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(54) Title: TRACER MATERIALS IN CEMENTITIOUS COMPOSITIONS AND METHOD OF IDENTIFICATION THEREOF

(57) Abstract: A method of identifying a cement-based composition comprising at least one nonamorphous tracer material is disclosed. The method comprises the steps of removing cement and the like of a sample using a strong acid, washing the residue and optionally filtrating and drying the same. The residue is preferably burnt at an elevated temperature remove organic content and located in a X-Ray Diffractometer. The angle and intensity of the diffracted rays are measured and compared with pre-determined data of specific tracer materials. The tracer materials are specifically selected from the group of talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax and kolemanite, which are suitable materials for use in cementitious compositions with their crystal molecular shapes and chemically inert features providing assistance during the X-Ray diffraction analysis.

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TRACER MATERIALS IN CEMENTITIOUS COMPOSITIONS AND METHOD OF IDENTIFICATION THEREOF

Technical Field of the Invention

The present invention relates to a method of identification of a cement-based material for determining whether it is of a particular type or belonging to a certain producer and a cement based composition comprising the tracer materials of said method. The method incorporates use of specific tracer materials, admixed to various types of cementitious products such as; adhesives, filling materials, insulation mortars, repair mortars, grouts etc. The novel method allows determination of the source and type of the product before/after the usage through a rapid and reliable way of analysis comprising a pre-treatment step followed by a X-Ray Diffractometric analysis which provides the capability of identifying the product both in powder form i.e. prior to application and in hardened form i.e. after application on a building structure.

Background of the Invention / Prior Art

The present invention refers to cement-based materials comprising very fine trace materials as an additive and a novel method for determining the producer and the kind of cement based product comprising the tracer materials of said method.

Parallel to the tremendously high amount of application areas in daily life, cement and cement-based compositions take an important role to constitute part in various types of constructions. These widely used applications bring certain problems to the manufacturers that require a full pursuit of their own products even many years after application. There are cases where manufacturers are required to identify their own products even long years after they are sold and applied on a building structure. A major problem arises from the fact that producers are demanded to re-supply products or compensate for losses of a consumer when a product fails to meet with requirements specified by the producer itself or by government regulations.

When a cementitious product is applied on a building structure, it is generally very difficult to identify the exact producer and the type of a product. From the producer's point of view, the case is always to be handled with utmost care as failure to comply with the requirements is one of the major concerns of every reliable producer. It may be the case that the product which was applied on a building structure and which later on showed defects may be the product of a third party. Having a few pieces of cementitious product in hand, it is generally very difficult and expensive to find the producer and the type of a cement based product long years after application on a

structure. As a second possibility, it may also be the case that the product which failed to meet with the requirements is the product of concerned producer, but the type of the product was inappropriate for application on the building structure for which the consumer demands compensation. A third possibility is that the defective product was produced by concerned producer and the type of the product was appropriate for the structure on which it was applied. In all three cases, it is important to the concerned producer to reliably identify at low cost whether the cement based material used in the pieces of cementitious product in hand was his own product and if yes, was it of the correct type for applying on the structure at which damage occurred.

Basically, a cementitious material includes a number of chemical admixtures depending on their functions, such as; air-entraining, water-retaining, retarding, accelerating and plasticizer additives. In addition to these, the present invention proposes use of tracer materials within the cementitious composition, the tracer particles being invisible or hardly visible to the human eye under normal conditions. At this point, the present methods offer some tracer particles characterized in their physical properties. These include using tracer particles having colors or sizes which are different to those of the cementitious composition and the detection method being based on distinguishing particles based on their physical properties using simple techniques such as screening. One such method is disclosed in US 5,324,356 granted to Goodwin et al. Goodwin basically suggested pulverizing and screening a building material e.g. pieces hardened cement based material to determine the absence or presence of a tracer material within that building material. Other suggestions of Goodwin are adding tracer materials which can be distinguished using their shape, color, density, refractive index, insolubility and fluorescence effect. One of the major drawbacks of using tracer materials identifiable by such physical properties is that the identification process is likely to fail in case that a cementitious composition of any third party naturally comprises an ingredient having physical properties similar to that of the tracer material. Those skilled in the art will easily appreciate how difficult and non-reliable it could be to find out the type and the producer of a cement based material solely by means of separation in physical properties such as identifying color, shape, particle size, density or solubility.

