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METHOD OF RENDERING ASBESTOS ORE PARTICLES DIFFERENTIALLY FLUORESCENT

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ABSTRACT OF THE DISCLOSURE

A method of rendering asbestos in asbestos-containing rocks differentially fluorescent in relation to host rock thereby adapting the rocks for mechanical separation into fractions having commercially valuable and commercially non-valuable asbestos contents. The rocks are contacted with a liquid dispersion of particles comprising a fluorescent dye, which particles are preferentially trapped on the fibrous asbestos surfaces.

This invention relates to the sorting of rocks containing asbestos from barren rocks. The term "barren rocks" as used herein is intended to mean rocks which either do not contain asbestos or which contain asbestos in a quantity insufficient to enable economical separation from the rock.

The invention has been devised to provide a method of rendering asbestos in asbestos-containing rocks differentially fluorescent in relation to host rock as a preliminary step in the process of separating the asbestos from the rock. The principal advantage resulting from the invention is that asbestos can be separated more cheaply and quickly than hitherto because barren rock can be located and discarded prior to mill processing.

Asbestos deposits are frequently associated with a number of hard minerals. For example, crocidolite asbestos ore mined at Wittenoom, Western Australia, contains on the average 6–7% of crocidolite in a matrix of host rock comprising: quartzite (hardness 7 on the Mohs' scale), hematite and magnetite (both, hardness 5.5 to 6.5 on the Mohs' scale), together with accessory dolomite and chlorite. The crocidolite is separated from the ore comprising these minerals by a process which includes mill grinding; and because of the hardness of the host rock, it will be appreciated that there will be less wear and tear on the mill machinery when lumps of barren rock are eliminated before processing in an initial sorting step.

Apart from this aspect, the more significant advantage to be gained from sorting is that the output of asbestos can be very appreciably increased. The source of this increased output is to be found in two effects associated with the consequential reduction in the amount of barren rock being processed, viz. (i) higher plant capacity, and (ii) less tailings, hence less asbestos lost in tailings.

According to the prior art, the sorting of asbestos-containing rocks has been done by hand; and in the case of Wittenoom ore, about one quarter of the barren rock has been rejected in this way before mill processing. While hand picking is reliable, it suffers from the disadvantage of being slow, costly and wasteful of manpower.

The principle of electro-pneumatic sorting has been applied by D. Van Douwe in U.S. Patent No. 2,776,747 to the sorting of falling objects according to their reflectivity characteristics; and the same principle has been applied by James F. Hutter and Leonard Kelly in U.S. Patent No. 3,011,634 and Australian Patent No. 223,683 to the sorting of falling pieces of rock which naturally emit value-identifying radiations, e.g. rocks containing radioactive or fluorescent minerals.

While asbestos is not naturally fluorescent, it has been found by the present inventors that it can be rendered artifically fluorescent by taking advantage of its relatively high sorbent properties compared with host rock.

When an asbestos-containing rock is dipped into a fluorescent dye solution and is washed and inspected under suitable radiation (e.g. ultraviolet light), it is found that the exposed seams of asbestos can be identified by the relative brilliance of their fluorescence. However, for practical purposes, the ratio of light emitted by exposed asbestos to light emitted by host rock is not sufficiently great to enable easy identification of asbestos-containing rocks by this method. The low value of this ratio derives from the removal of a large proportion of dye from the asbestos fibre surface during washing.

It has now been found that the selective sorption of a fluorescent dye on sorbent asbestos surfaces can be improved markedly by employing it in a precipitated form.

Accordingly, the invention includes a method of rendering asbestos in asbestos-containing rocks differentially fluorescent in relation to host rock, which comprises:

(a) contacting the rocks with a liquid dispersion of a precipitated fluorescent dye;

(b) removing non-sorbed material from the rocks, e.g. by washing, sufficiently to render exposed asbestos differentially fluorescent in relation to host rock.

