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[54] METHOD FOR STABILIZING CHROMOGENIC TEST REAGENT FOR ALDEHYDE

[72] Inventors: **Rudolph L. Iannacone**, Cranbury; **Anthony J. Revukas**, Cranford, both of N.J.

[73] Assignee: **Cities Service Oil Company**

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[58] **Field of Search** ..... 23/253 TP; 252/408

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Primary Examiner—Morris O. Wolk
Assistant Examiner—R. E. Serwin
Attorney—J. Richard Geaman

[57] **ABSTRACT**

A chromogenic reagent normally unstable upon exposure to air is stabilized for use in an aldehyde detection test. The chromogenic reagent, preferably 3-methyl - 2-benzothiazolinone hydrazone hydrochloride monohydrate (MBTH), is prepared by adsorption on a suitable supporting media and drying in an inert atmosphere.

12 Claims, No Drawings

METHOD FOR STABILIZING CHROMOGENIC TEST REAGENT FOR ALDEHYDE

BACKGROUND OF THE INVENTION

The present invention relates to the stabilization of a chromogenic reagent for use in the indication of ethylene glycol antifreeze contamination in crankcase oil. More particularly, the invention discloses a method for the preparation of a stabilized reagent such as 3-methyl - 2-benzothiazolinone hydrazone hydrochloride monohydrate (MBTH).

The presence of contaminants in engine oil may have damaging effects upon the performance of the engine and its internal parts. The cleanliness of the internal parts of an engine depends upon the equilibrium between the oil polluting substances and the remaining effective oil lubricating molecules. Various methods are available for testing engine oils as to their effective lubrication and cleansing properties upon engine parts. Both laboratory and field tests have shown that ethylene glycol is one of the more particularly hazardous contaminants which may enter engine oil. The ethylene glycol is derived from the antifreeze added to the engine's cooling system. Through abusive wear of the engine and failure of sealing members within the engine's parts, glycol may enter the crankcase and lubricating system of the engine and cause pasty emulsions which may plug oil filters, pump screens, oil feed lines and passages within the engine. The presence of ethylene glycol also presents a problem in the engine combustion chamber where temperatures are high enough to convert the glycol into a varnishlike substance which causes valves to stay open, valve lifters to bend in their guards, and piston rings to stick in their grooves. Consequences of the above-mentioned malfunctions of the engine may result in extreme engine abuse, engine lifetime diminishment and eventual engine failure. The elimination of ethylene glycol in the crankcase oil is a matter of extreme importance in maintenance of the engine in that no engine oil additives appear available on the market to combat the incompatibility properties of glycol.

The most common method used to combat ethylene glycol contamination in engine oil and subsequent seizure of engine parts is to change the engine oil periodically so that the concentration of ethylene glycol never exceeds a maximum tolerable concentration which would damage the engine's moving members. What is required is an ethylene glycol testing method which will indicate the first detectable concentration of ethylene glycol after certain periodic intervals of engine hour usage, such that the engine may be serviced and the oil changed. This ethylene glycol test method must include a procedure by which servicing personnel may periodically check engine oil for glycol concentration without a rigorous analytical technique being required. The test must, therefore, be simple enough for layman's usage and also provide positive indentification of the ethylene glycol content. To date, no suitable ethylene glycol test method is available for service station or industrial usage. It has been suggest that the presence of glycol in engine oil may be detected by treating a sample of oil with an oxidizer to oxidize any glycol present to aldehyde and then utilizing a chromogenic reagent to detect the presence of the aldehyde. An inherent problem with this test method is the rapid deterioration of available chromogenic reagent on exposure to air.

It is an object of the present invention to provide a method for preparing a chromogenic aldehyde reagent for the detection of oxidized glycols which will be stable on exposure to air.

It is still another object of the present invention to provide a method for preparing a stabilized chromogenic reagent with which the ethylene glycol content of the crankcase oil may be determined.

With these and other objects in mind, the present invention is hereinafter presented with particular reference to the following description.

