Title: A METHOD FOR MARKING FIBROUS PRODUCTS USING LUMINESCENT MATERIALS, AND METHODS FOR DETECTING MARKED PRODUCTS

Abstract: The present invention is related to a method for marking of fibrous products, in particular fibrous cementitious products, using luminescent materials by introduction of said luminescent materials in the fibrous product. The invention is further related to methods of detecting the mark by admission of energy to the fibrous product and inspection by the human eye or by a preferably automated spectroscopic or spectrometric technique, that capture (specific wavelengths of) the emitted light.
A METHOD OF MARKING FIBROUS PRODUCTS USING LUMINESCENT MATERIALS, AND METHODS FOR DETECTING MARKED PRODUCTS

Field of the Invention

[0001] The present invention is related to the fabrication of fibrous products, more specifically fibrous cement products, using luminescent materials, with the aim to distinguish them from asbestos cement products through marking with luminescent materials.

Background art

[0002] Asbestos cement products have been produced for a long time. The negative effects on the human health of the fibres of asbestos materials, e.g. chrysotile have been recognised and have led to the gradual replacement by alternative fibrous materials in many products such as plates and tiles for roof coverage. The best-known process for the production of plates of fibrous cement is based on the repeated formation of a layer of asbestos or fibrous cement product on a sieve in the shape of a roll making use of the hydrostatic pressure difference that exists between the inside and outside of the sieve. The production process is in general referred to as the Hatschek process.

[0003] Hardening of the product takes place according the so-called hydraulic reaction of cement with water. The main difference between asbestos and the fibres in fibre cement is that asbestos fibres are very small and split easily to even smaller fibres. This is
contrary to fibres of fibre cement which consist of cellulose fibres and synthetic fibres. These fibres do not pose any threat to human health.

[0004] The inability to distinguish hazardous asbestos cement products from harmless fibre cement products has been a disadvantage for a long time. Although fibre cement has nothing to do with asbestos cement products, users are not willing to recycle FC products. In some cases FC products are treated like asbestos cement with very high disposal costs.

[0005] Luminescence is the general name for the phenomenon where light is emitted as a result of a so-called excitation process at which energy is being absorbed. There are various types of luminescence, denoted with a prefix according to the source of excitation that is considered. Photo-luminescence uses UV-light, visible light or IR-light as the excitation source. In addition, thermo-luminescence uses an increase of temperature for creating luminescence; electro-luminescence uses electrical energy, chemo-luminescence (e.g. the element ‘phosphor’) is based on the occurrence of a chemical reaction (e.g. oxidation,..); cathodo-luminescence is obtained by excitation of the material with electrons and radio-luminescence occurs after excitation of the material with e.g. X- or γ-radiation. Finally, bio-luminescence is a natural phenomenon, e.g. as the result of a natural chemical reaction.

[0006] Further, one distinguishes between 2 types of photo-luminescence. In the case where there is only a short time between excitation and emission of light, typically ~10^-8 sec. or less, the phenomenon is called fluorescence. So, fluorescence effectively stops once the source of excitation is removed. For longer times, the phenomenon is indicated with phosphorescence. Phosphorescence can last
for seconds or even minutes after removal of the source of excitation.

[0007] Photo-luminescent materials are constituted from a crystal lattice that acts as a host for doping with activator elements. There can be one or two doping agents. The ‘foreign’ activator ion will be able to function as a so-called luminescent centre. The operation of inorganic luminescent materials, also called ‘phosphors’ is represented schematically in figure 1. The energy of the emitted light is typically lower than that of the exciting radiation of longer wavelength. The increase in wavelength is being denoted with ‘Stokes shift’.

[0008] The host materials for phosphors fall in two main categories:

- insulating materials with ionic bonds, e.g. borates (e.g. Cd₂B₂O₇), silicates (e.g. Zn₂SiO₄) and calcium phosphates like apatite. In these materials, doping with an activator ion creates discrete energy levels as a result of local adaptation of the crystal lattice to the activator ion.

