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Asbestos treatment

Abstract

A method of treating ***asbestos*** comprising depositing on at least a portion of the ***asbestos*** a material consisting essentially of at least one metal ferrocyanide.

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References Cited [Referenced By]

U.S. Patent Documents

1907616	May., 1933	Tucker	162/153.
2096538	Oct., 1937	Durrant	427/343.

Other References

McNab, G. et al., Nature 214, 522-523 (1967).
Schnitzer et al., "***Asbestos*** Hemolysis", Environ. Res. 3, 1-13 (1970). pp. 1-13.

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Claims

What is claimed is:

1. A method of treating ***asbestos*** comprising depositing on at least a portion of the ***asbestos*** a sufficient amount of a material consisting essentially of at least one metal ferrocyanide to reduce the hemolytic activity of the ***asbestos*** to at least about 9 percent hemolysis.

2. The method of claim 1 wherein the ***asbestos*** is chrysotile.

3. The method of claim 1 wherein the metal is selected from the group consisting of cadmium, iron (III), nickel, tin (II), and titanium (IV).

4. The method of claim 1 wherein the metal is titanium (IV).

5. The method of claim 1 wherein the metal is tin (II).

6. The method of claim 1 wherein the depositing step comprises:

(a) contacting the ***asbestos*** with a solution of an ionizable salt of at least a first metal to deposit at least a portion of the ionizable salt on the ***asbestos***;

(b) contacting the ***asbestos*** with a solution solution of a ferrocyanide salt of a second metal to form a ferrocyanide of at least the first metal on at least a portion of the surface of the ***asbestos***.

7. The method of claim 6 wherein the first metal is selected from the group consisting of cadmium, iron (III), nickel, tin (II), and titanium (IV).

8. The method of claim 6 wherein the second metal is selected from the group consisting of sodium and potassium.

9. The method of claim 6 wherein the solution of the ionizable salt has a salt concentration of from about 1 percent by weight to about a concentration corresponding to a saturated solution of the salt.

10. The method of claim 6 wherein the solution of the ionizable salt has a salt concentration of from about 5 percent by weight to about 10 percent by weight of the salt.

11. The method of claim 6 wherein the ionizable salt includes at least one member selected from the group consisting of a chloride, a sulfate, and a nitrate.

12. The method of claim 6 wherein the ionizable salt is a chloride.

13. The method of claim 6 wherein the solution of the ferrocyanide salt has a concentration of from about 1 percent by weight to about the concentration corresponding to a saturated solution of the ferrocyanide of the second metal.

14. The method of claim 6 wherein the solution of the ferrocyanide salt has a concentration of from about 1 percent by weight to about 10 percent by weight of the ferrocyanide of the second metal.

15. The method of claim 6 wherein the solution of the ionizable salt is an aqueous solution.

16. The method of claim 6 wherein the solution of the ferrocyanide salt is an aqueous solution.

17. The method of claim 1 wherein the depositing step comprises spraying at least a portion of the ***asbestos*** with at least one metal ferrocyanide suspended in a liquid medium.

18. The method of claim 17 wherein the medium is water.

19. A method for treating ***asbestos*** comprising:

(a) slurrying the ***asbestos*** with a sufficient amount of an aqueous solution of an ionizable salt of at least a first metal selected from the group consisting of cadmium, iron (III), nickel, tin (II), and titanium (IV), to deposit at least a portion of the ionizable salt of the first metal on at least a portion of the ***asbestos***;

(b) slurrying the ***asbestos*** from step (a) with an aqueous solution of a ferrocyanide of a second metal selected from the group consisting of sodium and potassium to form a sufficient amount of a ferrocyanide of the first metal on at least a portion of the ***asbestos*** wherein the ionizable salt was deposited to reduce the hemolytic activity of the ***asbestos*** to at least about 9 percent hemolysis.

20. The method of claim 19 including agitating the ***asbestos*** and the aqueous solution of the ionizable salt of the first metal for a sufficient time to allow the ionizable salt to contact at least a portion of the ***asbestos***.

21. A fibrous ***asbestos*** material consisting essentially of ***asbestos*** fibers and at least one metal ferrocyanide deposited on at least a portion of the ***asbestos*** fibers in a sufficient amount to reduce the hemolytic activity of the ***asbestos*** fibers to at least about 9 percent hemolysis.

22. The material of claim 21 wherein the metal is selected from the group consisting of cadmium, iron (III), nickel, tin (II), and titanium (IV).

23. The material of claim 21 wherein the metal is titanium (IV).

24. The material of claim 21 wherein the metal is tin (II).

25. The material of claim 21 wherein the metal ferrocyanide is present in an amount of from about 0.05 to about 5.0 percent by weight, based on the weight of the ***asbestos***.

