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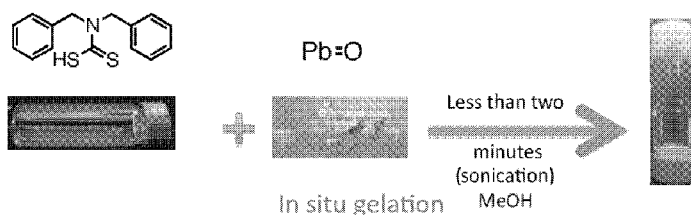
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Published:

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(54) **Title:** METHOD AND KIT FOR DETECTING LEAD IN A SOLID SAMPLE

FIG. 1



(57) **Abstract:** A method and kit for detecting the presence of lead in a solid sample is disclosed. The solid sample is brought into contact with a nonaqueous solution of a dithiocarbamate capable of forming a gel upon contact with lead, with the formation of a gel showing that lead is present in the solid sample.

METHOD AND KIT FOR DETECTING LEAD IN A SOLID SAMPLE**STATEMENT OF GOVERNMENTAL INTEREST**

[0001] This invention was made with government support under N00014-12-1-0604 awarded by the Navy/ONR. The Government has certain rights in the invention.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application claims the benefit of U.S. provisional patent application No. 61/987,786, filed May 2, 2014, incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0003] The present invention relates to the detection of lead in a solid sample, for example, a paint chip. More particularly, the present invention relates to a method and kit for the detection of lead in a solid sample wherein gelation of a reagent solution demonstrates the presence of lead in the solid sample.

BACKGROUND OF THE INVENTION

[0004] Lead has been used for centuries in coatings, for example, as a pigment in paints, a corrosion inhibitor, and a drier in paints and varnishes. The primary reasons for using lead in coatings are properties such as durability of a finished coating, the broad spectrum of available colors using lead compounds, and corrosion, water, and weather resistance.

[0005] When lead-containing coatings age, the coatings deteriorate and consequently create lead-containing or lead-contaminated dust. Similarly, when lead-containing coatings are disturbed by cutting, drilling, sanding, or other methods commonly employed to remove building materials, lead-containing dust is released from the disturbed coating, and the dust can readily disseminate and contaminate large areas. This is a well-known public health hazard because lead-contaminated dust has been identified as a significant health hazard, particularly to children. Lead-based paints therefore were banned in 1978, but it is estimated that greater than 20 million homes may still contain lead-based coatings.

[0006] Lead contamination is not limited to paint and related products because lead has been used for decades in a wide variety of applications, such as building construction materials (roofing material, cladding, flashing, gutters and gutter joints, and on roof parapets), ammunitions, lead-acid car batteries, weights, fusible alloys, radiation shields (lead glass), and cosmetics. The use of lead in paint (wall paint, oil and water-based paint in art,

paint used in toys), fuel, pipe, and plumbing material, solder for cars and pesticides has been greatly reduced over the last several decades because of the danger of lead poisoning.

[0007] Lead poisoning is a medical condition caused by increased levels of lead in the body. Exposure and accumulation to lead and lead-containing chemicals can occur through inhalation, ingestion, and/or dermal contact. Lead affects several organs in the body, and especially the nervous system. Lead also adversely effects bones (weakness in fingers, wrists, or ankles), teeth, kidneys (nephropathy and colic-like abdominal pain), the cardiovascular (blood pressure), immune, and reproductive (reduced fertility in males) systems, and can cause miscarriage in pregnant females. The adverse effects of lead on the nervous system is more pronounced in children than in adults.

[0008] Lead poisoning can be prevented by detecting lead or lead-containing compounds, and reducing or avoiding exposure to lead. To address the issue of the health risks from lead-containing dust, the United States Environmental Protection Agency (USEPA) promulgated regulations governing the appropriate methods and procedures to be used during remodeling and renovation of residential housing. These regulations stipulate that, for all housing built before 1978, the surfaces to be disturbed during renovation or remodeling must be checked for the presence of lead in the surface coatings. There are several ways lead testing can be accomplished, including Atomic Absorption spectroscopy, X-Ray Fluorescence, and chemical tests.