- Semi-conductors like ZnS with covalent bonds. Doping of these materials with activator ions leads to the creation of additional energy levels to the energy band structure of the ZnS crystal lattice. (Source for the above prior art, including fig. 1: A.R. West; ‘Solid State Chemistry and its applications’, chapter 17 page 583 -590 Ed. John Wiley and Sons Ltd, ISBN 0 471 90377 9, 1987)

[0009] In the past an enormous amount of combinations of host crystal lattice materials and activator elements have been studied. The addition of photo-luminescent materials to a fibre cement product with the aim of marking such a product, is unknown in the art, and not all of the known photo-luminescent materials would be of interest for the aim of marking fibre cement products.
[0010] Document US2003/0051638 describes a cementitious product with phosphorescence. The phosphorescent material in the form of a layer or coating on a substrate, e.g. a statue, is applied by trowel, brush or spray, and is aimed at obtaining a glowing effect after exposure to sunlight. The phosphorescent materials used, and the way of applying these materials, are unsuitable to obtain a marking of the cementitious products.

Aims of the invention

[0011] The present invention aims to provide a method for adding photo-luminescent materials to a fibre product, in particular a fibre cement product, so as to mark said products for subsequent identification. The invention is also related to methods of detection of the marks, and thus of distinguishing between marked and non-marked products.

Summary of the invention

[0012] The invention is related to methods as described in the appended claims, in particular to a method of marking a fibrous product by the introduction of an inorganic or organic luminescent material in said fibrous product, in particular in a fibrous cementitious product. Further, the luminescent materials can be applied either in mass (throughout the bulk) or localised e.g. in between two of the layers that build up the product. Further to this invention, the detection of the mark is realised by inspection of the cross-section with a (small, portable) UV-light source. Detection of the mark can be, again according to this invention, supported using a darkened environment enhancing the contrast between the mark and the matrix. In daylight the difference between a marked and an unmarked specimen will not be visible. Only when the
excitation is applied and when all other conditions for detection of the mark are sufficiently fulfilled, the difference will be visible. For the customer market, this is very important because no adaptation is required from the customer. It is sufficient, even preferable, for the photoluminescent material to produce only a briefly lasting luminescence (in the order of seconds).

[0013] In particular, the invention is related to a method for marking of fibrous products using luminescent materials by:
- Introduction of said luminescent materials in the fibrous product,
- Detection of the mark by admission of/introduction of energy to the fibrous product and inspection by the human eye or by a spectroscopic or spectrometric technique, that captures (specific wavelengths of) the emitted light. Preferably, the detection takes place in an automated way, for example by an automated spectroscopic or spectrometric technique.

[0014] The fibrous product may be a fibre cement product or an asbestos cement product. The inspection is preferably supported by using a darkened environment.

**Brief description of the drawings**

[0015] Figure 1, left: schematic presentation of the process of luminescence in which an activator atom is being excited and subsequently emits light; Figure 1, right: the process of luminescence in which a sensitizer atom is involved.

**Detailed description of the invention**

[0016] The invention is generally related to the use of photo-luminescent materials for the marking of fibrous products, in particular fibrous cement products. The
invention is related to a method for marking said products, by adding photo-luminescent material to a fibrous product, in such a way that the photo-luminescent material can be detected by applying an excitation to the product, preferably an excitation by light energy, preferably by placing the marked product in a darkened environment. Optimal marking effects can be obtained by the right choice of photo-luminescent material, and by the right choice of concentration of said luminescent material with respect to the fibre material to which it is added.

The luminescent material can be applied to the (fibrous) cement with the following methods:

Application in the mass of the cement by adding the luminescent substance to the mixture. This will result in a disperse mark. Any production method for producing fibrous cement products, e.g., the Hatschek process, starts from a mixture of the cement and other constituents with one or more types of fibres. By adding an amount of photo-luminescent material to said mixture, this material will be dispersed evenly over the volume of the cement product.