26. The material of claim 21 wherein the ***asbestos*** has a fiber length of at least about 0.5 microns.

Description

BACKGROUND OF THE INVENTION

This invention relates to ***asbestos***. More in particular, the present invention relates to a method of treating ***asbestos***.

"***Asbestos***" is a general term applied to a group of naturally occurring fibrous silicate minerals that are commercially important because of their fibrous characteristics. Four principal types of ***asbestos***

minerals generally enter world commerce. These are chrysotile, crocidolite, amosite and anthophyllite. Of these, chrysotile is perhaps the most important, accounting for about 95 percent of the world's ***asbestos*** production.

Chemically, chrysotile ***asbestos*** is the fibrous form of the mineral serpentine, a hydrated magnesium silicate having the general formula Mg.sub.3 Si.sub.2 O.sub.3 (OH).sub.4. Structurally the chrysotile ***asbestos*** is believed to consist of rolled up sheets formed from two layers. The first layer is a continuous network of silica (SiO.sub.2) tetrahedra. This layer is interlocked through common oxygen atoms with a second layer of magnesium hydroxide (Mg(OH.sub.2)) octahedra. The walls of the ***asbestos*** fibers are composed of a number of such individual sheets contorted into scrolls with the magnesium hydroxide layer on the outside. Consequently, one of the dominant chemical features of chrysotile ***asbestos*** is its alkaline surface characteristics.

The surface modification of asbestine minerals, such as chrysotile, has attracted a good deal of attention from research workers during recent years. A large number of surface treatment methods have been proposed and evaluated for the purpose of modifying certain predetermined properties of the ***asbestos*** fibers. These procedures include: coating the surface of ***asbestos*** fibers with a phosphate, polyphosphate, or corresponding acid to improve the filtration characteristic of the fibers (U.S. Pat. Nos. 3,535,150, 3,957,571); treating ***asbestos*** fibers with magnesium carbonate or an oxide of a polyvalent metal to enhance the tensile strength of the fibers (U.S. Pat. Nos. 1,982,542; 2,451,805; 2,460,734); coating an ***asbestos*** fabric with an insoluble inorganic oxide to render the fabric flame resistant and water repellent (U.S. Pat. No. 2,406,779); mixing a detergent organic surface-active agent with fibrous ***asbestos*** agglomerates to disperse the ***asbestos*** fibers (U.S. Pat. No. 2,626,213); and distributing small amounts of polymeric particles or a water-soluble macromolecular organic substance throughout an ***asbestos*** product to reduce dust emitted by the ***asbestos*** during handling and use (U.S. Pat. Nos. 3,660,148; 3,967,043).

An area of concern to the producers and users of asbestine material has been the potential health problems allegedly associated with ***asbestos*** exposure. It has been reported by the National Safety Council that persons who inhale large amounts of ***asbestos*** dust can develop disabling or fatal pulmonary and pleural fibrosis (asbestosis) and several types of malignancy of the respiratory tract ("***Asbestos***", National Safety Council Newsletter, R & D Section, June 1974). There is also speculation that ***asbestos*** may cause various forms of carcinogenesis, particularly carcinoma of the lung, pleura and peritoneum (R. F. Holt, "Asbestosis", Nature, 253, 85 (1975)). Since the pathogenicity of ***asbestos*** minerals is apparently unmatched by any other silicate, there has been much interest in developing a method of passivating ***asbestos*** to reduce any potential fibrogenic and carcinogenic effects on those exposed to it without adequate precaution.

Existing methodology for studying the in vivo fibrogenic effects of ***asbestos*** involves direct inhalation or intratracheal administration of ***asbestos*** fibers to animals. Subsequently, the experimentally treated animals are examined, usually months later, for pathological and histochemical evidence of fibrosis. Since the incubation period for ***asbestos***-induced diseases is reported to be unusually long, experiments of this type are complicated, expensive and time consuming.

However, recent work done by R. R. Hefner, Jr. and P. J. Gehring (American Industrial Hygiene Association Journal, 36, 734-740 (1975)) shows that a relationship exists between the in vivo fibrogenicity of ***asbestos*** and its in vitro hemolytic activity. Hemolytic activity, or hemolysis, is a measure of induced blood cell rupture when fibers are agitated with a suspension of blood erythrocytes. Numerous other authors have also made similar in vitro evaluations of a number of particulates.

The in vitro hemolytic model provides a rapid, relatively inexpensive test which reliably assesses the fibrogenic potential of ***asbestos***. Consequently, the hemolytic model has been employed in the present invention to test the effectiveness of certain ***asbestos*** treating procedures found to be potentially useful in alleviating some of the health problems reportedly associated with ***asbestos*** fibers.