Reliability of the simple physical treatments based on the physical visibility of the particles is quite doubtful and may easily cause failures during the detection experiments. Assuming that tracer materials are identified using their shape or color, it is possible that any hardened sample comprising a natural or foreign ingredient which has a similar shape or color to that of the tracer material is likely to lead in an

erroneous test result. It is quite common in latest products of the industry that the products comprise particles such as fibers which are proposed to be tracers materials as suggested by Goodwin et al. However, it is well known that many such products comprise fibers for reinforcement purposes. Any such component is likely to confuse the test staff as it is almost impossible to determine whether such particles are reinforcement fibers or flakes of a third party product or alternatively, the tracer materials of the concerned producer. Assuming that the tracer particles are identified using their size, the identification method is the most primitive and thus most questionable approach that could be employed. It is practically inappropriate to add a tracer material which does not have near sizes to the filler. Under such cases, it is generally not possible to obtain a trustworthy identification result. There is also no need to mention that producing an imitation product is an extremely easy process in all three aforementioned assumptions.

Using tracer materials having a specific weight which is different to that of the cementitious composition might be practically possible only if the tracers have a lower specific weight. However, one should also keep in mind that natural fillers having low weight are already used in many types of cementitious products, which accompany the fact that such products will not be identifiable among many of the third party products.

If the case is that the fluorescence effect of the tracer materials are sought, then the identification process would be more reliable compared to above mentioned assumptions whereas the process would require use of generally very expensive materials as the tracers. Alternatively, if the tracer materials are identified using their insolubility, then the identification method is again very questionable. Any natural or foreign content which is found e.g. in a hardened sample collected from a failed site and which is insoluble, may lead the identification process in an erroneous result. Under such a case, one should assume that all cement based products comprising non-dissolving agent should certainly belong to the concerned producer, which is no-doubt an erroneous.

The present invention aims to provide a method in which detection of tracer materials are conducted in the molecular level rather than in the macro level of physical properties. None of the present methods offer such reliable and efficient tracer materials and/or detection methods thereof applicable to cement-based compositions. The present invention offers an extremely reliable combination of specific tracer materials and their detection method including an XRD (X-Ray Diffraction) analysis in which specific identification parameters, namely the distance between atom row planes

of crystal lattices (d) and the intensity of diffracted light (I) are determined with a precision not open to debate.

Objects of the Invention

One of the objects of the present invention is to provide an efficient method which enables a producer of cement based materials to identify reliably his product and its type before or after use on a structure.

Another object of the present invention is to provide a tracer material identification method, in which very fine tracer materials admixed in a cement based composition can be identified, such identification taking place in the molecular level.

Another object of the present invention is to provide novel process for identifying tracer materials in a cement based composition, in which tracer materials show particle size, shape and color characteristics which are substantially similar to those of said cement-based composition.

A further object of the present invention is to provide a tracer material identification method in which the tracer materials admixed in a cement based composition are identified using their crystal structure.

A further object of the present invention is to provide a tracer material identification method in which the tracer materials to be admixed to the product can be selected from a group of elements which can not be naturally encountered in the products of other producers.

A further object of the present invention is to provide cement based material comprising at least one tracer material which is identifiable by the method of the present invention.

Summary of the Invention

The objects of the invention are achieved through use of specifically determined tracer materials such as talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax, kolemanite etc. These additives take their place inside the formulation of cement-based materials to which they are added and allow a reliable identification by means of XRD (X-Ray Diffractometry) either before use or after application on a structure, even followed by long years.