By "precipitated fluorescent dye" we mean a fluorescent dye which has been precipitated as an insoluble salt by a suitable cation (e.g. aluminum) or a suitable mixture of ctaions, or which has been incorporated in or adsorbed on a foreign precipitate or floc (e.g. clay or undissolved particles of gelatin).

The invention also includes a method of sorting rocks containing asbestos from barren rocks, which comprises:

(a) contacting the rocks with a liquid dispersion of a precipitated fluorescent dye;

(b) removing non-sorbed material from the rocks sufficiently to render exposed asbestos differentially fluorescent in relation to host rock;

(c) exposing the differentially fluorescent rocks individually to exciting radiation, examining the emitted fluorescent radiation by known photo-electric detection means in activating relationship with known sorting means;

(d) activating the sorting means in response to signals received from the photo-electric detection means whereby to sort rocks containing asbestos from barren rocks.

The invention is described hereinafter with particular reference to the sorting of rocks containing crocidolite asbestos from barren rocks, but it will be understood that the method is also applicable to the sorting of rocks containing other types of asbestos (e.g. chrysotile, amosite, tremolite, actinolite) from barren rocks.

The following is a typical sequence of steps in applying the invention to the sorting of crocidolite ore:

(1) After mining, the ore is crushed to a suitable rock size, e.g. between +2.5 and —10 centimetres.

(2) The rocks are washed with water to remove contaminating particles of dirt, etc.

(3) The cleaned rocks are conveyed to a second bath where they are brought into contact with an aqueous dispersion incorporating between 0.1 and 0.5 gram of a precipitated fluorescent dye per 100 millilitres of dispersion.

(4) The rocks are then conveyed to a site where:

(i) they are irradiated individually with ultraviolet light and simultaneously scanned by photo-electric detection means comprising a photo-multiplier fitted with suitable filters;

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(ii) when the signal from the photomultiplier reaches a predetermined level, a sorter mechanism is activated and rocks are thereby separated into those having a commercially valuable asbestos content and those which are barren rock, i.e. have an asbestos content so low that they are preferably discarded prior to mill processing. A suitable sorter mechanism is that described by Hutter and Kelly in previously noted U.S. Patent No. 3,011,634 or Australian Patent No. 223,683.

It is covenient to employ washing and dyeing tanks measuring about 10 feet long and 4 feet wide. Settling tanks, each of 5,000 gallons capacity, are associated with each of the washing tanks, and water is circulated between them all at the rate of 1,000 gallons an hour. Settled mud is pumped off from the first settling tank and settled dye is fed from the second settling tank back to the dyeing bath tank. Asbestos-containing rocks can be conveyed through such a system at a rate of about 4 feet per second. Water and dye are replenished as necessary.

There is evidence to suggest that the sorption of precipitated fluorescent dye by asbestos is a purely mechanical phenomenon. Thus, tightly packed crocidolite fibres sorb less dye than loosely packed fibres. Furthermore, the uptake of dye decreases with increased relative velocity between the dye dispersion and the rocks. For this reason it is preferred to apply the precipitated dye under conditions of comparatively low relative velocity between the dye dispersion and the rocks.

Not every fluorescent dye can be precipitated by a given cation and not every cation can precipitate a given fluorescent dye. Furthermore, different precipitated dye salts behave differently and therefore not all dye salts are equally suitable in carrying out the invention.

In a test to determine optimum combinations of dyes and cations, the comparative data shown in the following table were obtained when the method of the invention was invoked to render crocidolite in sample crocidolite-containing rocks differentially fluorescent in relation to host rock.

Uniform washing and dyeing procedures were employed throughout the test series, viz. (i) the sample rock was dropped into water at ambient temperature and shaken, (ii) it was transferred to the dye disperson for 1 second, and (iii) it was immersed in a bath of water at ambient temperature for 10 seconds without stirring. In each case, the dye dispersion was prepared by titrating to equivalence a solution containing the selected cation with a solution containing the selected dye. The exciting radiation used was ultra-violet light of wave length predominantly 360 millimicrons and the same photo-multiplier assembly was used throughout the series to analyse the fluorescent light emitted by the treated rocks.

