/or vary it without departing from the generic concept, and, therefore, such variations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed invention. It is to be understood that the phraseology or terminology employed herein is for the purposes of description and not of limitation.

What is claimed is:

1. An asbestos product which exhibits dustproof effects comprising an asbestos article impregnated in the interior substrate thereof by the reaction product of formaldehyde and a water-soluble organic compound reacted therewith to form a water-insoluble compound under weakly alkaline conditions in an atmosphere maintained at a high temperature and a high humidity, said reaction product being present in an amount of 0.05 to 10 wt.% based on the total weight of the asbestos product, said asbestos product having a surface layer of 0.04 to 0.09 wt.% based on the weight of the

said asbestos product of a film of a water-soluble macromolecular substance, said asbestos product having 1.5 – 30wt. % based on the weight of the asbestos product of a polyhydric alcohol plasticizer therein.

2. The asbestos product in accordance with claim 1 wherein said water-soluble organic compound is melamine, urea, phenol or phenol prepolymer, and said water-soluble macromolecular substance is polyethyleneoxide, polyvinyl alcohol or methyl cellulose.

* * * * *

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asbestosclaims.law/library/15947/10

United States Patent
Heron

[11] 3,660,146
[45] May 2, 1972

[54] TREATMENT OF ASBESTOS

[72] Inventor: Gordon F. Heron, Rochdale, England

[73] Assignee: Turner Brothers Asbestos Company Limited, Manchester, England

[22] Filed: Jan. 8, 1970

[21] Appl. No.: 1,635

[30] Foreign Application Priority Data

Jan. 10, 1969 Great Britain.....1,579/69

[52] U.S. Cl. .....117/126 AB, 117/161 UC, 117/161 UD, 117/162, 162/155, 161/92

[51] Int. Cl. B32b 19/02, B32b 19/08

[58] Field of Search.....117/126 AB, 161 UD, 161 UC, 117/162; 162/155; 161/92

[56] References Cited

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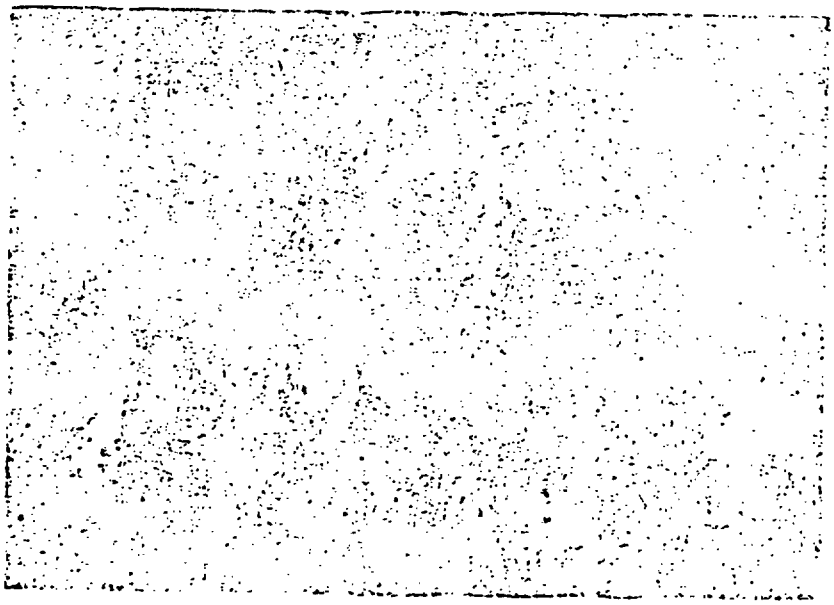
591,327 1/1960 Canada.....117/126 AB

Primary Examiner—William D. Martin
Assistant Examiner—D. Cohen
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] ABSTRACT

The invention comprises treating asbestos cloth and other asbestos products to reduce the dust emitted by them during handling and use. This is done by distributing a small amount of polymeric particles throughout the product to bind the fibers to one another thereby binding the loose particles except the dustiest essentially [illegible]. The preferred method consists in impregnating [illegible] with a solution or suspension of the polymeric material and removing the water.

