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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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(54) Title: LITHIUM ALKYLSILICONATE COMPOSITION, COATING, AND METHOD OF MAKING SAME

(57) Abstract: A method of making a lithium alkylsiliconate composition comprising adding an alkylalkoxysilane to a first mixture comprising lithium hydroxide and water to form a second mixture comprising a lithium alkylsiliconate and an alcohol, wherein i) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.9 to less than 1.1 and the water is from 89 to 93 mol %, or ii) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 1.1 to 1.4 and the water is from greater than 93 to 99 mole %.

LITHIUM ALKYLSILICONATE COMPOSITION, COATING, AND METHOD OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 62/324948 filed 20 April 2016 under 35 U.S.C. §119 (e). U.S. Provisional Patent Application No. 62/324948 is hereby incorporated by reference.

FIELD OF THE INVENTION

[0001] The present invention relates to a method of making a lithium alkylsiliconate composition comprising adding an alkylalkoxysilane to a mixture comprising lithium hydroxide and water. The invention also relates to the lithium alkylsiliconate composition made by the method; a method of making a coating comprising applying the lithium alkylsiliconate composition to a substrate; and the coating.

BACKGROUND OF THE INVENTION

[0002] Methods of making alkali metal alkylsiliconate compositions are known. For example, alkali metal alkylsiliconates have been made by the reaction of alkylsilanols, alkylalkoxysilanols, or organodisiloxanes with metal oxides and hydroxides in the presence of water. The alkali metal alkylsiliconate compositions made by current methods find use in coating compositions for application to various silica-containing materials, such as cement or concrete, to provide water repellency and resistance to degradation caused by weather, chemicals and other corrosive elements. Even though coatings formed with the current alkali metal alkylsiliconates provide water repellency benefits to silica-containing materials, the water repellency of these coatings can still be improved. Therefore, there is still a need for new methods of making alkali metal alkylsiliconate compositions for use in coating compositions that form coatings with improved water repellency.

BRIEF SUMMARY OF THE INVENTION

[0003] The present invention is directed to a method of making a lithium alkylsiliconate composition comprising adding an alkylalkoxysilane to a first mixture comprising lithium

hydroxide and water to form a second mixture comprising a lithium alkylsiliconate and an alcohol, wherein i) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.9 to less than 1.1 and the water is from 89 to 93 mol %, or ii) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 1.1 to 1.4 and the water is from greater than 93 to 99 mole %.

[0004] The present invention is further directed to a method of making a coating comprising applying the lithium alkylsiliconate composition to a substrate.

[0005] The method of the instant invention produces a lithium alkylsiliconate composition that forms coatings providing superior water repellency properties to silica-containing materials, such as cement, stone, masonry and concrete, as evidenced by low 8-hour water absorption test results as described below. The lithium alkylsiliconate composition may be used in coating compositions for application to silica-containing materials.

DETAILED DESCRIPTION OF THE INVENTION

[0006] A method of making a lithium alkylsiliconate composition, the method comprising:

adding an alkylalkoxysilane to a first mixture comprising lithium hydroxide and water to form a second mixture comprising a lithium alkylsiliconate and an alcohol, wherein i) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.9 to less than 1.1 and the water is from 89 to 93 mol %, or ii) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 1.1 to 1.4 and the water is from greater than 93 to 99 mole %.

[0007] The alkylalkoxysilane has the formula $R_aSi(OR)_{4-a}$ (I), wherein each R is independently C_1-C_{10} alkyl or cycloalkyl; and the subscript a is 1, 2, or 3.

[0008] The alkyl groups represented by R typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms, alternatively 1 carbon atom. Acyclic alkyl groups containing at least three carbon atoms can have a branched or unbranched structure. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, decyl. Examples of cycloalkyl groups include, but are not limited to, cyclopentyl, methylcyclopentyl, cyclohexyl, and methylcyclohexyl.

[0009] Examples of alkylalkoxysilanes include, but are not limited to, those having the formulae: $CH_3Si(OCH_3)_3$, $CH_3CH_2Si(OCH_3)_3$, $CH_3Si(OCH_2CH_3)_3$, $CH_3CH_2Si(OCH_2CH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $(CH_3CH_2)_2Si(OCH_3)_2$, $(CH_3)_2Si(OCH_2CH_3)_2$, $(CH_3CH_2)_2Si(OCH_2CH_3)_2$, $(CH_3CH_2)_3Si(OCH_2CH_3)$, $(CH_3)_3Si(OCH_3)$, $(CH_3CH_2)_3Si(OCH_3)$, and $(CH_3)_3Si(OCH_2CH_3)$.