SUMMARY OF THE INVENTION

The objects of the present invention are accomplished by a method for the preparation of a chromogenic reagent for aldehydes which is normally unstable upon exposure to air. The invention comprises the dissolving of the chromogenic reagent in a solvent and subsequently pouring the solvent containing the dissolved chromogenic reagent onto a support medium, while constantly in the presence of an inert atmosphere. The support medium may be dried simultaneously with the adsorption of the chromogenic reagent. Some chromogenic reagents which may be utilized are salicylalhydrazone, p-nitrobenzalhydrazone, 2-hydrazinobenzothiazole, 2-hydrazinobezothiazole - 4-nitrobenzenediazonium fluoborate, etc., while 3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate (MBTH) is preferred. One of the solvents used to dissolve the chromogenic reagent to further its introduction onto the support medium is deionized and/or distilled water, while any solution which will dissolve the test reagent may be utilized. The support medium may consist of any suitable material such as anhydrous aluminum, silica gel, diatomaceous earth, firebrick or polymeric material. Suitable polymeric material includes polyethylene, nylon, etc. and is preferably present in particulate form such as chips or powder. The inert atmosphere may be provided such as by introducing a continuous flow of dry nitrogen gas through the support medium during the adsorption period. The drying process is generally conducted at a temperature less than about 100° C. during the entire preparation of the chromogenic reagent material.

By this procedure, the reagent is rendered in a stable form which will remain stable on exposure to air and give lasting tests for the aldehyde; for example, the aldehydes formed from the oxidation of glycols in the engine oil. Therefore, a method is developed by which oxygen sensitive chromogenic reagents may be placed on a support medium and rendered stable for long periods.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a method for preparing a chromogenic reagent for the detection of aldehydes such as those formed from the oxidation of ethylene glycol contaminants in engine oils. Many chromogenic reagents for the detection of aldehydes exist, but the reagent used must be highly specific for formaldehyde or other aldehydes. In the testing of engine oils the test reagent must not be influenced by other substances which may be oxidized or may be contained as additives or original components of the engine oil. In the particular application of the aldehyde test reagent for testing engine oils, the reagent will be subjected to an acidic media, therefore, the reagent must be able to respond to the presence of formaldehyde in an acidic media. This criteria eliminates a number of excellent reagents as they will not perform under acidic conditions. Many reagents such as 2-hydrazinobenzothiazol and 2-hydrazinobenzothiazol - 4-nitrobenzene diazonium fluorborate are excellent reagents to be utilized for the detection of aliphatic, aromatic, and heterocyclic aldehydes; however, the reagents fail in the criteria that they require an alkaline media. These reagents may be prepared by the particular method of the present invention for testing for aldehydes that are not present in an acidic media. Although they are specific to formaldehyde indication and prepared so as to be stable on exposure to air, they will not chromogenically perform under the conditions stated.

Another criteria for preferred reagents is the stabilization of the coloring test after introduction of the formaldehyde into the chromogenic reagent. The color should remain stable for several minutes so that the operator may observe the reagent color against predetermined charts or a blank for a quantitative determination of the amount of ethylene glycol present in the original sample. A study has been made by Sawicki, et al., *Analytical Chemistry*, Vol. 33, No. 1, Jan., 1961, p. 93, and has indicated that 3-methyl - 2-benzothiazoline hydrazone

hydrochloride monohydrate (MBTH) is an excellent reagent for the determination of aldehydes and this is a preferred reagent in practicing the present invention. We have found in particular that the application of the above-mentioned reagent adsorbed on particulate polyethylene, silica gel and other chromatographic supports has proven to be a stable reagent which may be kept for a long period of time and ultimately used in the field. Silica gels of wide mesh sizes may be used. In particular, the mesh size range of 28 to 200 mesh has proven favorable. Particulate polyethylene, chipped or powdered form provides an excellent support. Other chromatographic supports which may be used in the present invention may be selected from the group consisting of silica gel, anhydrous alumina, diatomaceous earth, polymeric materials and firebrick. Although it is preferred to use silica gel, or particulate polyethylene, the other chromatographic supports have proven satisfactory. As with the oxidizing agents, the chromatographic supports used to adsorb the formaldehyde reagent thereon should be translucent or opaque such that any color imparted from the support will not interfere with the chromogenic test. Therefore, it is a necessary criteria of the chromogenic support that it not have an interfering background color which would interfere with the color test. Therefore, many of the chromatographic supports available are not suitable for usage with the present invention.