6 Claims, 4 Drawing Figures



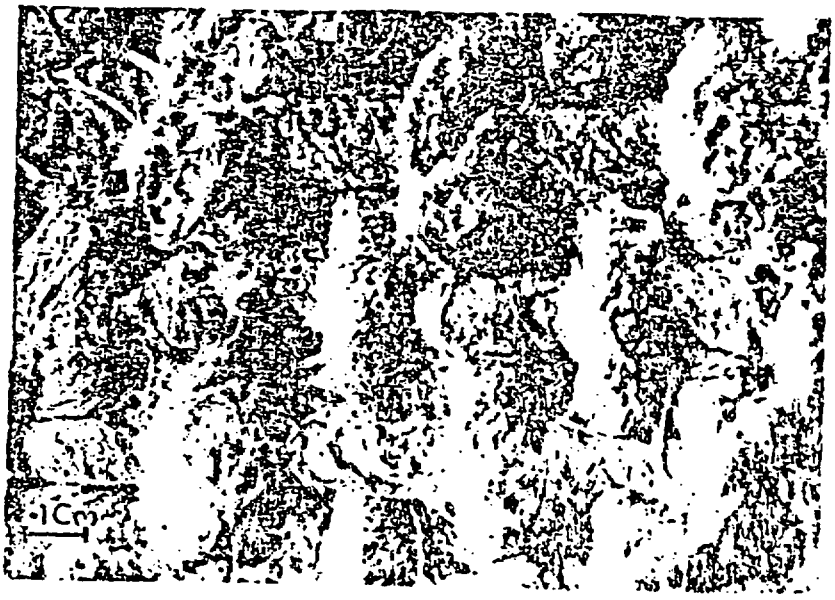


FIG. 1

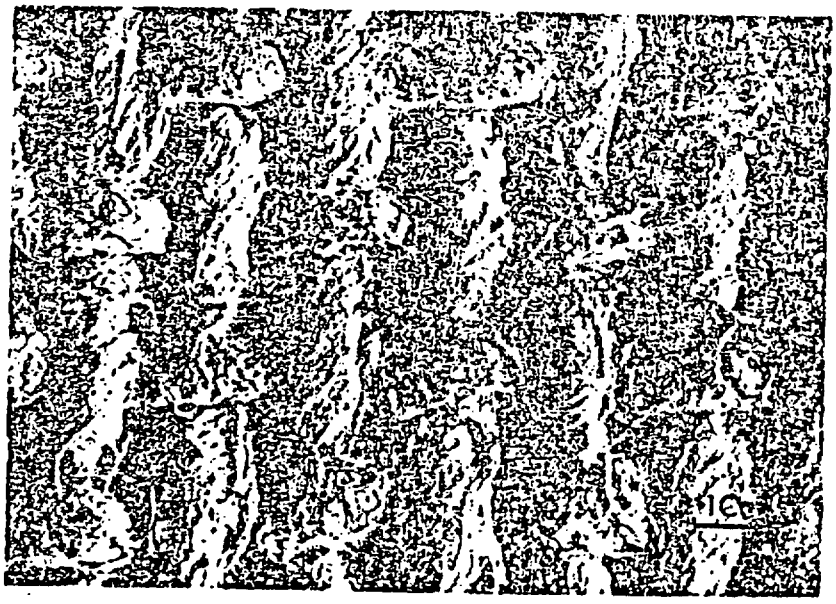


FIG. 2

INVENTOR
GORDON F. HERON
BY Sughrue, Rothwell, Mion, Zinn & Macpeak
ATTORNEYS

Fig. 3

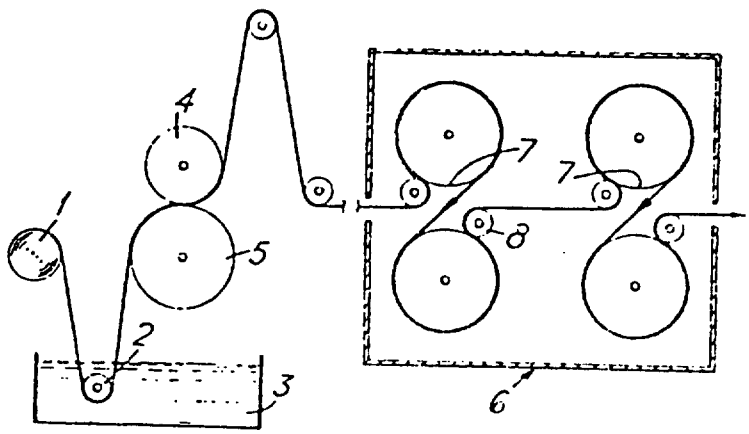
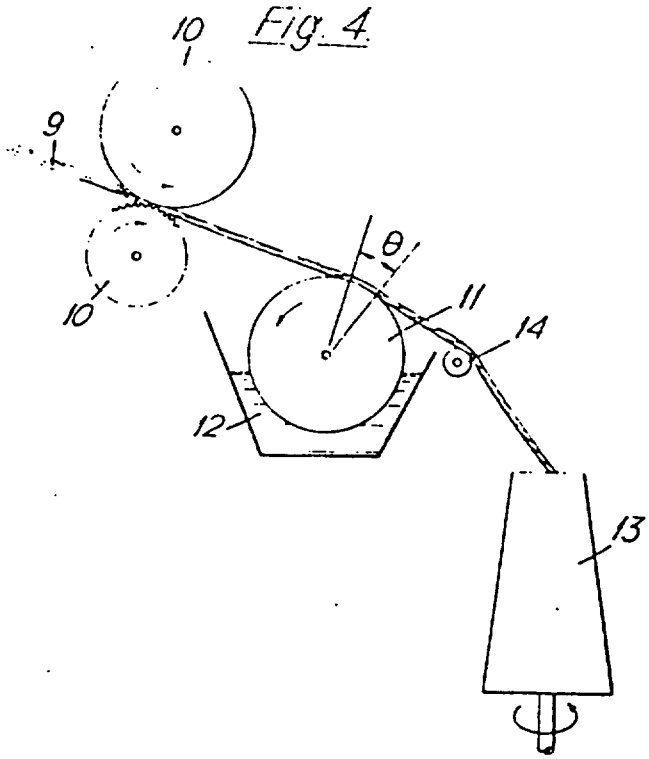


Fig. 4



Inventor
GORDON F. HERON

BY Sughrue, Rothwell, Mion, Zinn & Macpeak
Attorneys

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TREATMENT OF ASBESTOS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the treatment of asbestos products.

2. Description of the Prior Art

In recent years the risk of contraction of asbestosis by people who make or handle asbestos products has been increasingly appreciated. This risk arises when asbestos dust is present in the atmosphere. Dust control is usually achieved in manufacturing processes by the use of ventilation, or by enclosing or shielding machinery, but the users of the manufactured products frequently work in unprotected atmospheres. For example, asbestos cloth used as insulation is often torn by the installers, and asbestos clothing is often roughly handled. Then short fibers fluff and fibrous particles are given off as dust into the atmosphere.

The suppression of asbestos dust is accordingly an acute problem. Coating the product is an obvious approach, but has not proved successful.

The most important requirements for the majority of asbestos products in normal use are that the products should give rise to the minimum of dustiness in normal handling (not necessarily tearing), that the flexibility and handling characteristics of the product should not be substantially impaired, and that the product should be compatible with materials subsequently applied to it, such as resin, rubber or paint. In short, the product, though treated to suppress dust, should not lose any of its natural characteristics other than that of giving off dust.

The most important asbestos products which it is desirable to treat for dust suppression are asbestos cloth of all kinds, which normally contain a small proportion (say 10 percent) of cotton or other organic fibers Other materials advantageously treated include slivers, yarns, tapes and rope.

A solution of the problem proposed some thirty years ago involved brushing a synthetic resin diluted with acetone onto the outside of a garment of asbestos cloth and, after evaporation of the acetone, baking the garment to toughen the resin. However, the application of a surface layer to asbestos cloth impairs the handle and flexibility of the cloth and in practice does not solve the problem, because dust in the interior of the cloth is still liable to escape, for example when the cloth is torn. As far as we are aware this old process has never come into use in practice.

To proof asbestos cloth with rubber or other material is also known, but this is no remedy, as the cloth is completely changed in handle, flexibility and appearance by the proofing.

SUMMARY OF THE INVENTION

I have surprisingly found that asbestos cloth and other products can be rendered substantially less dusty without essential modification of any other property of the cloth or other material if a suitable polymeric material is so introduced into the asbestos product as to bond as many as possible of the fibers to one another.

To be suitable, the polymeric material must have two essential properties. First, it must possess the ability to bond the fibers in the asbestos product, and a suitable criterion of this is film-forming ability, that is to say ability to form a coherent film on drying from solution, emulsion or dispersion. Second and most important, it must be flexible; a suitable criterion of flexibility is the extension at break of the material under the A.S.T.M. tensile test D 882–61I and under this test the polymeric material must have an extension to break of at least 10 percent, and preferably at least 50 percent. Advantageously the polymeric material is thermoplastic or elastomeric.

According to the invention at least the majority of the fibers in an asbestos product are bonded by particles of such a polymeric material distributed throughout the asbestos product in an amount of from 0.1 to 5 percent by weight of the product. This distribution can be effected by impregnating the asbestos product throughout with a dispersion, emulsion or solution of the polymeric material, and removing the continuous phase of the dispersion or emulsion or the solvent of the solution to leave polymer particles adherent to and bonding together at least the majority of the fibers at points of contact with other fibers. On the other hand, spreading a melt of the polymeric material on asbestos cloth is of no value, as it merely proofs the cloth.