Another production technique is the application between different layers by spraying a suspension of the luminescent substance on the surface. In particular, said suspension is sprayed on the surface of an intermediate layer formed during the course of Hatschek processing for producing sheet material. The result is a narrow stripe of luminescent material, e.g., near the middle of the cross-section of the fiber cement product.

Also, the luminescent material can be applied between the layers by pneumatically blowing powder of pure luminescent material or of luminescent material diluted with another inert powder, that meets the requirements of the application on the surface, preferably on the surface.
of an intermediate layer formed during the course of Hatschek processing. The transport of the powder from the gun to the target can be electrostatically supported by application of an electric field. This method will also result in a narrow stripe of luminescent material, e.g. near the middle of the cross-section of the fiber cement product.

According to the invention, said luminescent materials may be introduced in the fibrous product in a concentration between 50 weight% and 0.00000001 weight%, or between 5 weight% and 0.000001 weight% or between 0.5 and 0.0001 weight%, or below 0.1 weight%.

Preferred photoluminescent materials for use according to the present invention preferably have the following characteristics:

- stable at a pH of 13 in order to withstand the hydraulic reaction during hardening of the product,
- service life of 50 years or more,
- not radioactive,
- safe with respect to human health,
- environmentally friendly.

In case the marking is to be recognised by the human eye (cheap and easy), than the material preferably demonstrates the largest part of its emission near the top of the eye sensitivity curve, i.e. the material preferably demonstrates a maximum emission at 555 +/- 20 nm where the human eye shows the highest sensitivity. In other words, for cheap and easy detection the materials preferably emits green coloured light.

The photo-luminescent material preferably can be excited at 365nm or at 254nm: this makes a cheap excitation source possible. Excitation at 365nm is preferred for following 2 reasons:
- safer wavelength for the eyes
- cheaper light source

Photoluminescent materials which may be used in pure form or as part of a mixture, are: \( \text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}, \text{Mn} \) (i.e. matrix of \( \text{BaMg}_2\text{Al}_{16}\text{O}_{27} \) doped with \( \text{Eu} \) and \( \text{Mn} \)); \( \text{Zn}_2\text{SiO}_4: \text{Mn} \); \( (\text{Sr}, \text{Ba})_2\text{SiO}_4: \text{Eu} \); \( \text{Y}_2\text{O}_2\text{S}: \text{Eu} \); \( \text{ZnS}: \text{Cu}, \text{Al}, \text{Au} \); \( \text{ZnSiO}_3: \text{Mn}, \text{As} \). Other possible materials that are suitable (pure or in a mixture) are: \( \text{Y}_2\text{O}_3: \text{Eu} \); \( \text{MgAl}_{11}\text{O}_{19}: \text{Ce}, \text{Tb} \); \( \text{Y}_3\text{Al}_5\text{O}_{12}: \text{Ce} \); \( \text{MgB}_5\text{O}_{10}: \text{Ce}, \text{Gd} \); \( \text{LaPO}_4: \text{Ce}, \text{Tb} \). The above lists are not

limitedative for the present invention.

[0023] The invention is further related to a method for detecting the luminescent marking of the product, by admitting energy to the product, preferably in a darkened environment.

[0024] According to a first embodiment, light energy is admitted, and the inspection is performed by using a light level below 1000 lux, or below 100 lux, or below 10 lux. The energy may be admitted by irradiation with UV-, visible or IR-light.

[0025] Alternatively, energy may be admitted to the fibrous product by irradiation with X-rays or gamma-rays, or by heating, or by application of an electrical voltage over the product, causing electrical current, or by chemical reaction. In the above cases, the photo-luminescent material used is chosen appropriately with the energy source used for excitation, i.e. radiation sensitive photoluminescent material, electro-luminescent material, or chemo-luminescent material.