The type of the tracer material shall be appropriate for use within the cementitious composition and be detectable either in powder form prior to use or after setting. It is important that selected tracer particles are chemically inert and do not indicate an amorphous structure in X Ray diffraction. The method may be applied to both powdered and already hardened structures, comprising a number of pre-treatment steps such as removing foreign materials (soil, stone, dust, mortar etc.), washing the residue with a concentrated acid, filtration, drying, burning and finally analyzing in an X-Ray Diffractometer. The pre-treatments applied before the XRD analysis serve to the purpose of obtaining precise results in the diffractometer.

XRD detection is conducted by subjecting the residue in an X-ray field, measuring the distance (d) between the atom row planes of the crystal lattices and the intensity (I) of the diffracted light using the rays diffracted from the residue. The distance (d) and the light intensity (I) values for each kind of the tracer material selected for use in the method of the present invention are known and shown on charts comprising such predetermined data as in the case of ASTM charts. Values obtained from the diffractometer are then compared with the values shown on the chart and used to determine whether the residue comprises or not and, if yes, the type of the tracer material used by the concerned producer.

Brief Description of the Figures

Accompanying figures are given solely for the purpose of schematically exemplifying the principle of the method of the present invention.

Fig. 1 is a schematic 2-dimensional demonstration of an x-ray diffraction occurring on a residue material surface intended to simulate, by way of an example, an X ray being diffracted on plane surface of a residue and rebounded with a specific light intensity.

Detailed Description of the Invention

Cement-based materials are compositions generally comprising 30 to 60% Portland Cement, aggregates and additives like cement-based adhesives, filling materials, insulation mortars, repair mortars, grouts etc. which are used for different purposes in constructions through use of a setting or a hardening component, generally water. Hydrolysis occurs in the structure of the formulation as soon as the hardening agent contacts the cementitious material. At this stage the calcium aluminates, calcium silicates and other compounds are hydrolyzed and pH of the composition increases immediately to over 12 and a large amount of heat release occurs due to the release of alkaline hydroxide (OH^-) ions. At this point said specifically selected tracer materials

perform a highly resistant property against those highly alkaline pH values and against hard conditions having the ability to stay in the structure for many years and coinciding to micro level particles of cementitious and additive phases.

The present invention comprises a number of steps for precisely detecting the existence of a tracer material in a residue to provide an indication for the producer and type of the product. These steps include removing the solid bulk materials (soil, sand, stone etc.) around the residue, washing the same using any strong acid e.g. HCl, drying, burning and finally locating the residue in an X-Ray Diffractometer. Preferred tracer materials of the present invention are talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax and kolemanite in very fine form.

Aforementioned pre-treatment steps are, selectively and as necessary, applied to a hardened composite sample, aiming to obtain a relatively pure material for a precise identification in the diffractometer step. Assuming an aged residue of cement based product in hand, the sample is to be cleaned out from the rough materials and preferentially washed out in a strong acid, such as hydrochloric acid. The acid-wash substantially provides removal of cement and filling materials from the sample. Subsequently, the sample is optionally washed with water, filtrated and dried. It is of utmost importance during these steps that the tracer material sought in the sample should of a type insoluble and non-reactant to the materials involved in these treatments or shortly, the tracer material shall be capable of retaining its crystal structure during the pre-XRD treatments. Organic materials are removed by optionally burning the sample for a preferred duration of 1 hour at an elevated temperature between 250 to 650 °C. It is found out during the tests that burning the sample is not an essential step of the identification process, but it is preferred due to the fact that the tracer materials are frequently surrounded by organic components which reduce the detectability of the tracers in the x-ray diffractometry. A clear tracer component which is free of organic materials can be more sharply detected in the XRD analysis while accompanying the additional benefit of adding a lower tracer content in the cement based composition.

It is further noted during the laboratory experiments that the amount of organic compound content can be used in combination to existence of a tracer material to determine the type of a product. The amount of organic material can be measured during the burning step.