DETAILED DESCRIPTION OF THE INVENTION

While a solution gives maximum penetration and bonding of the asbestos, the most suitable polymeric materials are not water-soluble, and the use of organic solvents leads to problems in solvent recovery. Preferably, therefore, the polymeric material is applied in the form an aqueous dispersion or emulsion. A particularly advantageous process comprises immersing the asbestos product in an aqueous emulsion or dispersion, e.g. by passing it through a bath of the emulsion or dispersion, mechanically expressing water from the material, e.g. by passing it between two rolls, and then drying it, e.g. by passing it through a dryer. To ensure uniform distribution of the polymeric material in the asbestos product, its concentration in the dispersion or emulsion should be low, preferably no more than 5 percent by weight and better still no more than 2 percent.

What is required is that the pick-up of the polymeric material shall be from 0.1 to 5 percent weight of the asbestos product, and preferably from 0.5 to 3 percent by weight, and the concentration of the polymeric material, the duration of the immersion, the amount of water expressed, and the nature of the cloth or other asbestos product must be correlated to give the desired pick-up.

Asbestos slivers or yarn may be impregnated by passage over a damping roller which dips into a bath of a dispersion or emulsion; in this case the concentration of the polymeric material may be higher, say up to 10 percent.

Polymeric materials of very different chemical compositions have been found to give satisfactory results, though some such as polyvinyl acetate must be plasticized if they are to have the required extension to break without which satisfactory results are not obtained. Suitable polymeric materials with their approximate percentage elongations at break include polyvinyl acetate plasticized with 20 percent dibutyl phthalate (450 percent), terpolymers of vinyl acetate, unsaturated acid and vinyl caprate (300 percent), copolymers of vinyl acetate and 25% 2-ethyl-hexyl-acrylate (320 percent), plasticized polyvinyl chloride (50 percent), copolymers of vinyl acetate and an acrylate and copolymers of styrene and an acrylate, (which are too soft to test for extension), natural rubber latex (2,000 percent), styrene-butadiene rubber latex (2,000 percent) and neoprene (1,500 percent). In contrast unplasticised polyvinyl acetate (8 percent) renders the product stiff and harsh to handle, as do emulsions of polystyrene (3 percent) and emulsioms of phenol-formaldehyde resins (3 percent). These polymeric materials so modify properties of the product as to be of no value.

In the drawings,

FIGS. 1 and 2 are photomicrographs of, respectively, untreated asbestos cloth and asbestos cloth treated according to the invention.

FIGS. 3 and 4 diagrammatically show two ways by which asbestos products can be treated according to the invention.

Referring to FIG. 3, a roll of asbestos cloth 1 is unwound to pass round a roller 2 in a bath 3 containing an emulsion or dispersion of the polymer, and leaves the bath to pass between rollers 4 and 5 which express liquid from it, this liquid dropping back into the bath. The impregnated cloth then travels through a dryer 6, which is essentially formed by a housing for four cylinders 7 internally steam-heated to and from which the cloth is guided by rollers 8.

Some examples of the treatment of different asbestos cloths in apparatus such as that diagrammatically shown in FIG. 3 will now be given.

Union Carbide trial exhibit UC-715: H. B. Rhodes to R. E. Byrne, Jr. on a Possible Montello Patent on Oil-Wetted A... Published by AsbestosClaims.Law
ACL Doc 15947 · Page 14 of 26 asbestosclaims.law/library/15947/14

EXAMPLE 1

A general purpose asbestos cloth, weighing 28 ounces per square yard with a plain weave was passed at 80 feet per minute through an emulsion of a copolymer of vinyl acetate and maleic ester containing 1.7 percent solids by weight. The amount of liquid left in the cloth after passing through the rollers 4 and 5 was 45 percent by weight of the cloth. The cloth emerged dry from the dryer 6 and contained 0.7 percent dry polymer by weight. The suppression of dust and the general handling characteristics were both excellent.

EXAMPLE 2

A further roll of the same cloth as in Example 1 was treated in the same way by passage through a bath of an emulsion of methacrylic ester homopolymer. The pick-up of the polymer was 0.7 percent. The dust suppression was excellent, but the handle was not quite so good.

EXAMPLE 3

An asbestos cloth weighing 78 ounces per square yard with a twill weave, normally used for insulating lagging, was treated exactly as in Example 1, but the amount of liquid left in the cloth after passing through the rollers 4 and 5 was 50 percent by weight. The pick-up was 0.8 percent. The results were as good as in Example 1.

EXAMPLE 4

Equally good results were obtained on the cloth used in Example 3 when the emulsion of the copolymer was replaced by natural rubber latex..

EXAMPLE 5

A cloth weighing 36 ounces per square yard with a plain weave was treated with a styrene-butadiene rubber latex, the pick-up being 0.6 percent. The dust suppression and handle were both excellent.

EXAMPLE 6

The same cloth as in Example 5 was treated in the same way with an emulsion of a copolymer of styrene and an acrylic acid ester, the pick-up being again 0.8 percent by weight. The dust suppression was excellent, but the treated cloth, though satisfactory, was a little stiffer.

EXAMPLE 7

The same cloth as in Example 1 was treated with an emulsion of polyvinyl chloride plasticized with 15 percent tricresyl phosphate, the pick-up being 0.7 percent. The dust emission was much reduced, but the improvement was not as great as in Example 1.

EXAMPLE 8

Example 1 was repeated with neoprene latex as the polymeric material. The dust suppression was good, but the product became stiffer and discoloured with age, so neoprene is most suitable only when the product is to be used shortly after treatment.

In contrast, when the cloth of Example 1 was treated with an emulsion of a phenolic resin of 2 percent concentration by weight, with a pick-up of 1 percent, the dust suppression was poor and the cloth became excessively stiff and harsh. When the same cloth was treated with an emulsion of unplasticised polyvinyl acetate to give a pick-up of 0.8 percent there was no significant improvement in dust emission, and the cloth was unacceptably stiff and harsh.

A practical test for the emission of dust is "mark-off," that is to say the appearance of fibers on a dark cloth against which the product is rubbed. Untreated asbestos products leave numerous small fibers on the cloth, whereas products of Examples 1 to 8 mark the cloth to a very much smaller extent.

Since dust may be produced by normal handling, which includes chafing and flexing, or by tearing, tests have been devised to enable comparisons to be made. The number of fibers in air can be measured both by a Royco electro-optical particle counter, and by collecting the fibers on a membrane filter and counting them under an optical microscope. In chafing tests a sample of cloth is repeatedly drawn through a right-angle across the edge of a metal plate inside a box through which air flows, and the fibers carried out of the box are assessed. The results can be expressed as fibrous particles per cc of air (p/cc). In the tearing tests a mechanism in the same box is externally operated to tear cloth.