[0009] Atomic Absorption Spectroscopy and X-Ray Fluorescence involve sophisticated instrumentation and are expensive procedures. Several commercially-available, do-it-yourself lead test kits are available, but these kits are not quantitative and often lack credibility because they lead to false positive results. The chemical tests also often lack selectivity because test samples often contain additional compounds that can interfere with the assay for lead. Such additional compounds can include chromium, mercury, cadmium, zinc, barium, nickel, cobalt, copper, antimony, bismuth, titanium, and other metals present in pigments.

[0010] In addition, in order to achieve the different benefits of lead in various types of coatings, different forms of lead and lead-containing compounds have been incorporated into the coatings. Lead compounds that have been used in coatings include, but are not limited to lead sulfate, lead chromate, lead monoxide (litharge), lead silicate, lead sulfate blue basic, lead linoleate, lead naphthenate, and lead carbonate. While each type of lead compound has

certain properties that differentiate the compound from the other lead compounds, the commonality of lead in each compound renders each compound a health risk. It is important that a detection method has the capability of detecting each type of lead compound that may be present in the solid sample. For example, some chemical assays fail to detect lead chromate.

[0011] In addition, although chemical tests to detect lead are commercially available, the tests may not properly detect lead levels at thresholds promulgated by regulatory authorities, e.g., lead equal to or exceeding 1.0 milligram per square centimeter (mg/cm^2) or 0.5 percent by weight (equivalent to 5,000 parts per million or ppm). In such cases, either false positive or false negative results may arise, which in the case of a false negative can lead to health issues and in the case of a false positive to unneeded and expensive remediation measures.

[0012] A need therefore still exists in the art for a fast and accurate method and test kit to detect levels of lead in a solid sample, while avoiding false positive and false negative assay results. A method and test kit that can be used by a homeowner or in the field, without the need to submit samples for testing or to require substantial user training, also is an unmet need in the art.

BRIEF DESCRIPTION OF THE FIGURES

[0013] Fig. 1 illustrates the reaction which forms a gel between lead and a dithiocarbamate.

[0014] Fig. 2 illustrates the selectivity of gel formation upon contact with a lead-containing sample vs. other metal-containing sample.

[0015] Fig. 3 illustrates various nonlimiting nonaqueous solvents used in the method of the present invention.

SUMMARY OF THE INVENTION

[0016] The present invention is directed to a testing kit and method of assaying a solid sample for the presence of lead. The method accurately determines the presence of lead in the solid sample without interference from other metals that may be present. In one embodiment, the kit includes (a) a dithiocarbamate compound that is capable of complexing with lead to form a gel and (b) a nonaqueous solvent. In other embodiments, the kit further contains a resealable container in which to conduct the assay.

[0017] Another aspect of the invention is to provide a method of determining the presence or absence of lead in a solid by adding a small sample of the solid to a nonaqueous solution of a dithiocarbamate capable of complexing with lead, then visually observing the resulting mixture for the formation of a gel. The dithiocarbamate is capable of complexing with additional metals, but the resulting complexes do not form a gel.

[0018] These and other aspects of the invention will become apparent from the following nonlimiting detailed description the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

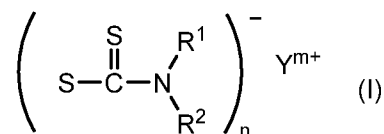
[0019] Six criteria for a lead detection method have been identified. The method should be (a) capable of detecting lead concentrations of 1 mg/cm², (b) non-hazardous, (c) suitable for use as a nondestructive or minimally destructive field method, (d) suitable for use by non-technical personnel, (e) sufficiently reliable, precise, and accurate, and (f) rapid. The present invention is provides an inexpensive, more reliable lead detector that meets each of these six criteria.

[0020] The present invention provides a portable test kit to detect lead in solid samples, such as paints. The test kit contains a dithiocarbamate that gels upon binding to lead, either immediately or within a short reaction time period.

[0021] The method provides an unambiguous visual change in the physical properties/appearance of the dithiocarbamate solution upon binding to lead. The present method enables the detection of lead by naked eye with no additional instrumentation or training. The method has low critical gel concentration facilitating detection of lower analyte concentrations, i.e., as low as about 200 ppm of lead.