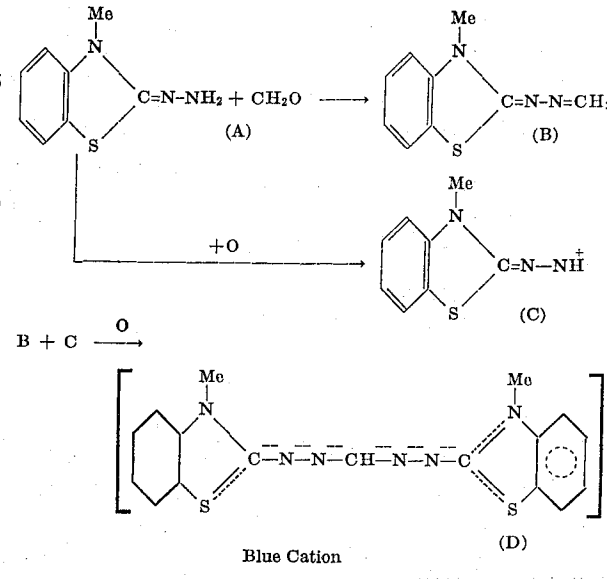
In the preparation of a chromogenic reagent, which would generally be unstable on exposure to air and unsuitable for the determination of aldehydes contained in samples, the chromogenic reagent generally is dissolved in a solvent. In most applications, the solvent used for the solution makeup would be deionized and/or distilled water. After the solution is formed, it is introduced onto a suitable support medium which will adsorb the chromogenic reagent. An inert atmosphere is maintained about the support medium during the adsorption process so that no oxidation of the chromogenic reagent will occur during its preparation. The adsorbing step may be enhanced by drying the chromogenic reagent on the support medium to strip off the solvent. This drying process may take from 5 minutes to an hour, depending on the amount of solution introduced onto the adsorbing medium. As mentioned, a preferred reagent to be used is 3-methyl - 2-benzothiazolinone hydrazone hydrochloride monohydrate. The MBTH solution in deionized water would generally be a 0.5 to 5 percent solution.

The inert atmosphere is maintained by introducing an inert gas such as nitrogen into a column of support medium with the MBTH adsorbed thereon and the solvent thereabout. The column may consist of a graduated cylinder or buret. A nitrogen containing cylinder may be connected to the column and nitrogen transferred therethrough so that an inert atmosphere is continuously in contact with the MBTH and support medium. The drying procedure utilizes temperatures up to about 100° C. so that no destructive degradation of the MBTH takes place during the adhesion process and is preferably carried out in an inert atmosphere. While satisfactory stability is achieved by adsorbing and preferably drying the chromogenic reagent in an inert atmosphere, the effective shelf life of the reagent may be even further extended by sealing the adsorbed, dried reagent in a container until it is used. If desired, this step may, however, be omitted and the adsorbed reagent may be exposed to air without excessive loss of stability. The MBTH in effect forms a complex with the support material so that after it is adsorbed on the active surfaces of the silica gel or other support medium used, it will remain stable and will not be subject to attack by oxygen in the atmosphere about it. It has been found that 0.01 to 10 grams of chromogenic reagent adsorbed for each 10 grams of support material, such as silica gel or particulate polyethylene, preferably 0.1 to 1 gram per gram, provides sufficient indicator to give the results desired.

To detect the aldehyde produced from the oxidation of glycols, a sample of the aldehyde-containing aqueous phase is introduced onto the support material containing chromogenic reagent. Generally, about 0.5 to about 1.0 milliliter of the aqueous phase containing the aldehyde is used per milliliter of chromogenic reagent. The container is then closed, vigorously shaken, generally for about 5 to 10 seconds, and then allowed to set until the color change is indicated. The test reagent will turn blue if ethylene glycol is present in the oil.