The results of such tests on both the untreated and the untreated cloths of Examples 1, 2, 5, 6 and 8 are given below.

Cloth	Chafing Test p/cc Royco	Tearing Test p/cc Royco
Untreated cloth of Examples 1 and 2	7.8	53 5
Example 1	0.17	13.1
Example 2	0.2	9 0
Example 8	0.25	14 0
Untreated cloth of Examples 5 and 6	2 7	46 1
Example 5	0 22	11.5
Example 6	0 25	12 0

As an indication of the reduction of dust in practice, specimens of the untreated cloth of Example 1, the cloth as treated in that example, and the same cloth treated with natural rubber latex were torn and then fitted round a steam pipe. Samples of the air were taken during the tearing processes, and continuous air samples were taken during the fitting and sewing of the cloth in position. The Table below shows the results obtained.

Cloth	During Tearing p/cc	During Fitting and Sewing p/cc
Untreated Cloth	61.0	6 0
Cloth treated as in Example 1	8.6	2 2
Cloth treated with natural rubber latex	6.0	2.3

That the treatment according to the invention does not interfere with post-treatments of the cloth is shown by a test in which untreated cloth of the kind used in Examples 5 and 6 and the same cloth treated with natural rubber latex according to the invention were proofed with rubber, and then pieces of the proofed cloths were plied together under heat and pressure. The resultant laminates were then tested for strength between the plies by a peeling test. It was found that the laminate produced from the cloth treated according to the invention resisted peeling better than the laminate produced from the untreated cloth.

FIG. 4 diagrammatically shows the impregnation of asbestos sliver as it passes through a spinning frame.

The asbestos sliver, shown at 9, passes between rollers 10 and then over a damping roller 11 which dips into a bath 12 of a dispersion or emulsion of the polymeric material and from this to a flyer frame package 13 shown purely diagrammatically. In passing from the bath to the package 13 the sliver passes over a bar 14, the position of which determines the angle of contact θ between the damping roller 11 and the partially twisted sliver. The twist runs back from the package 13 to the rollers 10 with the result that the sliver is rotating while

in contact with the roller 11, the uniformity of impregnation being accordingly improved.

The advantage obtained by means of the invention is shown by dust measurements made in the atmosphere close to a spinning frame in which asbestos sliver was impregnated with an emulsion of the copolymer of polyvinyl acetate and maleic ester of 8 percent concentration, and also when more of the same untreated sliver passes to the frame. The pick-up of the copolymer was 0.5 percent by weight of the sliver. The Royco measurement in p/cc was 1.0 for the untreated sliver but only 0.35 for the treated sliver.

The yarns spun in the frame were tested for dust emission by being wound from the spinning bobbins into cheeses in a box of the kind used for the chafing and tearing tests. During the winding, the Royco counts in p/cc air were 2.8 for the untreated yarn, but only 0.65 for the treated yarn. Moreover, the treated yarn, except for the improvement in dust emission, was essentially similar to the untreated yarn.

An important property of asbestos cloth is inflammability. Since the process according to the invention introduces a combustible product into the cloth, it might be thought that there would be an adverse effect on inflammability. In fact, the difference is negligible.

Asbestos cloth according to the invention presents the additional advantages that it is of improved appearance and improved weave stability, and that when cut it frays less than similar untreated cloth.

I claim:

1. An asbestos product rendered substantially less dusty without essential modification of any other property by particles of a film-forming polymeric material having an extension to break of at least 50 percent, distributed throughout the product in an amount of from 0.1 to 5 percent by weight of the product and bonding at least the majority of the fibers at points of contact with other fibers.

2. The product of claim 1 in the form of asbestos cloth.

3. A product according to claim 1 in which the polymeric material is a thermoplastic or elastomeric material.

4. A product according to claim 1 in which the polymer particles amount to from 0.5 to 3 percent by weight of the product.

5. A product according to claim 1 in which the polymeric material is a copolymer of vinyl acetate and maleic ester.

6. A product according to claim 1 in which the polymeric material is natural rubber or styrene-butadiene rubber.

* * * * *

United States Patent [19]
Xanthos et al.

[11] 3,965,284
[45] June 22, 1976

[54] CHEMICALLY OPENING CHRYSOTILE ASBESTOS AND ENCAPSULATING

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[51] Int. Cl.² B32B 17/00

[58] Field of Search ..... 117/126 AB, 126 AQ, 117/100 S, 62.1, 62.2; 162/155; 427/299, 221, 340, 341; 428/404, 407

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[57] ABSTRACT

Chrysotile asbestos is chemically opened into the individual fibrils by soluble vinylic polymer polyelectrolytes containing carboxylic acid groups in aqueous media. Polyacrylic acids, polymethacrylic acids, maleic anhydride polymers and water-soluble copolymers thereof are preferred polyelectrolytes and form stable colloidal dispersions. The polyelectrolytes are neutralized to alkaline pH with inorganic or organic bases, but preferably with basic vinylic monomers when complete encapsulation is desired. By a further aspect of the invention the polyelectrolyte-coated fibrils in aqueous dispersion are encapsulated by copolymerization with (a) a basic vinylic comonomer (used for pH control) such as dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate or a vinylpyridine; and (b) a non-basic vinylic comonomer such as styrene, divinylbenzene, vinyl chloride or fluoride, vinyl acetate, methyl methacrylate, ethyl acrylate, acrylonitrile, and methacrylonitrile. The encapsulated fibrils are advantageous for forming reinforced composites including laminates and foamed or cellular products.

13 Claims, 4 Drawing Figures

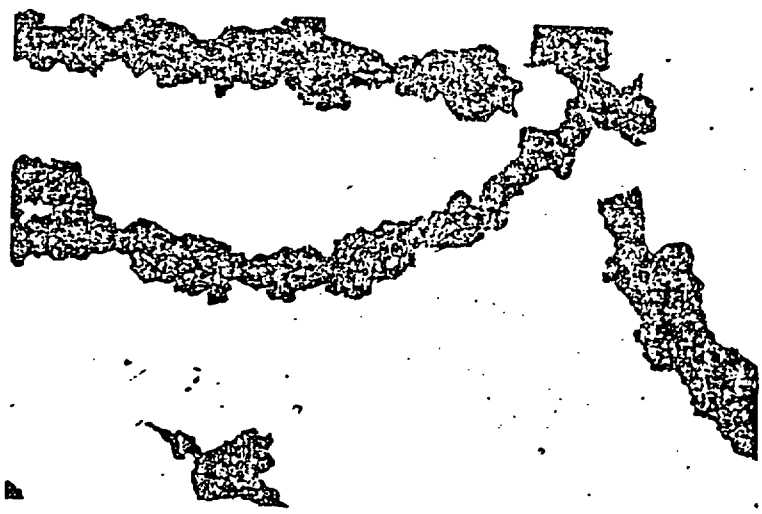




FIG. 1

Polymerization of styrene in the presence of polymethacrylic acid neutralized with sodium hydroxide.