It is guaranteed by the pre-XRD treatments that all the minerals and other foreign materials which may inadvertently affect x-ray diffractometry are removed. It is further more stated that aforementioned pre-XRD treatments are found to be helping the tracer material concentration in the sample increase. In return, this feature provides the advantage of freedom to use a lower amount of tracer content in the final product while still remaining in the detectable limits.

It is obvious for those skilled in the art that X Rays can easily detect minerals and inorganic materials having formal crystal shapes. X Rays are conventionally created in a vacuum tube and emitted from an anode electrode. The regularly ordered atoms of the lattice structures of the minerals diffuse the X Rays causing interferences and consequently these indicate the proper constitution of the secondary dispersion of the emission. Bragg Law is employed to understand the diffractometry behavior during the XRD analysis. According to the same, X Rays should come through a mineral with a definite angle and the difference of distance between the incoming and outgoing rays should be equal to a multiple of the wave length.

$$(BA' + CA' = n\,\lambda)$$

The Bragg Law further defines that :

$$n\,\lambda = 2\,d\,\sin\Theta$$

in which

n, is the diffraction coefficient
Θ, is the diffraction angle
λ, is the X Ray wave length
d, is the distance between the atom row planes in the crystal lattice.

In the exemplified X Ray diffraction analysis, it is aimed to determine two single parameters. One is the distance (d) between the main atom row planes in the crystals and the other is the X Ray diffraction light intensity (I) about the plane. Table-1 indicates four different d and I values for each tracer material to be used with the present invention.

	d – distance				I - Intensity			
Talc	9.34	3.12	4.66	2.48	100	100	90	65
Albite	4.03	3.22	3.66	3.20	100	25	20	20
Orthoclase	3.24	3.29	4.22	2.16	100	65	65	55
Chloride	7.11	4.75	3.57	14.13	100	100	100	35
Zeolite	3.48	3.22	9.10	6.61	100	100	90	90
Mica	10.00	3.35	2.60	2.50	100	95	85	75
Vollastonite	2.98	3.83	3.52	3.31	100	100	80	80
Barite	3.44	3.10	2.12	2.10	100	97	80	76
Pirofillite	3.05	9.16	4.46	2.41	100	40	40	40
Bentonite	15.00	4.50	5.01	3.02	100	80	60	60
Serpentine	7.30	3.63	2.52	2.42	100	75	18	10
Chromite	2.51	1.08	1.47	1.60	100	90	80	60
Borax	2.57	2.84	4.86	3.96	100	53	47	40
Kolemanite	3.13	5.64	3.85	2.55	100	50	50	50

Table-1) d and I for the elements of the present invention

In accordance with the present invention, the sample to be put under X-rays is preferentially brought into powder form in order to increase the intensity of the reflection. Each mm^3 contains approximately 110 particles and their different locations provide intensive reflections. The X Rays, generated in the generator part of the XRD equipment with high voltage, are directed towards the pulverized sample and the diffracted X Rays with definite angles are converted to electronic data by means of a sensor located on a mobile goniometry arm. Each mineral and each crystallized material has a characteristic spectrum, which is also indicated in ASTM charts. Mineral identification is achieved through a brief comparison of experimental analysis results with the values e.g. indicated on ASTM charts.

Table-2 is a typical ASTM chart prepared upon XRD identification of a certain mineral, four conventional d and I values, exact diffraction list and surfaces and crystallographic-chemical-instrumental information used in the XRD.

d	3.34	4.26	1.82	4.26	SiO_2
I/I$_1$	100	35	17	35	SILICON II OXIDE ALPHA QUARTZ

Rad. CuKα$_1$ λ 1.5405 Filter Ni
Dia. Cut off Coll.
I/I$_1$ G.C. DIFFRACTOMETER d corr. abs.?
Ref. SWANSON AND FUYAT, NBS CIRCULAR 539, VOL. III, (1953)

Sys. HEXAGONAL S.G. D_3^4 - $P3_121$
a_o 4.913 b_o c_o 5.405 A C 1.10
α β γ Z 3
Ref. Ibid.

