⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 211 689**
B1

⑫ EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of the patent specification: **27.06.90**

(51) Int. Cl.⁵: **C10M 177/00**, G01N 33/28, F01M 11/10

㉑ Application number: **86306424.2**

㉒ Date of filing: **19.08.86**

---

(54) **Determination of metal source in used oil.**

㉚ Priority: **21.08.85 US 767744**

㊸ Date of publication of application:
25.02.87 Bulletin 87/9

㊺ Publication of the grant of the patent:
27.06.90 Bulletin 90/26

(84) Designated Contracting States:
DE FR GB IT

(56) References cited:
EP-A- 0 024 146
US-A- 2 744 069

JOURNAL OF THE AMERICAN SOCIETY OF LUBRICATION ENGINEERS, vol. 34, no. 11, November 1978, , pages 625-628; J.E. STEENBERGEN: "Comprehensive lube oil analysis programs: A cost-effective preventive maintenance tool"

(73) Proprietor: **EXXON CHEMICAL PATENTS INC., 200 Park Avenue, Florham Park New Jersey 07932(US)**

(72) Inventor: **Munsell, Monroe Wallwork, 180 Sutton Drive, Berkeley Heights New Jersey 07922(US)**
Inventor: **Finn, Richard Francil, 64 Juniper Way, Basking Ridge New Jersey 07920(US)**

(74) Representative: **Northover, Robert Frank et al, ESSO Chemical Limited Esso Chemical Research Centre P.O. Box 1, Abingdon Oxfordshire, OX13 6BB(GB)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

ACTORUM AG

Description

The present invention relates to oil compositions, particularly motor oils, containing a tracer metal component to determine the source of another metal component, such as metal wear, corrosion, contamination, and/or an additive component of the motor oil.

BACKGROUND OF THE INVENTION

Current motor oil additives are either non-metal containing, or if they do contain metal, then the metals are generally calcium, magnesium, zinc, or sodium.

Recently, it has been found that copper additives are particularly useful in motor oil as antioxidants. Such use has been described in Canadian Patent 1,170,247 and European Patent 24146. There is generally little or no problem in formulating passenger car crankcase oils with copper additives. However, a problem has arisen in applying these copper additives to motor oils for diesel engines which are extensively used in trucks. It has become a common practice for many truck fleet operators to have samples of the engine oil periodically analyzed for metals in order to diagnose contamination, corrosion and particularly excessive wear and impending failure of engine parts. Such metal analysis will typically include: copper, which can indicate excessive wear of copper-lead bearings; iron, which can indicate excessive wear or rust of the engine; chromium, which can indicate excessive wear of chrome faced piston rings, etc. Adding a copper additive to the motor oil interferes with the copper analysis as there was no way to tell from the used oil analysis whether a high level of copper found by the analysis is due to excessive wear of copper-containing engine parts, and/or whether the copper is a component of the motor oil being used. Even if the fleet operator knows that the crankcase was initially filled with oil of a known copper content, the operator still does not generally know from the analysis if wear is occurring, particularly if make-up oil was added. Thus, the make-up oil may be obtained from different suppliers, who may or may not have a copper additive in the oil. Furthermore, even if both the original oil and all make-up oil are from the same supplier, there may be an accumulation of metals, including copper, due to varying oil losses due to volatility of the base oil, which accumulation interferes with determining accurately the source of the copper.

The problem is to find a reliable method of determining whether any copper in the oil is due to a copper additive used by the oil manufacturer, or is due to other sources such as wear of copper-containing parts, or whether the copper is from both an oil additive and wear. It also becomes important to determine the relative amount of copper individually due to an oil additive and to wear to indicate whether the wear is excessive.

Summary of the Invention

It has been found that the above problems in determining the source of a first metal in engine oil after use can be solved in an economical fashion by the addition of a second and different tracer metal to the engine oils. While the first or primary metal may be present in said oil both as an additive in fresh oil and as a result of engine wear, the tracer metal is introduced in said oil solely as an additive.

From the amount of the tracer metal in the used oil and the known predetermined ratio of primary metal and tracer metal in the fresh oil, the amount of the primary metal in the used oil due to wear can be determined.

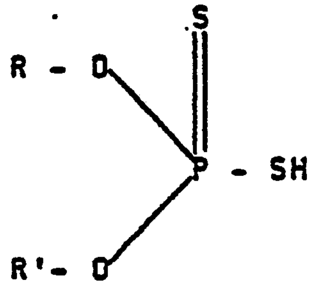
Thus, in the case of copper, by adding a small amount of a tracer metal, other than copper and other than a metal which is associated with engine wear or corrosion, the source of copper may be determined. The technique may also be used, for example, for iron, lead and chromium.