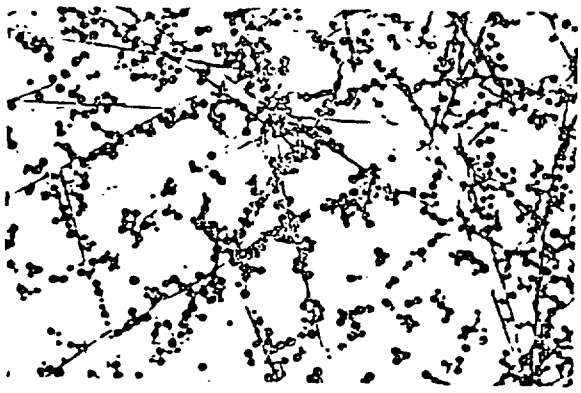


FIG. 2

Polymerization of styrene in the presence of a copolymer of styrene -acrylic acid neutralized with ammonia.



FIG. 3

Electron micrograph showing completely coated Chrysotile fibrils. Copolymerization of styrene/dimethylaminoethyl methacrylate (3/1) in the presence of polyacrylic acid. 6,340x.



FIG. 4

Electron micrograph showing completely coated chrysotile fibrils. Copolymerization of methyl methacrylate/ dimethylaminoethyl methacrylate (3/1) in the presence of polyacrylic acid. 7 940x.

CHEMICALLY OPENING CHRYSOTILE ASBESTOS AND ENCAPSULATING

The asbestos minerals comprise the fibrous form of serpentine, known as chrysotile, and five minerals of the amphibole group, namely: anthophyllite, crocidolite, actinolite, tremolite and amosite. Chrysotile, one of the most useful and plentiful forms of asbestos, may be opened into discrete fibrils (a) mechanically by a combination of crushing and high speed air turbulence and/or (b) by chemical methods of opening employing various known chemical opening agents.

Chemical opening agents used previously include selected surfactants including fatty acid soaps, acrylic acid, methacrylic acid or maleic anhydride monomer (at acid pH), and saturated amines such as triethanolamine. Inorganic salts have also been used. In many cases, the degree of opening or the stability of the aqueous dispersion is less than desirable, or the residue of the agent remaining on the fibrils is deleterious in subsequent use and difficult to remove. The present invention is believed to have several important advantages over former methods.

The asbestos employed in the processes and products of this invention is known as Chrysotile. Chrysotile, being a common and plentiful form of asbestos, is widely used as a filler in synthetic organic polymer compositions. However, in order to make best use of its reinforcing properties, the mechanically-opened mineral must be separated into its primary fibrils of an average diameter of 250 – 500 A. This mineral should first be broken up in a preliminary way mechanically as in a crusher or chopping mill and then further opened e.g. by turbulent, high speed air jets. Mechanical agitation is not able to separate the individual fibrils from each other and form a stable dispersion. The presence of a dispersing agent is therefore necessary to disperse and stabilize the individual fibrils of Chrysotile in water.

It has been discovered that polyelectrolytes having free carboxylic acid groups and in particular polyacrylic acid, polymethacrylic acid, maleic anhydride polymers and water-soluble copolymers thereof are excellent aqueous dispersing and opening agents for Chrysotile. The pH of the solution used for the chemical opening should be carefully adjusted to the alkaline side for best results; preferably a pH of 8–10 is maintained, resulting in dispersions of excellent stability. In a typical example a 0.5% solution of polyacrylic acid neutralized to pH 8 with sodium hydroxide is added to a weighed quantity of mechanically-opened Chrysotile. In order to hasten the process of chemical opening the suspension is subjected to high shear agitation for few minutes, such as in a Waring Blendor. A uniform colloidal suspension results which shows excellent separation of the individual fibrils when examined under the electron microscope.

The amount of dispersing agent may be as little as about 0.1% based on the weight of dry asbestos or as great as 1000% for some purposes. The aqueous dispersion of asbestos is usually in the range of 1–10% solids since concentrations above 10% become too viscous to handle. In cases where the polyelectrolyte may act subsequently as a binder, the proportion of polymeric dispersing agent may be greater than necessary for complete dispersion. Such dispersions are easily spun into continuous fibres, the resulting fibres showing good strength after drying to remove excess water. The dispersion may be spun through an orifice into a coagulatinng medium such as for example an organic liquid, an aqueous solution of alkaline earth metal ions (e.g. calcium, barium) or by passing into an aqueous solution of low pH e.g. below about 5.

Mats or papers of asbestos may be formed simply by depositing a layer of the chemically-opened fibres on a surface and then removing the water. The polyelectrolytes will act as a binder, becoming insolubilized on heating and producing a tough sheet of material. Other uses for these dispersions include the preparation of rigid, low density panels for sound and heat insulation and battery separators.

In the attached Figures which illustrate embodiments of and the advantages of a preferred aspect of, the invention (see Example XIII)

FIG. 1 is a photomicrograph at magnification 10450 of Chrysotile fibrils opened with polymethacrylic acid neutralized with sodium hydroxide and showing globules of styrene polymerized in situ.

FIG. 2 is a photomicrograph at magnification 10450 of the fibrils opened with a copolymer of styrene-acrylic acid neutralized with ammonia and showing fine uniform-sized globules of styrene polymerized in situ.

FIG. 3 is a photomicrograph at magnification 6340 of the fibrils opened with polyacrylic acid and neutralized and copolymerized with styrene/dimethylaminoethyl methacrylate (3/1) in situ.

FIG. 4 is a photomicrograph at magnification 7940 of the fibrils opened with polyacrylic acid and neutralized and copolymerized with methyl methacrylate/dimethylaminoethyl methacrylate (3/1) in situ.

In a preferred aspect of the invention, a basic vinylic monomer is used to neutralize and polymerize onto the polyelectrolyte, and has basic amino groups or basic heterocyclic nitrogen atoms in the molecule. Suitable basic monomers include dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate and a vinylpyridine (as any isomer) or mixtures thereof. If the basic monomer is used as the sole neutralizing agent it should be present in equivalent amount to neutralize or combine with the free carboxylic acid groups of the polyelectrolyte. Mixtures of the various neutralizing agents may be advantageous for particular purposes e.g. ammonia with vinylpyridine.

Operative inorganic neutralizing agents which may be used in whole or in part include the alkali metal and ammonium hydroxides.

In some cases, it is advantageous to employ a volatile base as a neutralizing agent, i.e. ammonia, although any volatile organic amine may be chosen. The resulting dispersion can be converted to filaments or mats which after moderate heating to remove the volatile base are less sensitive to moisture. In such cases the reactive carboxyl groups are believed to form insoluble salts with the magnesium ions present in the asbestos.