[0026] The energy may be admitted to the surface of the fibrous product, if the luminescent powder has been admixed throughout the bulk. Alternatively, the energy may be admitted to a cross-section of the fibrous product, by breaking the fibrous product in order to create fresh
surface area. Inspection by the human eye may be supported by comparing a marked and a non-marked product. Luminescent materials used in the invention preferably are inorganic materials.

According to various embodiments, said luminescent materials emit light with a wavelength in between 400 and 700 nm, or between 500 and 600 nm, or between 530 and 580 nm.

Example 1:
50 mg of ZnSiO₃:Mn inorganic luminescent powder is added to 100g of the cement slurry, containing also the other constituents like portland cement, amorphous silica, limestone and the necessary fibres, a.o. cellulose fibres and synthetic fibres. The Hatschek process is applied to make flat cementitious plates that are later curved to yield sheets of corrugated plate. As such the marked product is obtained, after drying. After application and use for either short or long service life of up to 50 years, the plate is recovered for recycling. A cross-section is obtained by breaking the plate. This cross-section is inspected upon irradiation with UV-light, eg. with wavelength of 254nm and/or 365nm, making use of commercial light sources in a slightly darkened environment. The cross-section is compared with a cross-section of non-marked material (i.e. not containing luminescent material) and/or an additional cross-section of marked material. Since the marked product will emit visible light of green colour, it will be recognised and processed as non-hazardous material, in comparison to non-marked cementitious fibrous products that are likely to contain asbestos fibers.
Example 2:
A suspension of 5g BaMg2Al16O27:Eu,Mn inorganic luminescent powder is prepared in 0.1l of water, possibly containing constituents like dispersant, etc. This suspension is fed to a spray gun and sprayed on the surface of an intermediate layer formed during the course of Hatschek processing. The spraying of the phosphor suspension is synchronised with the Hatschek process, such that the spraycoating is applied to one of the middle layers of the resulting fiber cement product. Detection is done as in example 1, with the difference that the mark will show up as a distinct, thin line near the middle of the cross-section.
CLAiMS


2. The method according to claim 1, wherein said product is a fibre cement product.

3. The method according to claim 2, wherein said photo-luminescent material is added to a slurry comprising constituent materials of said fibre cement product, and wherein said product is produced from said slurry.

4. The method according to claim 2 or 3, wherein said product is a fibre cement sheet, produced by the Hatschek process, and wherein said photo-luminescent material is applied on a surface of an intermediate layer of said sheet product during production thereof.

5. The method according to claim 4, wherein a suspension of said photo-luminescent material is sprayed on said surface.

6. The method according to claim 4, wherein a powder of said photo-luminescent material is blown onto said surface.

7. The method according to any one of the preceding claims, wherein said photo-luminescent material is chosen from the group consisting of: $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}, \text{Mn}$; $\text{Zn}_2\text{SiO}_4:\text{Mn}$; $(\text{Sr}, \text{Ba})_2\text{SiO}_4:\text{Eu}$; $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$; $\text{ZnS}:\text{Cu}, \text{Al}, \text{Au}$; $\text{ZnSiO}_3:\text{Mn, As}$; $\text{Y}_2\text{O}_3:\text{Eu}$; $\text{MgAl}_{11}\text{O}_{19}:\text{Ce}, \text{Tb}$; $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$; $\text{MgB}_6\text{O}_{10}:\text{Ce}, \text{Gd}$; $\text{LaPO}_4:\text{Ce}, \text{Tb}$. 
8. The method according to any one of the preceding claims, wherein said photo-luminescent material is added in a concentration between 50 weight% and 0.0000001 weight%.

9. The method according to any one of claims 1 to 7, wherein said photo-luminescent material is added in a concentration between 5 weight% and 0.000001 weight%.

10. The method according to one of claims 1 to 7, wherein said photo-luminescent material is added in a concentration between 0.5 and 0.0001 weight%.