εα nωβ 1.5441 γ 1.553 Sign +
2V D_x 2.647 mp Color
Ref. Ibid.

MINERAL FROM LAKE TOXAWAY, N.C. SPECT. ANAL.: <0.01% Al; <0.001% Ca, Cu, Fe, Mg.
X-RAY PATTERN AT 25°C.

REPLACES 1-0649, 2-0458, 2-0459, 2-0471, 3-0419, 3-0427, 3-0444

d Å	I/I$_1$	hkl	d Å	I/I$_1$	hkl
4.26	35	100	1.228	2	220
3.343	100	101	1.1997	5	213
2.456	12	110	1.1973	2	221
2.282	12	102	1.1838	4	114
2.237	6	111	1.1802	4	310
2.128	9	200	1.1530	2	311
1.980	8	201	1.1408	<1	204
1.817	17	112	1.1144	<1	303
1.801	<1	003	1.0816	4	312
1.672	7	202	1.0636	1	400
1.659	3	103	1.0477	2	105
1.608	<1	210	1.0437	2	401
1.541	15	211	1.0346	2	214
1.453	3	113	1.0149	2	223
1.418	<1	300	0.9896	2	402,115
1.382	7	212	.9872	2	313
1.375	11	203	.9781	<1	304
1.372	9	301	.9762	1	320
1.286	3	104	.9609	2	321
1.256	4	302	.9285	<1	410

Table-2) Sample ASTM chart

Example 1

A contractor informed that a repair mortar applied 3 months ago on the exterior wall of a sports hall failed at site and that the consumer demands warranty repair. Sample pieces or failed mortar in hardened form was brought into the laboratory and subjected to hydrochloric acid bath. The residue is then washed, filtrated and dried followed by a burning process at 400°C. Upon pulverization the residue was put into a Philips 1040 X-Ray Diffractometer having a CuKα anode with 36 kV 16 mA high voltage. A separate goniometric instrument with a speed of 1° 2Θ / min was employed for measuring angles of diffracted rays. The diffractometer was operated at 4 x 102 CPS (x-ray photon flow per second). While the repair mortar of the producer comprised talc tracers, the XRD analysis resulted no content of talc in the residue. It is understood that the contractor used a third party repair mortar in the exterior construction of the failed site.

The present invention proposes a very reliable identification method even in very low tracer material concentrations in the sample. Having the capability of reliably identifying tracer materials in very low concentrations, producers are able to reduce material costs while at the same time producing end products which comprise less foreign content to deteriorate desired features of a cement based composition.

While prior art methods essentially adopt some simple approaches such as sieving, floating, coloring, sizing etc. of tracer materials for further detection, the present invention introduces instrumental analysis conducted in molecular level. The novel process of the present invention also allowed the producers to reliably identify their products before or after application in a building through use of specific tracer materials which are capable of retaining their crystal structure throughout the entire identification process. The novel process of the present invention has also provided use of said tracer materials which show particle size, shape and color characteristics which are substantially similar to those of said cement-based composition in which they are added. These highly efficient tracer materials include, but are not limited to talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax, kolemanite which are specifically selected for cementitious materials and which do not show an amorphous characteristics.

Claims :

1. A method of identifying a cement-based composition comprising at least one tracer material which is non-amorphous and which is capable of retaining its crystal structure in the following steps that comprise:

a-) removing, through use of a strong acid, cement and additives of a sample comprising said cement based composition,

b-) washing the residue of step a) and optionally filtrating and drying the same,

c-) preferably burning the residue at an elevated temperature in the range of 250°C to 650°C,

d-) subjecting the residue under x-rays and measuring the angle and intensity (I) of the diffracted rays,

e-) comparing obtained data with pre-determined data of specific tracer materials and determining whether and which tracer material is included in the sample.

2. A method according to Claim 1 wherein the residue is pulverized prior to subjecting under x-rays of step d).

3. A method according to Claim 1 wherein said tracer material is selected from the group of consisting of talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax and kolemanite.