In practicing the invention using sodium periodate oxidizer and MBTH reagent, the reactions occurring may be summarized as follows:

Sodium periodate or some other suitable oxidizer is used to oxidize the ethylene glycol to formaldehyde. The aldehyde then contained in the aqueous phase is withdrawn and placed on the MBTH chromogenic reagent. The aldehyde reacts with the MBTH to form the azine. In addition, some MBTH is oxidized to a reactive cation which combines with the azine to form a blue dye. Therefore, a normally translucent chromogenic reagent contained on a support will turn a dark blue if aldehyde is present. A blank solution may be run by taking an uncontaminated sample of the oil, oxidizing it, and then introducing the aqueous phase, which is separated, onto the chromogenic reagent. The reagent turns green when silica gel is utilized and red when polyethylene is the support to give a blank test to indicate that no ethylene glycol is present. Deepening shades of blue indicate increased concentration of ethylene glycol. A color chart may be presented to quantitatively show the relative amount of ethylene glycol in parts per million which was contained in the engine oil. With this method, the operator knows at any time in the ethylene glycol contamination process what the ethylene glycol concentration is and when the oil must be changed. Each time the oil is checked the reading is recorded until a maximum tolerable concentration of ethylene glycol in the engine oil is experienced. The oil is then changed and the process repeated. The procedure is shown below diagrammatically for the reaction of formaldehyde with 3-methyl - 2-benzothiazolone hydrazone (A), to form the azine (B); oxidation of (A) to a reactive cation, (C); and the formation of the blue cation, (D).



The effectiveness of the stabilized aldehyde reagent may be observed by the following examples:

Five experiments were run with SAE 30 motor oil. Measured quantities of ethylene glycol were added to each of the five motor oil samples so that a precise indication of the effectiveness of the chromogenic-ethylene glycol detection method could be determined. Five to 10 milliliters of oil sample was placed in a one-ounce vial containing 10 milliliters of an aqueous 0.1 molar solution of sodium periodate. The vial was

EXAMPLE 1

sealed with a cap and shaken vigorously for 2 minutes to insure oxidation of the ethylene glycol contained in the oil to formaldehyde. The cap was then removed and the vial set on a flat surface in an upright position so as to allow the oil and aqueous liquid phases to separate. A second 1-ounce vial contained granular material which consisted of about 0.0005 to 0.05 gram of the chromogenic formaldehyde reagent MBTH adsorbed on 2 grams of 28 to 200 mesh silica gel. This material was prepared by dissolving 0.5 gram of MBTH in 100 milliliters of deionized water and immediately pouring the resulting solution into a glass column equipped with a stop cock and containing 100 grams of 28–200 mesh silica gel. The top of the column was connected to a nitrogen gas supply to provide an inert atmosphere during the coating of the silica gel with the reagent and to provide for a flow of nitrogen to aid in drying the coated silica gel. Drying of the coated silica gel was facilitated by exposing the column to a heating lamp. The dry silica gel coated with reagent was then stored in a stoppered vial. An eye dropper was inserted into the lower aqueous phase of the 1-ounce vial containing the aqueous and oil phases and a sample of the aqueous phase was removed by squeezing the rubber bulb upon insertion so that the clear liquid was raised into the dropper until 5 milliliters of liquid had been withdrawn. The eye dropper was wiped and the liquid added to the granular material in the other 1-ounce vial. The vial was stoppered and shaken vigorously for approximately 5 seconds. The vial was then placed on a flat surface. Color indication for each test was noted as shown in the following table. The color became apparent to be either a green, dark blue, or an intermediate color within a 15 minute period. No glycol was indicated by a negative response with a green color formed and glycol presence was indicated by different shades of blue color formation. As can be seen, the sensitivity to the silica gel based MBTH test for ethylene glycol was effective and stable to concentrations of 30 parts per million of ethylene glycol in the motor oil, therefore, giving a positive test for ethylene glycol content in motor oil.