11. The method according to one of claims 1 to 7, wherein said photo-luminescent material is added in a concentration below 0.1 weight%.

12. The method according to any one of the preceding claims, wherein said photo-luminescent material emits light with a wavelength in between 400 and 700 nm.

13. The method according to claim 12, wherein said photo-luminescent material emits light with a wavelength in between 500 and 600 nm.

14. The method according to claim 12, wherein said photo-luminescent material emits light with a wavelength in between 530 and 580 nm.

15. The method according to any one of the preceding claims, further comprising the step of detecting the mark by admission of energy to the fibre product and inspection by the human eye or by an automated technique, that captures the emitted light.

16. The method according to claim 15, wherein said detection takes place by a spectrometric or spectroscopic technique.

17. The method according to claim 15, said method being performed in a darkened environment.
18. The method according to claim 15 or 16, wherein said energy is light energy and wherein a light level below 1000 lux is used.

19. The method according to claim 15 or 16, wherein said energy is light energy and wherein a light level below 100 lux is used.

20. The method according to claim 15 or 16, wherein said energy is light energy and wherein a light level below 10 lux is used.
FIG. 1
### A. CLASSIFICATION OF SUBJECT MATTER

<table>
<thead>
<tr>
<th>INV.</th>
<th>C04B28/02</th>
<th>C09K11/59</th>
<th>C09K11/64</th>
<th>C09K11/74</th>
<th>C09K11/77</th>
</tr>
</thead>
</table>

According to international Patent Classification (IPC) or to both national classification and IPC.

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C04B
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 4 172 063 A (O'BRIll, ROBERT) 23 October 1979 (1979-10-23)</td>
<td>1-3, 7-15, 18-20, 4-6</td>
</tr>
<tr>
<td>Y</td>
<td>column 1, lines 43-56 column 2, lines 13,14,23,24,36-38,47-59 column 3, lines 15,16,23,24,39-41,44-50; example 1 examples 10,16,29</td>
<td>4-6</td>
</tr>
<tr>
<td>Y</td>
<td>paragraphs [0003], [0007], [0009], [0010], [0017], [0019]; examples 1,5,5a claims 1,8,9</td>
<td>4-6</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search

5 September 2006

Date of mailing of the international search report

12/09/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Hilversum
Tel. (+31-70) 340-2040, Tx. 31 051 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Vanier, C
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>column 1, lines 43-46, 60-63, 67 column 2, lines 1-18 column 3, lines 47-49 examples 1-8 claims 1-3</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>WO 02/070248 A (JAMES HARDIE RESEARCH PTY LIMITED; NAJI, BASIL; O’CHEE, MILTON) 12 September 2002 (2002-09-12) page 2, lines 13, 14 page 4, lines 3, 16-23 page 7, line 28 - page 8, line 19 examples 1, 2 claims 1, 7, 11, 12, 71</td>
<td>4-6</td>
</tr>
<tr>
<td></td>
<td>WO 02/02481 A (CROWLEY, GRAHAM, MICHAEL) 10 January 2002 (2002-01-10) page 2, lines 5-20 page 3, lines 12-14 page 4, line 19 - page 5, line 7 page 5, lines 8-16 page 6, lines 14-21 claims 1, 5</td>
<td>4-6</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>US 4172063 A</td>
<td>23-10-1979</td>
<td>NONE</td>
</tr>
<tr>
<td>US 2003051638 A1</td>
<td>20-03-2003</td>
<td>NONE</td>
</tr>
<tr>
<td>US 5849218 A</td>
<td>15-12-1998</td>
<td>NONE</td>
</tr>
<tr>
<td>WO 02070248 A</td>
<td>12-09-2002</td>
<td>NONE</td>
</tr>
<tr>
<td>US 6466135 B1</td>
<td>15-10-2002</td>
<td>NONE</td>
</tr>
</tbody>
</table>