[0022] The present test kit can comprise a container in which the assay for lead is performed. In some embodiments, the container is optional. In this case, the individual performing the lead assay can provide a suitable container to perform the present method. The container is manufactured from a transparent material, which allows an easy visual inspection for the formation of a gel. The container therefore can be prepared from glass or a transparent plastic, such as a polycarbonate, acrylate, or urethane, for example. The shape of the container is not limited, but often is in the shape of a cylinder. The container typically has a volume of about 3 to about 25 ml, and typically, about 4 to about 10 ml, which facilitates use of the test kit in the field.

[0023] An important feature of the present method and kit is to utilize a dithiocarbamate capable of complexing with lead to form an insoluble gel in a nonaqueous solvent. Useful dithiocarbamates have a structural formula (I):



wherein n is an integer 1 or 2; m is an integer 1 or 2; R¹ and R², individually, are selected from the group consisting of C₁-C₁₀ linear alkyl, C₃-C₁₀ branched alkyl, C₂₋₆ linear alkenyl, C₂₋₆ branched alkenyl, C₃-C₁₀ cycloalkyl, substituted and unsubstituted aryl, and substituted and unsubstituted (CH₂)₁₋₃aryl, or R¹ and R² are taken together with the nitrogen atom to which they are attached to form a five or six membered ring, optionally fused to an aryl ring; and Y is an element selected from Groups IA and IIA of the periodic table.

[0024] In preferred embodiments, R¹ and R², the same or different, are substituted or unsubstituted aryl, substituted or unsubstituted (CH₂)₁₋₃aryl, e.g., sodium dibenzylidithiocarbamate, or C₂₋₆linear alkenyl, e.g., sodium diallyldithiocarbamate..

[0025] Compounds of formula (I) include, but are not limited to, sodium dimethyldithiocarbamate (CAS# 128-04-1), sodium diethyldithiocarbamate (CAS# 148-18-5), sodium dibenzylidithiocarbamate (CAS# 55310-46-8), sodium diallyldithiocarbamate,

sodium allylbenzylidithiocarbamate, $\left(\begin{array}{c} \text{S} \\ \parallel \\ \text{S}-\text{C}-\text{N} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \end{array} \end{array} \right)^{-} \text{Na}^{+}$, and mixtures thereof.

[0026] The dithiocarbamate is used in a sufficient amount to complex with lead in the solid sample, for example, up to the solubility limit in the nonaqueous solvent used in the assay method. Typically, the dithiocarbamate is present in a nonaqueous solvent in an amount of about 0.05 to about 5%, preferably about 0.1 to about 3%, and more preferably about 0.25 to about 1%, by weight, of the nonaqueous solution.

[0027] In addition to the dithiocarbamate, the assay method utilizes a nonaqueous solvent. The identity of the nonaqueous solvent is limited solely by an ability to solubilize the dithiocarbamate in a sufficient amount to complex with lead in a solid sample. The time required to form a lead-containing gel after contact between a solid sample and the dithiocarbamate can vary depending upon the nonaqueous solvent used in the assay.

Selection of an optimum solvent, and selection of the concentration of dithiocarbamate, therefore can be readily determined by persons skilled in the art after considering the time requirements desired to obtain assay results. In preferred embodiments, the amount of water present in the nonaqueous solvent is less than 50% by volume, preferably less than 10%, by volume.

[0028] Examples of useful classes of nonaqueous solvents include, but are not limited to, alcohols, esters, glycols, glycol ethers, aliphatic and aromatic hydrocarbons, chlorinated solvents, and mixtures thereof. Specific nonlimiting examples of solvents include, but are not limited to, C₁₋₆alcohols, e.g., methanol, ethanol, propyl alcohol, and butyl alcohol, including isomers thereof; monoC₁₋₄alkyl ethers of ethylene glycol and propylene glycol; acetone; methyl ethyl ketone; isophorone; dichloromethane; chloroform; ethyl acetate; 2-methoxyethanol; DMF; DMSO; THF; acetonitrile; kerosene; mineral spirits; xylene; toluene; and mixtures thereof. Also useful are standard solvents used in the paint industry, e.g., paint thinner and turpentine.