Lightweight insulating materials have also been prepared by using the above asbestos mats after drying. The polyelectrolyte, after removal of the excess moisture serves to chemically bond the submicroscopic fibrils together. Furthermore the polyelectrolyte can be made completely insoluble by post-treatment with alkaline earth ions of calcium or barium.

The use of these polyelectrolytes particularly acrylic acid copolymers, methacrylic acid copolymers or maleic anhydride copolymers offer considerable control over the degree of chemical opening, the stability of the

resulting dispersion, binding efficiency after drying, and other factors associated with processing and performance. In addition to the composition of the copolymers and choice of neutralizing agent or basic comonomer, the molecular weight at each stage may be chosen so as to give optimum processability.

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

EXAMPLE I

Chrysotile asbestos, grade Plastibest No. 20 (trademark of Canadian Johns-Manville Co., Ltd.) was the type of asbestos used. Three grams of coarse mechanically-shredded fibres were suspended in 297 grams of distilled water containing 1.5 g. of polyacrylic acid (Acrysol A-3, Rohm and Haas Co.). After three minutes agitation at low speed in a Waring Blendor an equivalent amount of sodium hydroxide solution was added in order to raise the pH to 8. The thick, viscous suspension was further stirred at high speed for 10 minutes. Excellent, stable dispersions were formed by this process. No agglomerates or fibre bundles were visible under the microscope.

EXAMPLE II

Chrysotile shreds were treated in exactly the same manner as in Example I, but in this case polymethacrylic acid neutralized with ammonia was used as dispersing agent. A 2% asbestos dispersion in water was prepared, containing 0.25 g. polymethacrylic acid per g. of asbestos. Under the electron microscope the completely separated fibrils of average diameter 500 A were visible.

EXAMPLE III

0.75 g. of a styrene/acrylic acid copolymer (carboxyl content 0.75 g. equiv. —COOH per 100 g. of polymer) were dissolved in 300 cc of distilled water containing an equivalent amount of sodium hydroxide to give a pH of about 8. 3 g. of Chrysotile asbestos shreds (Plastibest No. 20) were added and the suspension was stirred in a Waring Blender for 10 minutes. A dispersion of excellent stability resulted which showed no agglomerates or visible particles.

EXAMPLE IV

3 g. of a methyl methacrylate/acrylic acid copolymer (carboxyl content 0.54 g. equiv. —COOH per 100 g. of polymer) were dissolved in 300 cc of distilled water containing an equivalent amount of sodium hydroxide to give a pH of about 8. 300 cc of an 1% asbestos dispersion were then prepared as in Example III with similar results.

EXAMPLE V

1.2 g. of a styrene/maleic anhydride copolymer (SMA 1420 A, Sinclair Oil Co.) were dissolved in 300 cc of distilled water containing an equivalent amount of sodium hydroxide. 300 cc of 0.75% asbestos dispersion were prepared as in Example III and IV (pH about 8). The resulting suspension was stable and showed excellent separation of the fibrils.

EXAMPLE VI

This example illustrates the preparation of a rigid, tough, lightweight expanded structure using the chemically-opened coated asbestos fibrils of this invention. 100 g. of an aqueous solution of 0.25% polyacrylic acid (made by adding 1.0 g. Acrysol A-3 (tradename) to 99 g. distilled water) was adjusted to pH 8 by the addition of ammonia. This solution was added to 5 g. of Chrysotile asbestos shreds (Plastibest No. 20) and thoroughly blended in a high-speed mixer of the Waring Blender type. The resulting thick, dough-like mass was placed in a beaker and heated to dryness in a radio frequency (RF) oven. The mass in this case retained its original shape and occupies a volume equal to that of the original mixture. The density was approximately 8 lb/ft³. The tough, rigid mass did not disintegrate even when boiled for a prolonged period in water, showing that the process is irreversible. Suitable adjustment of the viscosity of the original mixture can be employed to permit foaming or expansion to take place during the drying state, thereby resulting in a much lower density.

Such rigid foams are desirable for insulating purposes where high heat resistance is required. The composition of the polyelectrolyte dispersing agent can be selected to provide specialized properties for different applications.

EXAMPLE VII

2.0 g. Chrysotile asbestos shreds (Plastibest No. 20) were dispersed in 100 g. of a polyacrylic acid solution containing 0.5 g. polyacrylic acid adjusted to pH 8 with ammonia. The colloidal suspension was spun through a small orifice (a hypodermic syringe) into a coagulating bath containing dissolved barium acetate. The precipitated fiber was pulled under slight tension to induce orientation of the asbestos fibrils using a conveyor system in which the speed of drawing could be adjusted to conform with the speed of extrusion. A slight positive pressure of nitrogen could be employed to control the speed of extrusion through the orifice. A continuous thread was formed with an outer sheath of hardened material while the inner core remained fluid until heated to dryness. Reasonably strong, flexible fibers could be prepared by this technique. If desired, the polyacrylic acid binder could be removed completely by heating the fiber to temperatures above 500°C.

These continuous fibers can be used for filament winding application or in the manufacture of woven materials.

EXAMPLE VIII

A Chrysotile asbestos dispersion prepared as in the previous Example VII was filtered by suction. After the filtrate was dried, a very stiff, strong paper-like mat was obtained. A similar product was formed by centrifugal filtration. The polyacrylic acid provides strong binding forces which increase the toughness and rigidity of the sheet material. By adjusting the quantity of asbestos, the thickness of the resulting mat can be controlled, thicker sections being suitable for use in building panels and lightweight insulating panels for acoustic purposes, thermal insulation and fire protection.

Incorporation of the Chrysotile ultimate fibrils into the thermoplastic matrics by conventional techniques, i.e. latex compounding, does not always ensure uniformity of the resulting composition. The present invention includes a method for coating the individual asbestos fibrils (encapsulation) with a layer of polymer formed by free-radical polymerization in the presence of the aqueous colloidal Chrysotile dispersions described above. This technique is particularly advantageous in the case of asbestos. Encapsulation of opened asbestos fibers with polymer provides several advan-

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tages, namely, ease of molding, lower mixing costs, formation of translucent composites and several other advantages as will be discussed further.

Coating of some inorganic particles with polymers have previously been described in the literature. Particles of macroscopic dimensions are reported to be coated via free-radical or Ziegler-Natta polymerization. However, the method used in the present invention is believed to be unique in that an inorganic polyelectrolyte-treated substrate of colloidal dimensions (average diameter 500 A) can be coated by carrying out the polymerization in aqueous media, eliminating thus the use of expensive and usually nonrecoverable organic solvents. The encapsulated fibril products are also believed to be novel.

According to the present invention, a method is also provided which consists of opening and dispersing Chrysotile asbestos in water as described above, followed by copolymerization of unsaturated monomers with a basic amine monomer functioning both as a co-monomer and pH controller for the above dispersion.