[0010] The alkylalkoxysilane may be a single alkylalkoxysilane having the formula (I) or a mixture of two or more alkylalkoxysilanes, each having the formula (I). For example, a mixture of $CH_3Si(OCH_3)_3$ and $CH_3Si(OCH_2CH_3)_3$ may be used. Methods of preparing alkylalkoxysilanes are known in the art; many of these compounds are commercially available.

[0011] The first mixture comprising lithium hydroxide and water may be made by, for example, mixing solid lithium hydroxide or a lithium hydroxide hydrate ($LiOH{\cdot}H_2O$) with water or by diluting a more concentrated lithium hydroxide-water mixture. Lithium hydroxide is well known in the art and is available commercially in various forms.

[0012] The addition of the alkylalkoxysilane to the first mixture comprising lithium hydroxide and water to produce the lithium alkylsiliconate and alcohol can be carried out in any reactor suitable for contacting an alkylalkoxysilane with an alkali metal hydroxide solution. Suitable reactors include glass and Teflon-lined glass reactors. Preferably the reactor is equipped with a means of agitation, such as stirring.

[0013] The alkylalkoxysilane is added to the first mixture comprising lithium hydroxide and water. Reverse addition of the first mixture comprising lithium hydroxide and water to the alkylalkoxysilane may produce large amounts of gels and lithium alkylsiliconate compositions that will form coatings with inferior water absorption properties.

[0014] The method of the invention involves an exothermic reaction, so the addition rate of alkylalkoxysilane to the first solution is controlled to prevent the creation of an uncontrollable exotherm. Otherwise, there is no limit on the rate of addition.

[0015] The alkylalkoxysilane is typically added to the lithium hydroxide at a temperature up to 80 °C, alternatively from 20 to 80 °C, alternatively from 25 to 80 °C; alternatively 50 to 80 °C.

[0016] The time that the alkylalkoxysilane is added to the first mixture comprising lithium hydroxide and water to form the lithium alkylsiliconate and alcohol can vary depending on the structure of the alkylalkoxysilane and the temperature. For example, the

alkylalkoxysilane is typically added to the lithium hydroxide for from 10 to 120 min, alternatively from 20 to 60 min, at a temperature of from 20 to 70 °C. The optimum time can be determined by routine experimentation using the methods set forth in the Examples section below. The reaction of the alkylalkoxysilane is essentially complete after the alkylalkoxysilane has been added to the first mixture comprising lithium hydroxide and water. As used herein, "essentially complete" means that at least 90 mole %, alternatively at least 95 mole %, alternatively at least 98 mole %, of the alkoxy groups of the alkylalkoxysilane added to the first mixture have reacted.

[0017] The mole ratio of lithium hydroxide to alkylalkoxysilane varies with the mole % water as follows: i) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.9 to less than 1.1 and the water is from 89 to 93 mol %, alternatively the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.95 to 1.08 and the water is from 90 to 93 mol %, or ii) the mole ratio of lithium hydroxide to alkylalkoxysilane is from at least 1.1 to 1.4 and the water is from greater than 93 to 99 mol %, alternatively the mole ratio of lithium hydroxide to alkylalkoxysilane is from 1.2 to 1.4 and the water is from greater than 94 to 97 mol %, alternatively the mole ratio of the lithium hydroxide to alkylalkoxysilane is from 1.2 to 1.4 and the water is from 95 to 97 mole %. As used herein, the "mol ratio of lithium hydroxide to alkylalkoxysilane" means the moles of lithium hydroxide in the first mixture divided by the moles of alkylalkoxysilane added. As used herein in reference to the water, "mole percent" or "mol %" is based on the moles of alkoxysilane, lithium hydroxide, and water added. The mol % water is calculated by dividing the initial moles of water in the first mixture by the sum of the moles of the alkylalkoxysilane added, the initial moles of lithium hydroxide, and initial moles of water, then multiplying the quotient by 100. The mole percents of alkylalkoxysilane and lithium hydroxide are similarly calculated and on the same basis.

[0018] The method may further comprise separating the alcohol from the lithium alkylsiliconate composition. The separation may be accomplished by, for example, distillation. For example, when the alcohol is methanol, the lithium alkylsiliconate composition may be heated to from 90 to 98 °C, alternatively 90 to 95 °C, to distill the methanol. Alternatively, the alcohol may be separated using vacuum distillation.