[0029] In accordance with the present invention, a solid sample is assayed for the presence of lead by providing a reagent solution comprising a dithiocarbamate dissolved in a nonaqueous solvent. The reagent solution is placed in a transparent container and a sample of the solid is added to the solution. Alternatively, the reagent solution can be added to a transparent container containing the solid sample.

[0030] The resulting mixture optionally is shaken, then is allowed to stand uninterrupted. The container then is visually examined for the formation of a gel, as illustrated in Fig. 1. Gel formation occurs within 10 minutes, typically within 5 minutes, and usually within 2 minutes. The detection of lead in a solid sample therefore is rapid and can be performed at home or in the field.

[0031] The complexing reaction between lead and the dithiocarbamate to form a gel occurs at ambient temperature, e.g., about 20 to 30°C. To facilitate and speed gel formation, the reaction mixture can be heated above ambient temperature, for example, up to about 50°C, which temperature is limited by the identity and boiling point of the nonaqueous solvent used in the assay.

[0032] Various embodiments are envisioned for practice of the invention at home or in the field. In one embodiment, a kit comprising a ready-to-use reagent solution of a dithiocarbamate in a non-aqueous solvent in a transparent container is provided. The user

then merely adds a solid test sample to the container, and the container is visually observed for a response.

[0033] In other embodiments, the kit comprises the dithiocarbamate either neat or as a concentrated solution in a nonaqueous solvent. In use, the concentrated dithiocarbamate either is added to a container contained in a kit or is added to a container provided by the user, then the user adds a sufficient amount of nonaqueous solvent to the concentrated solution to provide a reagent solution for the lead assay.

[0034] In various embodiments, the kit contains an instruction sheet for proper use of the kit, e.g., amount of solid sample to add to the reagent solution or amount and identity of solvent to add to the neat or concentrated solution of dithiocarbamate.

Example 1 *In Situ* Gel Formation

[0035] An 8 mL vial was charged with sodium N,N-dibenzylthiocarbamate dissolved in methanol (0.8 mL), and the resulting mixture was heated to form a solution. A suspension of PbO in water (0.2 mL) then was added to the resulting solution. The vial was sealed, the resulting mixture was heated until homogeneous, then cooled to ambient temperature after about 20 seconds of sonication in a water bath at ambient temperature to form a gel.

[0036] In the above examples, sonication was used to speed formation of the lead-containing gel. In practical use at home or in the field, sonication is not required because the gel forms spontaneously over a slightly longer time period.

[0037] In addition to the PbO used in the examples, a lead-containing gel also forms when the solubilized dithiocarbamate forms complexes with other lead salts (e.g., PbCrO₄, PbCO₃, Pb(NO₃)₂, and Pb(OAc)₂). The solubilized dithiocarbamate also forms complexes with other metals, but the resulting complex does not form a gel. The present method therefore is specific for lead.

Example 2

[0038] To illustrate the selectivity of the present method and kit, a series of experiments was performed. In particular, an 8 mL vial was charged with sodium N,N-dibenzylthiocarbamate (3.3 mg, 0.012 mmol) and acetone (0.5 mL), which then was shaken to dissolve the dithiocarbamate. Then, a metal acetate salt (0.006 mmol) suspended in acetone (0.5 mL) was added to the dithiocarbamate solution. The vial was capped and heated to dissolve the metal acetate salt, and the mixture then was cooled to room temperature. Figure

2 shows that the dithiocarbamate forms a complex with a metal other than lead, but does not form a gel. The kit therefore is selective for the detection of lead.