TABLE

Sensitivity of Silica Gel Based MBTH Test for Glycol

Motor Oil SAE 30	Blue Color Formation
1000 p.p.m. glycol	Positive
100	Positive
60	Positive
30	Positive
0	Negative

EXAMPLE 2

To evaluate the present invention as contrasted with conventional chromogenic reagents utilized for the detection of ethylene glycol in oil, samples bearing various concentrations of ethylene glycol were made up with four different materials (water, SAE 20 oil, SAE 30 oil and SAE 50 oil). The samples were oxidized with sodium periodate solution as in Example 1. The chromogenic reagent utilized was p-rosaniline adsorbed on silica gel in an oxygen containing atmosphere. The following table discloses a very erratic determination, the results of which indicate an unstable chromogenic reagent was found.

TABLE

Evaluation of p-rosaniline test reagent

Glycol in p.p.m. added	P.p.m. found			
	Water	SAE 20 oil	SAE 20 oil	SAE 30 oil
1,000	←Less than 250→			
100	←60→			
60	←Faint to negative→			
30	←Negative→			

At a concentration of a thousand parts per million the p-rosaniline indicated the presence of aldehyde, although less than the apparent amount in the samples tested. Below 60 parts per million a negative test resulted which depicts the unstable nature of this chromogenic reagent. As the allowable ethylene glycol concentration in an engine oil would be generally be below about 50 parts per million, the determination with an unstable aldehyde reagent would not indicate the level of concentration of ethylene glycol which must be known.

EXAMPLE 3

To demonstrate the necessity for adsorbing chromogenic reagent on the supporting media in an inert atmosphere, a half gram of MBTH was dissolved in 100 milliliters of deionized water and poured over 100 grams of 28–200 silica gel contained in a beaker exposed to the air. The mixture was stirred to achieve a uniform distribution of the MBTH reagent on the silica gel and the placed in a drying oven at 100° C. to evaporate the water. The dry silica gel coated with MBTH was found to be tinted blue, thereby rendering it unfit for use as a test reagent.

The above method of preparation was then modified to shorten the period of exposure to the atmosphere. In this modified procedure, the mixture of water, MBTH and silica gel was poured into a buchner funnel inserted in a heavy walled, side arm filter flask. Immediately after mixing, a vacuum was applied to the flask to suck the treated silica gel free of moisture. Even though the silica gel was subsequently treated with nitrogen during drying, it was noted that the gel was tinted blue owing to oxidation of MBTH by the air passing through the gel during filtration.

It can be seen by the use of the present invention, for example, the detection of the ethylene glycol content in motor oils, that it will specifically determine the aldehyde concentration of a solution. The invention then enhances the capability of service attendants to detect the presence of ethylene glycol concentrations in engine oils and thereby remove the hazards of ethylene glycol varnish deposits causing valves to stay open, valve lifters to bend in their guards, and piston rings to stick in their grooves.

While the present invention has been described above with respect to certain embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention as set forth herein.

We claim:

1. A method for preparing a chromogenic reagent for aldehyde detection, consisting essentially of 3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate, which is stable on exposure to air which comprises the steps of:

a. dissolving a normally unstable chromogenic reagent in a solvent; and

b. contacting the solvent containing the dissolved chromogenic reagent with an adsorbent support media maintained in an inert atmosphere.

2. The method of claim 1 further comprising simultaneously drying the chromogenic reagent adsorbed on the support media in the inert atmosphere.

3. The method of claim 2 in which the adsorbed reagent is subsequently exposed to air.

4. The method of claim 3 in which the solvent is deionized or distilled water.

5. The method of claim 4 in which 0.1 to 1.0 gram of 3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate is adsorbed for each 100 grams of support media.

6. The method of claim 5 in which the support media is silica gel.

7. The method of claim 6 in which the inert atmosphere is provided by introducing a continuous flow of dry nitrogen gas through the silica gel.

8. The method of claim 6 in which the silica gel is of a 28 to 200 mesh size.

9. The method of claim 2 in which the chromogenic reagent and support media are dried at a temperature less than about 100° C.

10. The method of claim 9 further comprising sealing the dried chromogenic reagent adsorbed on the support media in a container.

11. The method of claim 2 in which the support media is particulate polyethylene.

12. The method of claim 11 in which the polyethylene is in chipped form.

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