TABLE

Cation [1]	Fluorescent dye [2]	Precipitate	Signal to background ratio
Na^+	Uvitex VR [4]	None [6]	3:1
Ca^{++}	do	Dense	3:1
Zn^{++}	do	do	4:1
H^+	do	do	6:1
CTA+ [3]	do	Viscous	10:1
Al^{+++}	do	Gelatinous	20:1
Na^+	Paper White BP [5]	None [6]	3:1
Fe^{+++}	do	Viscous	8:1
Al^{+++}	do	Gelatinous	20:1
Al^{+++}	Paper White SP	None [6]	3:1
Al^{+++}	Paper White BPN	Dense	3:1

[1] Provided in an aqueous solution of a soluble salt (0.5 gram of salt per 100 millilitres of solution).
[2] Provided in an aqueous solution (0.5 gram of dye per 100 millilitres of solution).
[3] CTA=cetyl trimethyl ammonium.
[4] "Uvitex" is the registered trade mark applied to a series of fluorescent dyes manufactured by Ciba Aktiengesellschaft.
[5] "Paper White" is the trade name of a series of fluorescent dyes manufactured by Du Pont de Nemours and Company.
[6] The sodium salts of Uvitex VR and Paper White BP and the aluminuim salt of Paper White SP are soluble and do not form precipitates.

It is clear that the most useful combinations are of cations and dyes which form viscous or gelatinous precipitates. Such precipitates are best suited for mechanical trapping by fibrous crocidolite surfaces and are not easily removed during washing. In the above test aluminium is the preferred precipitating cation for Uvitex VR and Paper White BP.

When it is desired to practise the invention using a dispersion of a preferred dye/cation combination (i.e. a combination promising high signal to background ratio), it is important to ensure that the prepared dispersion does not also contain a significant concentration of a contaminant cation whose combination with the selected dye would lead to a low signal to background ratio. Thus, it has been found that the effectiveness of Uvitex VR/aluminium (0.5 gram per 100 millilitres of dispersion) is much reduced if the dispersion has been prepared using water containing dissolved calcium in a concentration of 20 parts per million. On the other hand, the effectiveness of this dye salt is not greatly reduced if the dispersion has been prepared using water containing dissolved iron.

In a microscopic examination of a suspension obtained by titrating an aqueous solution of Uvitex VR (0.5 gram Uvitex VR per 100 millilitres of solution) with an aqueous solution of aluminium nitrate (0.5 gram aluminium nitrate per 100 millilitres of solution), the precipitated dye was found to form gelatinous globules of up to 200 microns diameter. When a crocidolite surface was brought into contact with such a dispersion, the water phase was seen to soak through it leaving a gelatinous mat of precipitated dye entangled in the loose upper fibres. Dye penetration did not exceed 1 millimetre. It was also found that dye deposition was much reduced if the water was unable to enter the bulk of the crocidolite. Vigorous washing or brushing of a dye-sorbed crocidolite surface led to breaking and dispersing of the gelatinous mat with consequential loss of fluorescence.

It has also been found that the fluorescent colour of a selected dye precipitate can be reversibly modified to heighten the differential fluorescence of asbestos in relation to host rock.

According to this preferred embodiment of the invention, a method is provided of rendering asbestos in asbestos-containing rocks differentially fluorescent in relation to host rock, which comprises:

(a) contacting the rocks with a liquid dispersion of a precipitated fluorescent dye in a form exhibiting second colour fluorescence;

(b) removing non-sorbed material from the rocks sufficiently to render exposed asbestos differentially fluorescent in relation to host rock, the precipitated fluorescent dye residually sorbed by the asbestos being characterised in that it is in said form exhibiting second colour fluorescence and the precipitated fluorescent dye residually adhering to the host rock being characterised in that it is in a form exhibiting first colour fluorescence.