Example 3

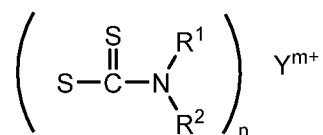
[0039] To illustrate that a variety of nonaqueous solvents can be used in the present method and kit, experiments were performed using a water-immiscible solvent and a water-miscible solvent were conducted. These solvents are known to dissolve latex- and oil-based paints. For example, an 8 mL vial was charged with sodium N,N-dibenzylthiocarbamate (4.8 mg, 0.016 mmol), oil-based exterior paint (0.05 mL), and commercial paint thinner (0.5 mL). The resulting mixture was shaken to form a solution. Then, $\text{Pb}(\text{OAc})_2$ (5.0 mg, 0.015 mmol) suspended in paint thinner (0.5 mL) was added to the solution in the vial. The vial was capped, heated to dissolve the lead salt, then cooled to room temperature to form a gel. In another example, an 8 mL vial was charged with sodium N,N-dibenzylthiocarbamate (4.4 mg, 0.015 mmol), latex-based paint (0.05 mL), and acetone (0.5 mL). The resulting mixture was shaken to form a solution. Then, $\text{Pb}(\text{OAc})_2$ (5.6 mg, 0.017 mmol) suspended in acetone (0.5 mL) was added to the solution in the vial. The vial was capped and heated to dissolve the lead salt, then cooled to room temperature. Upon cooling, a gel was formed. The results are illustrated in Fig. 3. The center vial of Fig. 3 shows that the present method is operative when both a latex- and oil-based paint are present in the same sample.

[0040] The present invention provides a simple to use method and a kit to assay solid samples for the presence of lead. The method and kit can be used at home or on site in the field to detect lead in paint during remodeling or renovation of older houses or buildings by general contractors and homeowners; lead in children's toys and play areas; lead in drinking water; lead in pipes, solders, and plumbing; and lead in cosmetics.

[0041] The present method and test kit provide advantages over existing assays including a simple and easy to use technology, an unambiguous detection of lead through a visible gel formation, no equipment or training to interpret test results, and an increased selectivity compared to existing lead assays.

CLAIMS

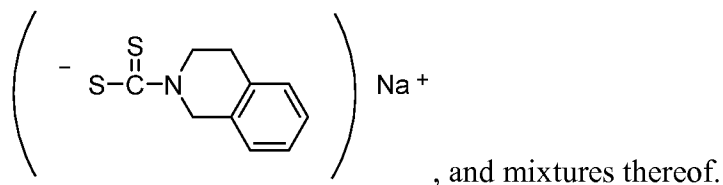
1. A kit for determining a presence or absence of lead in a solid sample comprising:
 - (a) a solution comprising:
 - (i) a dithiocarbamate capable of forming a gel upon contact with lead, and
 - (ii) a nonaqueous solvent;
 - (b) an optional transparent container for the solution; and
 - (c) an optional insert comprising instructions for use of the kit.
2. The kit of claim 1 comprising a transparent container.
3. The kit of claim 1 or 2 wherein the container has a sealable-resealable cap.
4. A kit for determining the presence or absence of lead in a solid sample comprising:
 - (a) a dithiocarbamate capable of forming a gel upon contact with lead; and
 - (b) an insert comprising instructions for use of the dithiocarbamate to determine the presence of absence of lead in the sample.
5. The kit of claim 4 wherein the dithiocarbamate is provided as a solid.
6. The kit of claim 4 wherein the dithiocarbamate is provided as a nonaqueous solution.
7. The kit of any preceding claim wherein the dithiocarbamate has a structure



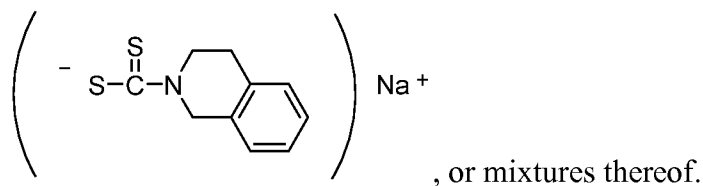
wherein n is an integer 1 or 2; m is an integer 1 or 2; R¹ and R², individually, are selected from the group consisting of C₁-C₁₀ linear alkyl, C₃-C₁₀ branched alkyl, C₂₋₆ linear alkenyl, C₂₋₆ branched alkenyl, C₃-C₁₀ cycloalkyl, substituted and unsubstituted aryl, and substituted and unsubstituted (CH₂)₁₋₃aryl, or R¹ and R² are taken together with the nitrogen atom to which they are attached to form a five or six membered ring, optionally fused to an aryl ring; and Y is an element selected from Groups IA and IIA of the periodic table.