The tracer metal should be oil soluble, or at least oil dispersible, and preferably should be easily and accurately measured in the used oil, as well as economical. While various metals such as potassium, lithium and tungsten could be used, barium has been found to be particularly desirable. Barium oil additives are well known and have been extensively used in the past in relatively large amounts in oil, but are now substantially obsolete and seldom used. By using both copper and barium additives together in a fixed predetermined ratio of copper to barium, e.g., a 1.6:1 ratio such as 80 ppm (parts per million) Cu to 50 ppm Ba, the source and amount of copper in used oil can now be accurately determined. For example, if the used oil showed no barium, then any copper is due to wear. If analysis showed 150 ppm copper and 60 parts of barium then the amounts of copper due to engine wear is $150 - 1.6 \times 60 = 54$, indicating both a metal build up as well as copper wear.

The copper may be blended into the oil as any oil soluble copper compound, i.e., soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form.

The copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples include C_{10} to C_{18} fatty acids such as stearic or palmitic, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting copper carboxylates.

The copper may be in the form of copper dihydrocarbyl thio- or dithio-phosphates wherein one mole of cuprous or cupric oxide may be reacted with one or two moles of the dithiophosphoric acid respectively. Copper dihydrocarbyl dithiophosphates may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P_2S_5 andthen neutralising the dithiophosphoric acid with a suitable copper compound. The dithiophosphoric acids may be represented by the formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater.

Other useful compounds are oil soluble copper dithiocarbamates of the general formula $(RR'NCSS)_nCu$ where n is 1 or 2 and R and R' are the same or different as described above for the copper dihydrocarbyl dithiophosphate. Copper sulphonates, phenates, and acetyl acetonates, etc. may also be used.

The barium may be present in the form of oil soluble lubricating oil additives such as neutral or basic metal salts of sulphonic acids, alkyl phenols, sulphurised alkyl phenols, alkyl salicylates, naphthenates, and oil soluble mono- and di-carboxylic acids, etc.

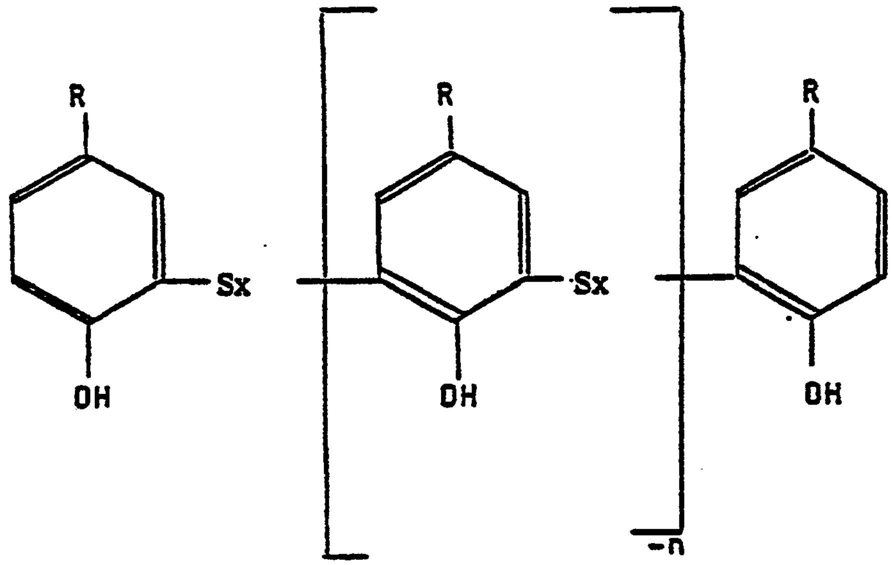
The neutral or basic barium sulfonates are usually produced by heating a mixture comprising an oil-soluble alkaryl sulfonic acid with a barium base such as the oxide or hydroxide sufficient for neutralization of the sulfonic acid. Excess barium base is used to prepare an overbased additive which contains a dispersed carbonate complex formed by reacting the excess metal base with carbon dioxide to provide the desired overbasing. The sulfonic aicds are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as for example, those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene with polyolefins as for example, polymer from ethylene, propylene, isobutylene, etc. The resulting alkaryl sulfonates usually contain from about 9 to about 70 or more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moiety.

Barium salicylate and naphthenate materials are known additives for lubricating oil compositions to improve their high temperature performance and to counteract deposition of carbonaceous matter on pistons (U.S. Patent 2,744,069). Salicylate/naphthenate rust inhibitors are preferably the barium salts of aromatic acids having the general formula:

$$HOOC\text{-}ArR_1\text{-}X_y(ArR_1OH)_n$$

where AR is an aryl radical of 1 to 6 rings, R_1 is an alkyl group having from about 8 to 50 carbon atoms, preferably 12 to 30 carbon atoms (optimally about 12), X is a sulfur (-S-) or methylene ($-CH_2-$) bridge, y is a number from 0 to 4 and n is a number from 0 to 4.