When aluminium nitrate solution is titrated to equivalence with Uvitex VR, the precipitated aluminium dye glows with a predominantly blue fluorescence (first colour fluorescence: wavelength 420 to 700 millimicrons) under ultraviolet light of wavelength predominantly 360 millimicrons. However, if titrated with a slight excess of Uvitex VR, the precipitate glows with a green fluorescence (second colour fluorescence: wavelength 500 to 700 millimicrons) under ultraviolet light. This green colour is probably due to surface adsorption of the dye on the precipitate, and the fluorescence is found to revert to blue when the precipitate is adequately washed.

If a sample of crocidolite-bearing rock is treated with an aqueous dispersion of the green fluorescent form of this salt, and is then rinsed with sufficient water, it is found that the precipitate adhering to the bands of as-

bestos exhibits green fluorescence under ultraviolet light; on the other hand, residual precipitate on the non-sorbent rock surface is found to have reverted under washing to the blue-fluorescent form.

The present invention may be adapted to take advantage of this differential effect, and using a photomultiplier fitted with suitable filters (e.g. Wratten 8B), it is found that the signal to background ratio can be considerably improved (e.g. from 20:1 to 28:1) by using aluminium-precipitated Uvitex VR containing a slight excess of dye.

Applying these principles, the signal to background ratio can be improved similarly by using some other dye precipitates whose fluorescent colour can be significantly and reversibly modified.

The precipitated dyes described above have been dispersed in water to a concentration selected from the range 0.1 to 0.5 gram precipitated dye per 100 millilitres solution. It will be understood that the invention may be practised with other dispersing liquids and at other concentrations. On economic grounds, it is advantageous to use a minimum of dye; however, comparatively high concentrations of dye may sometimes be required to compensate for, e.g. faint fluorescence.

In many applications it will be a matter of indifference whether or not particles of precipitated dye are retained in the treated asbestos surfaces. In other cases it may be preferred to remove all traces of contaminating matter. As noted above, dye particles which are merely trapped mechanically by absestos surfaces may be detached therefrom by vigorous washing or brushing; alternatively, they may be dissolved in a suitable reagent.

The invention has been described in detail in relation to the post-mining operation of sorting asbestos-containing rocks from barren rocks. It will be appreciated however that the described method of rendering asbestos differentially fluorescent in relation to host rock finds further application in the field of prospecting.

In many cases, visual inspection of asbestos-containing surfaces (e.g. bore-hole walls) is impracticable; alternatively, seams of asbestos are not naturally adapted for delineation by normal photographic techniques. Assessments have shown, however, that cliff faces, stope faces and bore-hole walls can be treated (e.g. aerially sprayed in the case of cliff faces) with dispersions of precipitated dyes and, after washing, areas of significant sorption (including asbestos seams) can be detected in a simple manner by irradiating with ultra-violet light and scanning, e.g. with a cable-suspended television camera. A record of asbestos distribution and ore grades can thus be made possible.

We claim:

1. In the separation of pieces of rock at least some of which contain asbestos into a first portion comprising pieces containing asbestos in quantities which are economically recoverable and a second portion comprising pieces which contain no asbestos or quantities of asbestos which are not sufficient to permit economical separation of the asbestos from the rock associated therewith, the improvement which comprises:

(a) contacting all of the pieces of rock of both said first portion and said second portion with a liquid dispersion of a precipitated fluorescent dye dispersed in a dispersing liquid, whereby at least some of said precipitated fluorescent dye is sorbed by said pieces; and

(b) removing non-sorbed material from said pieces whereby the pieces of rock in said first portion are rendered differentially fluorescent in relation to the pieces of rock in said second portion.