[0019] The mole ratio of lithium to silicon of the lithium alkylsiliconate composition prepared according to the present method varies according to the solids content. When the mol ratio of lithium to silicon is from 0.9 to less than 1.1, alternatively from 0.95 to 1.08, the solids content is from 15 to 25% (w/w); alternatively from 18 to 22% (w/w); or when the mol ratio of lithium to silicon is from 1.1 to 1.4, alternatively 1.2 to 1.4, the solids content is from 3 to less than 15 % (w/w), alternatively from 5 to 12 % (w/w). Solids content can be determined by placing a known amount of lithium alkylsiliconate composition into a suitable weighing dish and placing the weighing dish in an oven at a temperature from 40-60 °C, for example 48 °C, until a constant weight is achieved. The solids content can then be calculated by dividing the ending sample weight by the starting sample weight and multiplying by 100. The mole ratio of lithium to silicon of the lithium alkylsiliconate composition may be determined by common analytical techniques known in the art, such as by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Wavelength Dispersive X-ray Fluorescence (WDXRF).

[0020] The lithium alkylsiliconate composition produced by the method of the invention provides coatings with an 8-hour water absorption of less than 1.2 milliliters, alternatively 1.0 milliliter or less, alternatively from 0.1 to 1 milliliters. As used herein, the "8-hour water absorption" is the milliliters of water absorbed over 8 hours by a 3 x 5 x 3/8 inch (nominal) slab comprised of a medium aggregate concrete mix according to the test method described and exemplified below in the Examples section. Water absorption is the measure of the water repellency of a coating formed by a particular lithium alkylsiliconate composition. The less water absorbed in the test the greater the water repellency provided by a lithium alkylsiliconate composition.

[0021] The coating of the present invention can be prepared by applying the lithium alkylsiliconate composition to a substrate and drying the lithium alkylsiliconate composition to produce a coating. Typically, the lithium alkylsiliconate composition is prepared as described and exemplified above and then applied to at least a portion of the surface of a substrate. The lithium alkylsiliconate composition may be applied as prepared, diluted, or as part of a formulation with other common coating composition ingredients. The application to the substrate may be accomplished with a brush, roller, trowel, or spray equipment. The substrates typically comprise metal, ceramic, wood, stone, masonry, cementitious, and

bituminous materials. For example, the lithium alkylsiliconate composition can be sprayed onto a horizontal cement surface and allowed to dry to produce the coating. The drying may be accomplished by any suitable means of drying a coating composition to form a coating. For example, the drying may be accomplished by allowing the lithium alkylsiliconate composition to air dry or by use of a mechanical device such as fan or blower. The lithium alkylsiliconate typically will polymerize and crosslink on drying to form the water repellent coating.

[0022] The coating composition of the invention comprises the lithium alkylsiliconate composition produced by the method described and exemplified above. The coating composition may also comprise other ingredients used in coating compositions. For example, the coating composition may also comprise alkali metal silicates, dyes, pigments, and colors. The coating composition may be prepared by methods know in the art. For example, the coating composition may be formed by diluting the lithium alkylsiliconate composition with water and adding any other common ingredients with mixing.

[0023] The lithium alkylsiliconate composition of the invention may be used to protect a substrate. The lithium alkylsiliconate composition used to protect a substrate is produced as described and exemplified above. The substrate is as described above; alternatively, the substrate has a horizontal surface, and the lithium alkylsiliconate composition is used to protect the horizontal surface, provided the substrate is not constructed from concrete, stone, or masonry or is not exposed flooring; alternatively the substrate has a vertical surface and the lithium alkylsiliconate composition is used to protect the vertical surface. The lithium alkylsiliconate composition may be used to protect a substrate by applying the lithium alkylsiliconate composition to the surface of the substrate to be protected and drying the lithium siliconate composition. For example, the lithium alkylsiliconate composition may be applied to the vertical surface of a substrate by, for example, spraying the lithium alkylsiliconate composition onto the surface. The lithium alkylsiliconate composition typically then dries to form a water repellent coating. As used herein, "protect" is intended to mean to prevent or slow the degradation of the substrate by weather, chemicals, or other corrosive elements. As used herein, "exposed flooring" is intended to mean flooring used inside of structures and exposed to the interior of the home, as opposed to flooring not exposed to the inside of the home such as underlayment.

[0024] Coatings produced from the lithium alkylsiliconate composition or the coating composition of the invention provide improved water repellency to, for example, silica-containing materials, such as cement, masonry, stone, and concrete, as evidenced by the results of the 8-hour water absorption testing described below. The increased water repellency results in improved protection of the silica-containing materials from degradation caused by weather, chemicals and other corrosive elements.