4. A method according to Claim 1 wherein said tracer material being admixed to the cement based material shows an inert characteristic at substantially high pH values in the cementitious media.

5. A method according to Claim 1 the cement based composition comprises between 0.1 to 5% by weight of said tracer material.

6. A method according to any of the preceding claims wherein the outcome of step c) is treated in an x-ray diffractometer having a goniometric instrument for measuring the angle of rays.

7. A method according to any of the preceding claims wherein the amount of inorganic compound content is used in combination to existence of a tracer material to determine the type of a product.

8. A cement based composition comprising at least one tracer material which is identifiable by the method of claim 1.

9. A cement based composition according to Claim 7 wherein said tracer material is selected from the group of consisting of talc, albite, orthoclase, chloride, zeolite, mica, vollastonite, barite, profillite, bentonite, serpentine, chromite, borax and kolemanite.

10. A cement based composition according to Claim 7 or 8 wherein said cement based structure comprises between 0.1 to 5% by weight of said tracer material.

11. A cement based composition according to Claim 7 wherein said tracer materials show particle size, shape and color characteristics which are substantially similar to those of said cement-based composition.

12. A cement based composition according to Claims 7 to 10 wherein the composition comprises at least two tracer materials having different crystal structures for coding the type of a product.

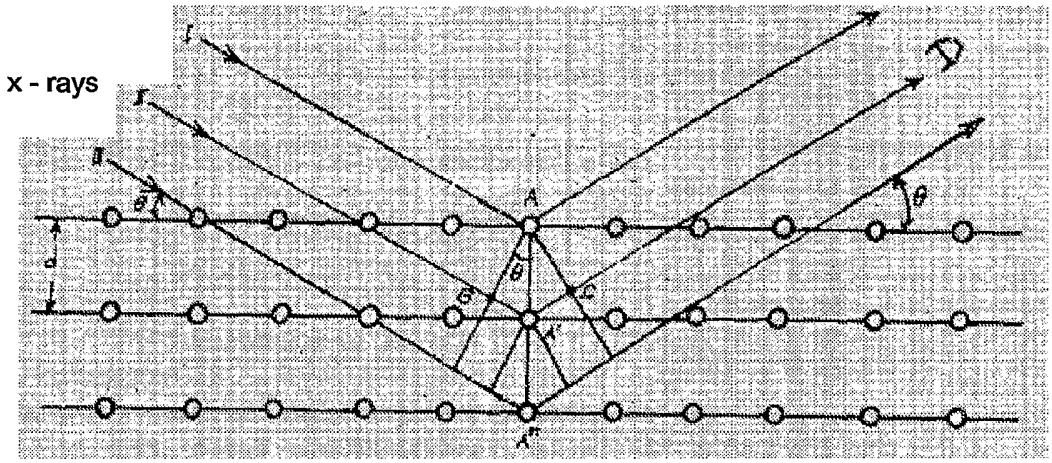


Fig -1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050890

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B40/00 G01N33/38

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)
IPC 7 C04B G01N

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 324 356 A (GOODWIN ET AL) 28 June 1994 (1994-06-28) cited in the application the whole document	8-11
Y		1-7
X	US 5 010 301 A (LEUNG ET AL) 23 April 1991 (1991-04-23) the whole document	8,9
Y		1-7
X	US 2002/117090 A1 (KU RICHARD) 29 August 2002 (2002-08-29) paragraphs '0018!, '0035!	8-11
Y		1-7

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
26 January 2005	07/02/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gattinger, I

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050890

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 624 489 A (FU ET AL) 29 April 1997 (1997-04-29) the whole document	8-12
Y		1-7
X	US 2 861 636 A (MESSENGER JOSEPH U) 25 November 1958 (1958-11-25) the whole document	8-12
X	EP 0 397 963 A1 (SIKA AG, VORM. KASPAR WINKLER & CO) 22 November 1990 (1990-11-22) table 1	8-12
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