8. The kit of claim 7 wherein R^1 and R^2 , the same or different, are substituted or unsubstituted aryl, substituted or unsubstituted $(CH_2)_{1-3}$ aryl, or C_{2-6} linear alkenyl.

9. The kit of any preceding claim wherein the dithiocarbamate comprises sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, sodium dibenzoyldithiocarbamate, sodium diallyldithiocarbamate, sodium allylbenzoyldithiocarbamate,



10. The kit of any preceding claim wherein the dithiocarbamate comprises a dibenzoyldithiocarbamate, diallyldithiocarbamate, allylbenzoyldithiocarbamate,



11. The kit of any preceding claim wherein the nonaqueous solvent comprises an alcohol, an ester, a glycol, a glycol ether, an aliphatic hydrocarbon, an aromatic hydrocarbon, a chlorinated solvent, and mixtures thereof.

12. The kit of any preceding claim wherein the nonaqueous solvent comprises a C_{1-6} alcohols, a mono C_{1-4} alkyl ether of ethylene glycol or propylene glycol, acetone, methyl ethyl ketone, isophorone, dichloromethane, chloroform, ethyl acetate, 2-methoxyethanol, DMF, DMSO, THF, acetonitrile, kerosene, mineral spirits, xylene, toluene, turpentine, paint thinner, and mixtures thereof.

13. The kit of any preceding claim wherein the nonaqueous solvent further comprises up to 50%, by volume, water.

14. A method of determining a presence or absence of lead in a solid sample comprising:

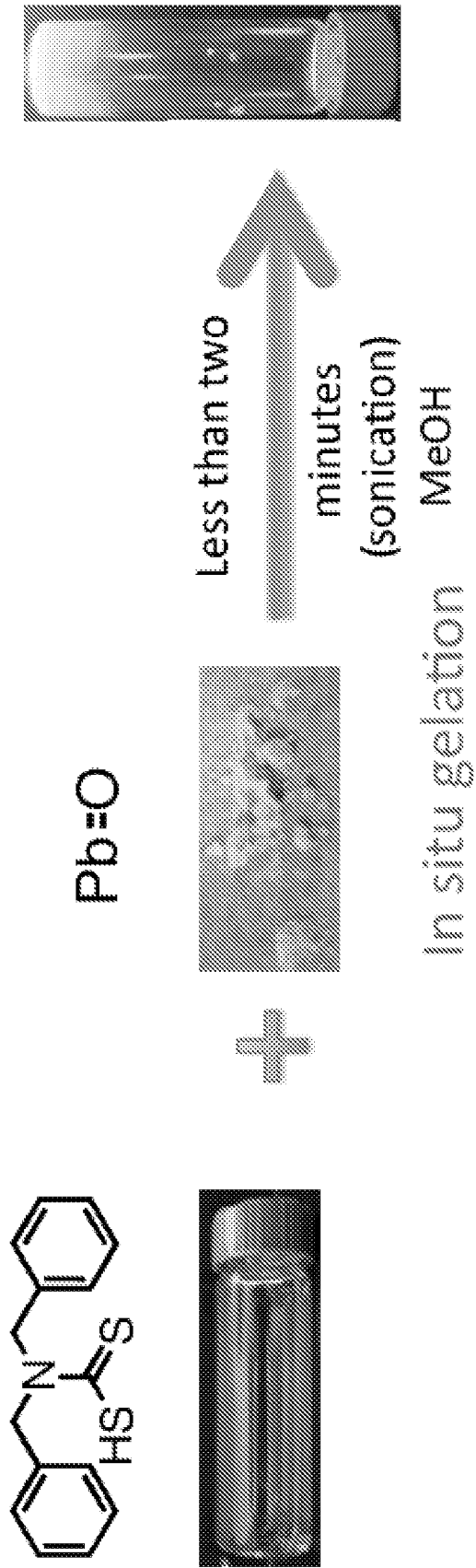
(a) providing a nonaqueous solution of a dithiocarbamate capable of forming a gel upon contact with lead;

(b) providing a test amount of a solid sample of interest;

(c) contacting the nonaqueous solution of (a) with the solid sample test amount of (b) and observing the resulting mixture for the formation of a gel.