2. A method according to claim **1**, wherein the precipitated fluorescent dye is selected from the group consisting of those fluorescent dyes which have been precipitated as a viscous insoluble salt and those fluorescent dyes which have been precipitated as a gelatinous insoluble salt, and the concentration of precipitated fluorescent dye in the dispersing liquid is selected from the range 0.1 to 0.5 gram per 100 millilitres of dispersion.

3. A method according to claim **2**, wherein the fluorescent dye has been precipitated as a gelatinous aluminium salt.

4. A method according to claim **3**, wherein the precipitated fluorescent dye is the aluminium salt of Uvitex VR.

5. In the separation of pieces of rocks at least some of which contain asbestos into a first portion comprising pieces containing asbestos in quantities which are economically recoverable and a second portion comprising pieces which contain no asbestos or quantities of asbestos which are not sufficient to permit economical separation of the asbestos from the rock associated therewith, the improvement which comprises:

(a) contacting said pieces of rock with a liquid dispersion of a precipitated fluorescent dye in a form exhibiting second colour flourescence dispersed in a dispersing liquid; and

(b) removing non-sorbed material from said pieces of rock, the precipitated fluorescent dye residually sorbed by the asbestos in said pieces of rock exhibiting second colour fluorescence and the precipitated fluorescent dye residually adhering to the non-asbestos surface areas of said pieces of rock exhibiting first colour fluorescence.

6. A method of sorting pieces of rock at least some of which contain asbestos into a first portion comprising pieces containing asbestos in quantities which are economically recoverable and a second portion comprising pieces which contain no asbestos or quantities of asbestos which are not sufficient to permit economical separation of the asbestos from the rock associated therewith, said method comprising the following sequence of steps:

(a) contacting both of said classes of pieces of rock with a liquid dispersion of a precipitated fluorescent dye dispersed in a dispersing liquid; and

(b) removing non-sorbed material from said pieces of rock;

(c) exposing the so treated pieces of rock indivdually to exciting radiation, detecting the emitted fluorescent radiation and translating said fluorescent radiation into electrical signals diagnostic of the asbestos content of each piece of rock;

(d) sorting pieces of rock comprising said first portion containing asbestos in quantities which are commercially valuable from pieces of rock comprising said second portion consisting of pieces which contain no asbestos or quantities of asbestos below a desired amount in response to said diagnostic electrical signals.

7. A method according to claim **6**, further characterised by a preliminary step in which the rocks are crushed to a suitable size and cleaned.

8. A method according to claim **6**, wherein the precipitated fluorescent dye is selected from the group consisting of those fluorescent dyes which have been precipitated as a viscous insoluble salt and those fluorescent dyes which have been precipitated as a gelatinous insoluble salt, and the concentration of precipitated fluorescent dye in the dispersing liquid is selected from the range 0.1 to 0.5 gram per 100 millilitres of dispersion.

9. A method according to claim **8**, wherein the fluorescent dye has been precipitated as a gelatinous aluminium salt.

10. A method of sorting pieces of rock to effect separation of said pieces of rock into a first portion consisting of pieces containing asbestos in quantities which are economically recoverable and a second portion comprising pieces which contain no asbestos or quantities of asbestos which are not sufficient to permit economical separation of the asbestos from the rock associated therewith, said method comprising the following sequence of steps:

(a) contacting all of said pieces of rock with a liquid dispersion of a precipitated fluorescent dye in a form

exhibiting second colour flourescence dispersed in a dispersing liquid;

(b) removing non-sorbed precipitated fluorescent dye from said pieces of rock, the precipitated fluorescent dye residually sorbed by the asbestos in said pieces of rock exhibiting second color fluorescence and the precipitated fluorescent dye residually adhering to the non-asbestos surface areas of said pieces of rock exhibiting first color fluorescence;

(c) exposing all of said pieces of rock individually to exciting radiation and detecting the emitted fluorescent radiation and translating said emitted radiation into electrical signals diagnostic of the asbestos content of each piece of rock; and

(d) sorting said pieces of rock into said first portion and said second portion in response to said diagnostic electrical signals.

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