Various materials have been examined which interact with the surface of ***asbestos*** fibers and reduce its hemolytic activity. Such material includes disodium ethylenediamine tetraacetic acid (EDTA), simple phosphates, disodium versenate, polyvinylpyridine N-oxide and aluminum (G. Macnab and J. S. Harington, Nature 214, 522-3 (1967), and certain acidic polymers (R. J. Schnitzer and F. L. Pundsack, Environmental Research 3, 1-14 (1970). In addition, West German Pat. No. 1,642,022 discloses that ***asbestos*** coated with polyvinylpyridine N-oxide minimizes the risk of asbestosis.

Some of these known materials, such as EDTA, are solubilized in body fluids and do not reduce the long term hemolytic activity of the ***asbestos***. There is therefore a need to determine materials which will adhere to the ***asbestos*** and reduce its hemolytic activity. Such passivating materials should not adversely affect the useful commercial properties of the ***asbestos***.

SUMMARY OF THE INVENTION

The present invention is a method for treating ***asbestos*** comprising depositing on at least a portion of the ***asbestos*** a material consisting essentially of at least one metal ferrocyanide.

Using the hemolysis test, as an in vitro screening test to assess the effectiveness of the metal ferrocyanide treatment, it has been surprisingly found that ***asbestos*** fibers with at least one metal ferrocyanide deposited thereon have reduced hemolytic activity in comparison with untreated ***asbestos*** fibers.

For the purposes of this specification, the oxidation state (valence) of metals which commonly exhibit more than one valence is indicated by a Roman numeral in parentheses following the metal to which it refers.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, ***asbestos*** is treated to deposit at least one metal ferrocyanide on at least a portion of the ***asbestos***.

The method of treating ***asbestos*** includes depositing an ionizable salt of at least one suitable first metal on at least a portion of the ***asbestos***. In this context an ionizable salt is defined as a salt which dissociates spontaneously into ions of opposite electrical signs when dissolved in a suitable polar solvent, such as water, methanol, mixtures thereof and the like. Examples of suitable first metal cations are barium, cadmium, cobalt, iron (II), iron (III), lead, manganese, nickel, potassium, silver, tin (II), tin (IV), titanium (III) titanium (IV), zinc and mixtures thereof. However other first metal cations which are capable of forming a ferrocyanide salt can also be used.

The ionizable salt can be deposited on the ***asbestos*** by contacting ***asbestos*** fibers with a solution of the ionizable salt of the first metal, preferably an aqueous solution of the ionizable salt of the first metal, to deposit at least a portion of the ionizable salt on the ***asbestos***. A number of suitable techniques are known for depositing compounds on ***asbestos***. These techniques include spraying the compound onto the ***asbestos*** fibers or soaking ***asbestos*** fibers in a solution of the coating compound. In the present process, a

preferred method of contacting the ***asbestos*** with the ionizable salt is by slurrying the ***asbestos*** in the solution of the ionizable salt for a sufficient time to allow the surface of the ***asbestos*** fibers to be contacted and wetted by the solution.

The ionizable salt employed in the present process is preferably a chloride, a sulfate, a nitrate, or a mixture thereof of the above first metals. More preferably, the ionizable salt is a water soluble chloride salt of the first metal. However, any salt that will ionize in solution to produce a cation of one of the first metals can be used in the present process. Furthermore, the ionizable salt can contain more than one type of cation and one type of anion. For example, a mixture of chloride salts of two first metals, or a mixture of the chloride and sulfate salts of the same first metal is suitable.

The concentration of the solution of the ionizable salt employed in the present process is from about 1 percent by weight of the salt to about the concentration corresponding to a saturated solution of the particular first metal salt. For example, when nickel chloride hexahydrate is the ionizable salt, the concentration of the salt in the aqueous solution at 20.degree. C. and 1 atmosphere pressure is from about 1 to about 72 percent by weight. Preferably, the concentration of the solution of the ionizable salt is from about 5 to about 10 percent by weight.

Advantageously, the mixture of ***asbestos*** and the salt solution can be agitated at room temperature for a sufficient time to allow the solution to contact at least a portion, and preferably substantially all of the ***asbestos*** fiber surfaces. The agitation of the mixture is accomplished by use of agitation means well-known in the art. These include mechanical, air, hydraulic or magnetic means for inducing agitation.

Following agitation, the ***asbestos*** fibers in solution can be separated from the filtrate by any suitable solid-liquid separation technique such as vacuum filtration. The ionizable salt-treated ***asbestos*** fibers are then contacted with a solution, preferably an aqueous solution, of a ferrocyanide salt of a second metal. Examples of suitable second metal cations are sodium, potassium or a mixture thereof. Various suitable techniques for contacting the salt-treated ***asbestos*** fibers with the ferrocyanide solution can be used as indicated previously. However, it is preferred to slurry the salt-treated ***asbestos*** fibers with the ferrocyanide solution. The salt-treated ***asbestos*** fibers are maintained in contact with the ferrocyanide solution for a sufficient time to allow at least a portion, and preferably substantially all the ferrocyanide solution to contact the salt-treated ***asbestos*** and react with the ionizable salt thereon to form a metal ferrocyanide compound wherein the cation of said compound is originally the cation of the first metal associated with the ionizable salt.