The use of anionic polyelectrolytes (polyacrylic acid, polymethacrylic acid, maleic anhydride polymers and water-soluble copolymers thereof) as asbestos opening and dispersing agents has been described above. The pH of these dispersions is carefully adjusted to about 8–10 by using inorganic or organic bases, in order to obtain coated fibril dispersions which are stable.

According to this preferred aspect of our invention the organic bases used to neutralize the polyelectrolyte may include cationic organic compounds having polymerizable sites such as dimethylaminoethyl methacrylates, t-butylaminoethyl methacrylate or vinylpyridine. Organic or inorganic bases which may be present also, include ammonia, amines, sodium hydroxide, potassium hydroxide or lithium hydroxide as described above. Vinylic non-basic comonomers, are preferably present along with the basic comonomer.

In a typical example, a 0.5 % solution of polyacrylic acid neutralized with dimethylaminoethyl methacrylate was added to a weighed quantity of asbestos shreds and the mixture agitated in a high-speed Waring Blender for 10 minutes. To the resulting stable opened dispersion was added a non-basic monomer such as styrene which contained an oil-soluble initiator such as azobisisobutyronitrile (AIBN). The weight ratio of basic amine comonomer to non-basic monomer (styrene) should be at least about one-third for complete encapsulation. After the polymerization, completely-coated individual Chrysotile fibers were precipitated out and easily recovered. This material after filtering and drying can be easily molded to give translucent specimens of excellent properties.

Encapsulation with other polymers is feasible by this method and is independent of the aqueous solubility of the added non-basic monomers, provided that the weight ratio of amine to non-basic monomer is not less than one-third. Use of oil-soluble initiators such as benzoyl peroxide, lauryl peroxide, methylethylketone peroxide, diisoproplyperoxydicarbonate, and AIBN is preferable in order to minimize the formation of excessive free polymer, i.e. polymer not attached to the surface of the fibrils.

The non-basic vinylic comonomer incorporated to polymerize with the basic monomer (and thus onto the polyelectrolyte), may be any other vinyl monomer polymerizable in aqueous systems. Such monomers include styrene, divinylbenzene, vinyl chloride or fluoride, vinyl acetate, methyl methacrylate, ethyl acrylate, acrylonitrile, and methacrylonitrile.

The concentrations of the individual components for a 1% by weight solids asbestos dispersion ensuring complete encapsulation should be the following: polyelectrolyte at least about 0.15 g. per g. asbestos, an equivalent amount of amine monomer, and weight ratio of amine to non-basic monomer at least about 0.33. The amount of polymer in the final asbestos composite may ary from about 2% to 100% by weight of the asbestos. The polymerization may be carried out in sealed containers under nitrogen with appropriate agitation and temperature control for instance at 60°C and for time periods varying from about 1–16 hours (until the polymerization is completed as desired).

Use of such encapsulated Chrysotile asbestos fibrils is advantageous for several reasons.

a. Greater ease of molding. Time periods required for molding are greatly reduced because the resin surrounds completely, and can wet-out thoroughly the filler.

b. Preparation of translucent composites. The material can be more easily pigmented and better gloss and color potential results from the translucent nature of the encapsulated filler.

c. Lower mixing costs and elimination of the use of expensive organic solvents. Cheaper grades of asbestos can be employed in many cases.

d. Reduced die and tool wear during injection molding or extrusion due to inherent lubrication.

e. High heat distortion temperatures due to the large surface area of the opened asbestos fibrils.

f. Greater ease of handling, less dusting and consequently less danger of cancer and lung disorders ("asbestosis").

Another application is the manufacture of asbestos foams. The polymerization-encapsulation may be carried out in the presence of an oil-soluble blowing agent which decomposes during molding, forming a lightweight encapsulated asbestos foam. Examples of suitable blowing agents are azobisformamide, azobisisobutyronitrile, N,N'-dinitrosopentamethylene tetramine, and toluene-4-sulfonyl hydrazide.

This further aspect of the invention will be better understood by reference to the following representative examples:

EXAMPLE IX

3 g. Chrysotile asbestos, grade Plastibest No. 20 were added to 300 cc of a 0.3 % aqueous polyacrylic acid solution (Acrysol A-3, tradename of Rohm and Haas Company) and the mixture was agitated for three minutes at low speed in a Waring Blendor. 1.96 g. dimethylaminoethyl methacrylate were then added dropwise to pH 8 and stirring was continued at high speed for a total period of 10 minutes. A stable dispersion of colloidal Chrysotile (average diameter 500 A) was produced. 5.88 g. styrene containing 0.5% azobisisobutyronitrile (AIBN) were then added. After 16 hours at 60°C, completely coated asbestos fibers precipitated. The material was then filtered, dried and molded to give excellent translucent specimens. The asbestos content of the encapsulated material, determined by ashing, was found to be 27.8% by weight, in good agreement with the feed composition.

EXAMPLE X

The same procedure was repeated as in Example IX, but in this case the amount of polyacrylic acid was 0.15 g. per g. of asbestos. Equivalent amounts of dimethylaminoethyl methacrylate and amine/styrene weight ratio 1/3 were used. The final encapsulated material containing 46.6% asbestos was easily molded to give a uniform, translucent specimen.

EXAMPLE XI

The same procedure was repeated as in Example IX and X, but in this case methyl methacrylate was used instead of styrene. A very desirable product was obtained.

EXAMPLE XII

1 g. Chrysotile asbestos was dispersed in 100 cc water with 0.15 g. polyacrylic acid and 0.3 g. dimethylaminoethyl methacrylate. 0.9 g. ethyl acrylate containing 0.5% AIBN were then added and polymerization proceeded at 60°C for 16 hours. After the completion of the reaction, 2 g. styrene containing additional catalyst were added and the polymerization continued at the same temperature for 12 hours. Coated Chrysotile with two successive layers of polymer were precipitated in the form of easily filtered spheres. Specimens prepared from this material showed improved Izod impact strengths, due to the pressence of the energy-absorbing polymeric layer on the surface of the fibrils.

EXAMPLE XIII

Typical polymer-fibril products were examined under the electron microscope. In each case the asbestos fibrils were chemically opened with the vinyl polymer polyelectrolyte having carboxylic acid groups, giving very good opening and dispersion of the individual fibrils. In FIGS. 1 and 2, the fine individual fibrils are clearly shown.

FIG. 1 shows the polymerization behaviour of styrene when sodium hydroxide was used to neutralize polymethacrylic acid the latter acting as the asbestos opening and dispersing agent. There was hardly any polymer attached onto the fibrils in this case, and the major part of the polymer precipitated during polymerization. In FIG. 2, the effect of a more efficient dispersing agent (a copolymer of styrene-acrylic acid neutralized with ammonia) is shown. Many small polystyrene particles partly attached to some of the fibrils are formed when styrene is polymerized in situ. (AIBN initiator was used for the styrene polymerization in both these cases). Upon filtration of this suspension the bulk of the polymer is recovered in the filtrate.