[0025] The method of invention can be used to produce various lithium alkylsiliconate compositions and coating compositions; the lithium alkylsiliconate and coating compositions have utility in producing water repellent coatings of silica-containing materials.

EXAMPLES

[0026] The following examples are presented to better illustrate the method of the present invention, but are not to be considered as limiting the invention, which is delineated in the appended claims. Unless otherwise noted, all parts and percentages reported in the examples are by weight. The following table describes the abbreviations used in the examples:

Table 1. List of abbreviations used in the examples.

Abbreviation	**Word**
g	gram
Me	methyl
wt	weight
%	percent
mol	mole
hr	hour
NA	Not Applicable
mL	milliliters
cm	centimeter

The following methods and materials were employed in examples 1-9:

Water Absorption

[0027] Water absorption was measured using a test apparatus referred to as a water absorption tube, or RILEM (Reunion Internationale des Laboratoires D'Essais et de Recherches sur les Materiaux et les Constructions) tube, and the procedure used was based on RILEM method 11.4. The tube configuration was for measurement on horizontal surfaces. The tubes were graduated, with an overall dimension of 15 cm in height and an inner diameter of 0.5 cm. The water column in the RILEM tube itself being approximately 13 cm. The RILEM tubes were adhered to the substrate with plumber's putty.

[0028] The substrate used for the water absorption testing was a slab measuring 3 x 5 x 3/8 inch (nominal) comprised of a medium aggregate concrete mix. The mix ratio was 4.5 parts aggregate, 3 parts silica sand and 2 parts Portland Cement. The slabs were prepared by Masonry Test Block Inc. of Saginaw Michigan. The slabs were conditioned to constant weight in a laboratory environment and had no loose or residual material on the surface.

[0029] Before testing, the slabs were treated with a particular test formulation. For comparison purposes, all lithium alkylsiliconate compositions were diluted to 3% (w/w) active ingredient (i.e., 3% lithium alkylsiliconate), with the balance being water, and were applied to the substrate at four grams per slab. The slabs were then allowed to dry and cure for at least 24 hours before performing the testing.

[0030] Eight (8)-hour water absorption for a particular test was determined by recording the water height difference in the RILEM tube after 8 hours.

Solids Content

[0031] The solids content was determined by drying a 2 g sample in a 48 °C vented oven until a constant weight was achieved. The solids content is the dry sample weight, divided by the initial sample weight, multiplied by 100.

Examples 1-9

Lithium Alkylsiliconate Synthesis Procedure

[0032] In a 3-neck, 2-liter flask equipped with a Barrett type moisture test receiver connected to a condenser, a heating mantle, a thermal couple, an addition funnel and a

magnetic stirrer, LiOH·H2O (lithium hydroxide monohydrate) was dissolved in water to form a first mixture of lithium hydroxide and water. The first mixture of lithium hydroxide and water was heated to and maintained at 70 °C while $MeSi(OMe)_3$ was added into the flask through the additional funnel over about 1 hour to form a second mixture. As soon as the addition of $MeSi(OMe)_3$ was complete, the temperature of the second mixture was increased to 90-95 °C and methanol was removed (stripped) over 15 to 60 minutes. Finally, residual methanol was removed under vacuum in a rotary evaporator, such as a Brinkman/Büchi Rotary Evaporator, for 15 minutes.

[0033] The difference between the preparations of individual samples of examples 1-9 was in the amount of lithium hydroxide, water and methyltrimethoxysilane combined. This difference provided variation of the mol ratio of lithium hydroxide to alkylalkoxysilane, the initial mole percent of water, and in the solids content of the lithium methyl siliconate composition. Also, the water absorption reported for example 1 is the average of nineteen trials; examples 2 and 3 are the average of seven trials; example 4 is the average of four trials; comparative example 5 is the average of eight trials; comparative examples 6 and 7 are the average of two trials; comparative example 8 is the average of twenty trials; and example 9 is the average of nine trials. The moles of lithium hydroxide, alkylalkoxysilane, and water, along with other test parameters, for each example are listed in Table 2 below.

Table 2. Mole percents, Li:Si, solids content, and water absorption.