15. The method of claim 14 performed at a temperature of 20°C to 50°C.
16. The method of claim 14 performed at a temperature of greater than 20°C to 30°C.
17. The method of claim 14 wherein the nonaqueous solvent further comprises up to 50%, by volume, water.
18. The method of claim 14 wherein the solid sample contains 200 ppm or more of lead.

FIG. 1



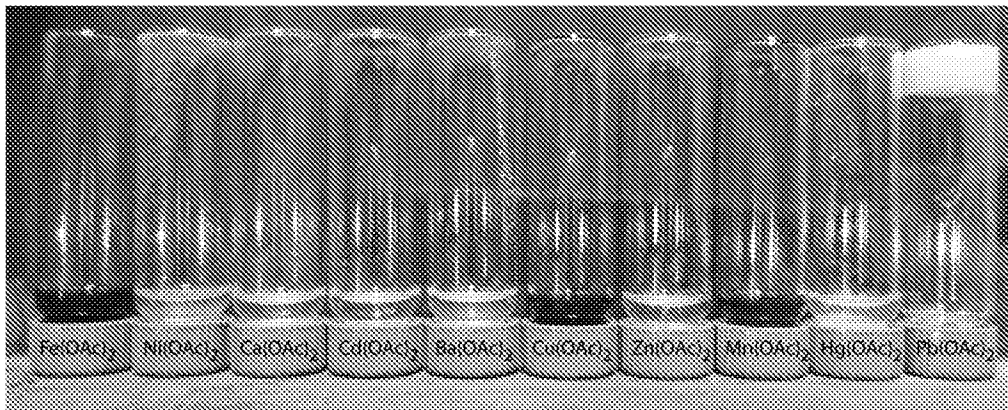


Fig. 2

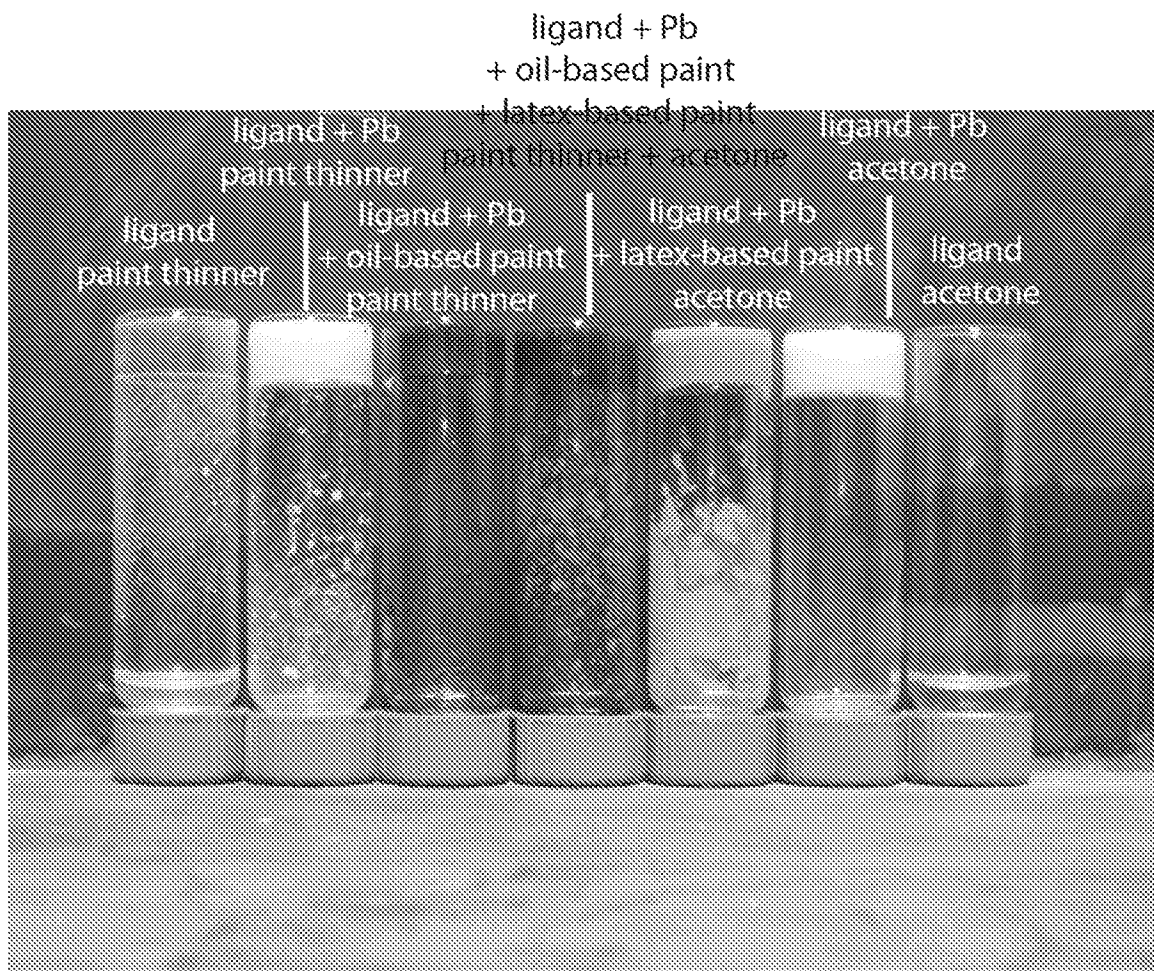


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/028766**A. CLASSIFICATION OF SUBJECT MATTER****G01N 31/22(2006.01)i, G01N 33/20(2006.01)i**

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)

G01N 31/22; C08F 38/02; C07F 1/12; G01N 21/76; G01N 33/20; C07D 401/12

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: gelation, gelator, dithiocarbamate, gel, lead, Pb, solid sample, paint, kit, determining, contact, analysis, dibenzylidithiocarbamate, transparent container, cap

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4786604 A (MICHAEL, ROBERT C.) 22 November 1988 See abstract; column 2, line 54 - column 4, line 54; claims 1-3 and 6-8; and Figure 1.	1-6, 14-18
A	KR 10-2012-0097794 A (EWhA UNIVERSITY-INDUSTRY ACADEMIC COLLABORATION FOUNDATION) 05 September 2012 See abstract; paragraphs [0118]-[0136]; claims 1, 4 and 11-15; and Figures 5 and 6.	1-6, 14-18
A	KR 10-2012-0053404 A (CHUNG ANG UNIVERSITY-INDUSTRY ACADEMIC COLLABORATION FOUNDATION) 25 May 2012 See abstract; paragraphs [0015] and [0063]-[0068]; claims 1, 16 and 17; and Figure 1.	1-6, 14-18
A	WO 2007-055846 A1 (ILLINOIS TOOL WORKS INC. et al.) 18 May 2007 See abstract; paragraphs [0014]-[0023]; and claims 1, 7 and 10.	1-6, 14-18
A	KR 10-2012-0119934 A (GYEONGSANG UNIVERSITY-INDUSTRY ACADEMIC COLLABORATION FOUNDATION) 01 November 2012 See abstract; paragraphs [0133]-[0140]; claims 1, 11 and 13; and Figure 7.	1-6, 14-18



Further documents are listed in the continuation of Box C.



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 July 2015 (22.07.2015)

Date of mailing of the international search report

24 July 2015 (24.07.2015)

Name and mailing address of the ISA/KR

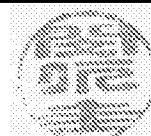
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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2015/028766**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 8
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 8 refers to an unsearchable claim which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 7,9-13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/028766

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4786604 A	22/11/1988	None	
KR 10-2012-0097794 A	05/09/2012	KR 10-1252506 B1	09/04/2013
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WO 2007-055846 A1	18/05/2007	CA 2628157 A1	18/05/2007
		CN 101317088 A	03/12/2008
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KR 10-2012-0119934 A	01/11/2012	None	