FIG. 3 shows individual fibrils opened and dispersed with polyacrylic acid and completely coated with copolymer formed in situ from styrene/dimethylaminoethyl methacrylate (3/1) using AIBN initiator. In FIG. 4 the fibrils were opened and dispersed with polyacrylic acid, and coated with copolymer formed from methyl methacrylate/dimethylaminoethyl methacrylate (3/1) and AIBN initiator. In both these Figures, the polymer is seen to completely encapsulate and adhere to the individual fibrils.

Encapsulated asbestos fibrils may be partially fused into sheets, tubes, or other shapes to be used as porous filter webs of extreme fineness such that only the finest particles may pass through the reticulated structure. The type of polymeric encapsulation may be selected to resist acids or bases, or other corrosive environments which would normally destroy the asbestos. Solvent-resistant sheaths may be provided using acrylonitrile copolymers as the encapsulating material. It is apparent that only a continuous coating would provide a coherent network, and that encapsulation must be essentially complete. The individual coated fibrils may be fused or joined together at their crossover points by the mild application of heat and pressure.

We claim:

1. A method of chemically opening chrysotile asbestos into individual fibrils and at least partially encapsulating with polymer comprising:
   a. physically breaking up the asbestos and shredding the fibres to a preliminary stage,
   b. dispersing the resulting asbestos shreds in an aqueous alkaline medium of alkaline pH up to about 10 containing a soluble vinylic polymer polyelectrolyte having free carboxylic acid groups, with agitation to chemically open and coat the individual asbestos fibrils, and
   c. insolubilizing the polyelectrolyte on the fibrils, and separating coated fibrils from the aqueous medium.

2. The method of claim 1 wherein the polyelectrolyte is selected from the group consisting of polymers of acrylic acid, polymers of methacrylic acid, and copolymers of maleic anhydride

3. The method of claim 1 wherein the pH of the aqueous medium is adjusted to about 8-10.

4. The method of claim 1 wherein the polyelectrolyte is insolubilized in (c) with an inorganic or volatile organic base.

5. The method of claim 1 wherein the polyelectrolyte on the fibrils is reacted and polymerized with a basic vinylic monomer.

6. The method of claim 1 wherein the polyelectrolyte is insolubilized and reacted and polymerized with both a basic vinylic comonomer and non-basic vinylic comonomer to encapsulate the individual fibrils with polymer, the weight ratio of basic to non-basic comonomer being at least about 0.33

7. A method of chemically opening chrysotile asbestos into individual fibrils and encapsulating the fibrils with polymer as in claim 1 comprising:
   a. physically breaking up the asbestos and shredding the fibres to a preliminary stage,
   b. dispersing the resulting asbestos shreds in an aqueous medium of pH about 8–10 containing both soluble vinylic polymer polyelectrolyte selected from the group consisting of polymers of acrylic acid, polymers of methacrylic acid, and copolymers of maleic anhydride and a basic vinylic monomer selected from the group consisting of dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate and a vinylpyridine, with agitation to chemically open and coat the individual asbestos fibrils, and
   c. insolubilizing the polyelectrolyte, polymerizing the monomer and separating the encapsulated fibrils from aqueous media.

8. A method of chemically-opening chrysotile asbestos into individual fibrils and encapsulating the fibrils with polymer comprising:
   a. physically breaking up the asbestos and shredding the fibres to a preliminary stage,
   b. dispersing the resulting asbestos shreds in an aqueous medium of alkaline pH up to about 10 containing

i. a soluble vinylic polymer polyelectrolyte selected from the group consisting of polymers of acrylic acid, polymers of methacrylic acid, and copolymers of maleic anhydride;

ii. basic vinylic monomer selected from the group consisting of dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate and a vinylpyridine; and

iii. non-basic vinylic comonomer and a polymerization initiator therefor; to chemically open and coat the individual asbestos fibrils, the weight ratio of basic monomer to non-basic comonomer being at least about 0.33, and

c. insolubilizing the polyelectrolyte, copolymerizing the basic and non-basic monomers to encapsulate the fibrils with polyelectrolyte and copolymer, and separating the encapsulated fibrils from aqueous media.

9. The method of claim 8 wherein the non-basic monomer is a styrene and an oil-soluble initiator is used.

10. Chemically-opened, chrysotile asbestos fibrils encapsulated with polymer comprising a vinylic polymer polyelectrolyte and polymerized basic vinylic monomer, the polyelectrolyte having carboxylic acid groups neutralized by the basic groups of said monomer, the amount of polymer being from about 2 to 100% by weight of the asbestos.

11. The encapsulated fibrils of claim 10 wherein the basic vinylic monomer is selected from the group consisting of dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate and a vinylpyridine.

12. The encapsulated fibrils of claim 10 wherein the polymer comprises non-basic vinylic monomer copolymerized with said basic monomer.

13. The encapsulated fibrils of claim 10 wherein the polyelectrolyte is selected from the group consisting of polymers of acrylic acid, polymers of methacrylic acid, and copolymers of maleic anhydride.

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CUSTOMER CALL REPORT

CUSTOMER & LOCATION: Montello - Tulsa, Oklahoma

INDUSTRY CLASSIFICATION: Distributor

SALESMAN: J.E. Walsh REGION: Southern DATE OF CALL: 5-3-79

ASBESTOS HEALTH & REGULATORY DOCUMENTS PROVIDED:

- ☐ MSDS
- ☐ Health & OSHA Information Blue Book
- ☐ Dust Count Report
- ☐ Other, specify below

PERSONS INTERVIEWED:

Ken Campbell - President
Chuck Petri - Office Manager

CALL OBJECTIVE:

Call made at the home office of our distributor to the oil well industry.

RESULTS OF CALL:

This was the first visit to Montello's new showplace office location since they moved out of their combination office-warehouse in Sand Springs. Montello owns this one story 11M sq. ft. building and occupies about 4M sq. ft. with luxury decor. This has been another good business year for Montello Ken said and they expect to close their fiscal year on June 30 with about $5MM sales vs $3.5MM last year. The oil wetted pellet project has been going along smoothly with Chemical Sealing in Kansas City, but they have experienced a slight delay in getting bags. They need polypropylene lined kraft bags as the oil used seeps through polyethylene and they will be using an International Paper bag currently being manufactured to package explosives and ammunition type products. The oil wetted product will be known simply as "Univis" and Ken expects a complete shift from Supervis and Shurelift sales to the oil wetted material. The Univis bags will have the asbestos warning and Ken expects that sales should grow back up to around 5,000 tons a year again. After a successful trial it looks like full scale production will occur at Chemical Sealing's West Coast plant in Union City, California to help reduce the transportation costs.

FOLLOW-UP ACTION REQUIRED:

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