Example	Mol % LiOH	Mol % MTM	Mol % water	Li:Si	Solids Content (%)	Water Absorption (mL)	Standard Deviation
1	3.48	3.62	92.90	0.96	18.5	0.65	0.44
2	4.52	4.18	91.30	1.08	21.0	0.98	0.48
3	2.13	1.78	96.09	1.2	9.5	0.9	0.5
4	3.33	2.58	94.09	1.29	13.5	1.0	0.92
5 (Comparative)	1.77	1.85	97.38	0.95	9	1.24	0.91
6 (Comparative)	2.38	2.76	94.86	0.86	14.3	1.40	0.07
7 (Comparative)	1.35	1.25	97.39	1.08	6.8	1.95	0.35
8 (Comparative)	2.88	2.67	94.46	1.08	12.3	1.45	0.51
9	4.19	3.49	92.32	1.2	17.8	1.16	0.57

(Comparative)							

[0034] Thus, the examples with coatings formed from compositions made according to the invention provided superior water absorption compared to the comparative examples, where coatings were formed from compositions not made according to the invention.

That which is claimed is:

1. A method of making a lithium alkylsiliconate composition, the method comprising:

adding an alkylalkoxysilane to a first mixture comprising lithium hydroxide and water to form a second mixture comprising a lithium alkylsiliconate and an alcohol, wherein i) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 0.9 to less than 1.1 and the water is from 89 to 93 mol %, or ii) the mole ratio of lithium hydroxide to alkylalkoxysilane is from 1.1 to 1.4 and the water is from greater than 93 to 99 mole %.

2. The method of claim 1, wherein the method further comprises separating the alcohol from the second mixture.

3. The method of claim 1 or 2, wherein the alkylalkoxysilane has the formula

$$R_aSi(OR)_{4-a} \quad (I),$$

wherein each R is independently C_1-C_{10} alkyl or cycloalkyl; and the subscript a is 1, 2 or 3.

4. The method of any one of claims 1-3, wherein the alkylalkoxysilane is $CH_3Si(OCH_3)_3$.

5. The method of any one of claims 1-4, wherein the mixture comprising lithium hydroxide and water is at a temperature from 25 to 80 °C.

6. The lithium alkylsiliconate composition produced by the method of any one of claims 1-5.

7. A method of making a coating, the method comprising: applying the lithium alkylsiliconate composition of claim 6 to a substrate and drying the lithium alkylsiliconate composition to produce a coating.

8. The coating formed according to the method of claim 7.

9. The coating of claim 7, wherein the coating has an 8-hour water absorption of less than 1.2 milliliters.

10. A method of protecting a substrate, the method comprising: applying the lithium alkylsiliconate composition of claim 6 to a substrate and drying the lithium alkylsiliconate composition.

11. The method of claim 10, wherein the substrate has a horizontal surface, and wherein the lithium alkylsiliconate composition is used to protect the horizontal surface, provided the substrate is not constructed from concrete, stone, or masonry or is not exposed flooring.

12. The method of claim 10, wherein the substrate has a vertical surface, and wherein the lithium alkylsiliconate composition is used to protect the vertical surface.

13. The use of the lithium alkylsiliconate composition produced by the method of claim 1 to protect a substrate.

14. The use according to claim 14, wherein the substrate has a horizontal surface, and wherein the lithium alkylsiliconate composition is used to protect the horizontal surface, provided the substrate is not constructed from concrete, stone, or masonry or is not exposed flooring.

15. The use according to claim 14, wherein the substrate has a vertical surface, and wherein the lithium alkylsiliconate composition is used to protect the vertical surface.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/016628

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B41/49 C09D183/08 C07F7/18 C07F7/08 C08G77/398
ADD.

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 C09D C07F C08G

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2011 083109 A1 (WACKER CHEMIE AG [DE]) 21 March 2013 (2013-03-21)	6
Y	paragraphs [0002], [0028], [0029]; example 2	7-15

X	US 8 961 672 B2 (STEPP MICHAEL [AT] ET AL) 24 February 2015 (2015-02-24)	6
Y	column 8, line 10 - line 50; examples 1,2,4	7-15

Y	US 3 574 651 A (NITZSCHE SIEGFRIED ET AL) 13 April 1971 (1971-04-13) example 7	7-15

A	US 3 208 972 A (LYONS JAMES D) 28 September 1965 (1965-09-28) column 1, lines 16-39; claim 1; examples 4,13	1-15

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

[X] See patent family 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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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 May 2017	15/05/2017

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/016628

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 2 438 055 A (FRANKLIN HYDE JAMES ET AL) 16 March 1948 (1948-03-16)	6
Y	claims 1,2	7-15

X	DE 11 76 137 B (GOLDSCHMIDT AG TH) 20 August 1964 (1964-08-20)	6
Y	claims 1,3; example 1	7-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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