The ferrocyanide solution has a concentration of from about 1 percent by weight to about the concentration corresponding to a saturated solution of the ferrocyanide of the second metal. For example, when sodium ferrocyanide is employed, the concentration of the salt in an aqueous solution at 20.degree. C., 1 atmosphere pressure, is from about 1 to about 32 percent by weight of the ferrocyanide of the second metal. Preferably, the ferrocyanide solution has a concentration of from about 1 to about 10 percent by weight of the second metal ferrocyanide.

The ***asbestos***-ferrocyanide solution slurry is preferably agitated at about room temperature for a sufficient time to insure contact between the ***asbestos*** fibers and the solution.

Following agitation, the ***asbestos*** fibers in solution are separated from the filtrate by any suitable solid-liquid separation technique, such as vacuum filtration. Preferably the filtered ***asbestos*** fibers are subsequently washed with a suitable solvent, such as deionized water, to remove any non-adherent

ferrocyanide compound. The ***asbestos*** fibers can then be dried by any suitable techniques, such as air drying, heating, vacuum and the like.

The present method of treating ***asbestos*** has been described in terms of initially contacting ***asbestos*** fibers with a solution of an ionizable salt of at least one first metal and subsequently contacting the thus treated ***asbestos*** with a solution of a ferrocyanide salt of at least one second metal to form a coating of a ferrocyanide of at least one first metal. However, the present invention is not limited to this sequence. For example, if desired, the ***asbestos*** can initially be contacted with a solution, preferably an aqueous solution, of ferrocyanide of at least one second metal, for example sodium or potassium ferrocyanide. If it is desirable to have another metal ferrocyanide other than the second metal salts deposited on the ***asbestos, the asbestos*** can be subsequently contacted with a solution of an ionizable salt of at least one first metal, to deposit on the ***asbestos*** a ferrocyanide of at least one of the first metals. Suitable first metals are those that have been described previously.

Alternatively, the metal ferrocyanide can be deposited on the ***asbestos*** by directly contacting the surface of the ***asbestos*** fibers with at least one first metal ferrocyanide suspended in a liquid medium, such as water. One suitable deposition technique involved suspending a particulate first metal ferrocyanide in water, spraying the suspension onto the surface of the ***asbestos*** fibers, and removing the water by drying. First metal ferrocyanides which can be suitably applied in this manner include those that are insoluble in the suspending medium.

The ***asbestos*** treated by the present method is characterized as being a fibrous ***asbestos*** material consisting essentially of ***asbestos*** fibers with a coating of at least one first or second metal ferrocyanide deposited on at least a portion of the ***asbestos*** fibers. Suitable first metals include any metal cation capable of forming a ferrocyanide salt. Preferably the first metal cation is barium, cadmium, cobalt, iron (II), iron (III), lead, manganese, nickel, potassium, silver, tin (II), tin (IV), titanium (III), titanium (IV), zinc and mixtures thereof. More preferably, the first metal cation is either titanium (IV), tin (II) or a mixture thereof. Suitable second metal cations are potassium, sodium, or mixtures thereof.

The ***asbestos*** treated by the present invention can include chrysotile, crocidolite, amosite, or anthophyllite ***asbestos***. Chrysotile, being the most abundant type of ***asbestos,*** is the preferred material for treatment by the present process. The physical form of ***asbestos*** treated includes fibrous mineral bundles of fine crystalline fibers, or individual fibers. Preferably the ***asbestos*** is in the form of bundles of crystalline fibers. Generally, the individual fibers of the bundle have a fiber length of at least about 0.5 micron, and a diameter of at least about 0.01 micron. However, other fiber lengths and diameters can be employed.

The exact mechanism by which the deposited metal ferrocyanide forms an adherent coating on the ***asbestos*** is not completely understood. It is believed that the coating is due to the alkaline outer surface of the ***asbestos*** fiber. The individual fibers are composed of a network of magnesium hydroxide tetrahedra. The outermost portion of the tetrahedra contains hydroxyl groups. There is some evidence that hydroxyl hydrogens are being displaced by the metal cation, to form a bond between the metal ferrocyanide and the ***asbestos***. Since each ***asbestos*** fiber is composed of a number of individual sheets having outer hydroxyl groups, and because these sheets are contorted into concentric scrolls, the deposition of the metal ferrocyanide may occur on more than just the outermost exposed surface of the ***asbestos*** fiber. Some of the metal ferrocyanide can impregnate the interior scrolls of the fiber and deposit on the interior hydroxyl surface present.

The metal ferrocyanide that is deposited on the ***asbestos*** is preferably present in an amount of from about