Barium salts of sulfurized metal alkyl phenates may also be used. These salts, whether neutral or basic, are generally of compounds typified by the general formula:



where x = 1 or 2, n = 0, 1 or 2 or a polymeric form of such a compound, where R is an alkyl radical, n and x are each integers from 1 to 4, and the average number of carbon atoms in all of the R groups is at least about 9 in order to ensure adequate solubility in oil. The individual R groups may each contain from 5 to 40, preferably 8 to 20, carbon atoms. The metal salt is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal containing material to impart the desired alkalinity to the sulfurized metal phenate.

In general, the amount of added copper compound used in the oil formulations, such as crankcase motor oil, will be such to give copper concentrations of about 5 to about 500 ppm to weight of copper in the lubricant composition and preferably about 10 to 300, e.g. 60 to about 200 ppm. The amount of barium compound used is such as to give 5 to 500, e.g., 10 to 300, preferably 25 to 150, most preferably 40 to 100 ppm of barium. The copper and barium can be used in any relative ratio, such as 0.1 to 10, preferably about 1 to 5, most preferably 2 to 1 parts by weight of copper per part by weight of barium. Concentrates comprising about 5 to 90, e.g., 10 to 60 wt.%, copper and barium compounds in lubricating oil may be first formed in whatever ratio is desired and these may be included as components in various additive packages which will be used to blend finished lubricating oils. In this way, an accurate and constant copper/barium ratio can be maintained in the final oil formulations being produced.

The lubricants to which the products of this invention can be added include not only hydrocarbon oils derived from petroleum, but also include synthetic oils such as alkyl esters of dicarboxylic acids, polygylcols and alcohols; polyalphaolefins, alkyl benzene, organic esters of phosphoric acids, polysilicone oil, etc.

In the above compositions or concentrates, other conventional additives may also be present, including dyes, pour point depressants, antiwear agents such as tricresyl phosphate or zinc dialkyl dithiophosphates of 3 to 8 carbon atoms in each alkyl group, other antioxidants such as N-phenyl a-naphthylamine, t-octylphenol sulfide, 4,4'-methylene bis (2,6-ditertbutyl phenol), viscosity index improvers such as ethylene-propylene copolymers, polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers, and the like, as well as ashless dispersants such as polyisobutylene succinic anhydride reacted with amines, hydroxy amines, polyols, etc., calcium and magnesium metal detergents such as carbon dioxide overbased alkylaryl sufonates, etc.

Techniques for measuring metals in used oil include flame atomic-absorption spectroscopy, electrothermal atomic-absorption spectroscopy, optical emission spectroscopy, inductively coupled plasma emission spectroscopy, scanning electron microscopy-X-ray analysis and X-ray florescence spectroscopy (see P.K. Hon, O.W. Lau and C.S. Mok, "Direct Determination of Metals in Lubricating Oils and Aqueous Inorganic Standards", Analyst 1980, 105, pp. 919-921, and the references cited therein. Other related articles on analysis of used oils for metals are Lubrication, vol. 70(2), pp. 13–24 (1984); Lubrication Engineering, vol. 34, 11, pp. 625–628, November 1978; Analyst, February 1983, vol. 108, pp. 254–260; Canadian Spectroscopy, January 1970, pp. 17–24; SAE Paper 770 642, Used Engine Oil Analyses – Review by P.A. Asseff, Fuels and Lubricants Meeting, June 7–9, 1977; and a paper by E.D. Archer, entitled "Lubricants, Oils and Greases" in Analytical Chemistry, vol. 57, No. 5, April 1985.

The invention will be further indicated by reference to the following example.

Example

A concentrate was prepared consisting of 76.6 wt.% mineral lubricating oil, 3.4 wt.% of the neutral barium salt of alkaryl sulfonic acid, said sulfonic acid having an average molecular weight of about 1000 land being prepared by alkylation of benzene sulfonic acid with tetrapropylene and 20.0 wt.% of cupric oleate. The weight ratio of copper to barium in said concentrate was 1.6 to 1.0.

A finished 15W40 crankcase motor oil composition was prepared containing a major amount of mineral lubricating oil, zinc dialkyl dithiophosphate, ashless dispersant of the succinimide type, magnesium and calcium sulfonates and sufficient of the above-noted concentrate to give about 80 ppm and 50 ppm barium in said finished oil composition.

An analysis was made of said oil from a field test delivery truck having an oil capacity of about 8 quarts operating on the above motor oil after about 7500 miles of operation.

The analysis of the used oil together with the fresh oil is summarized in the following table:

TABLE 1

Analysis of 15W40 Oil

	Fresh oil	Used Oil
Cu, ppm	80	105
Ba, ppm	50	62
Pb, ppm	Nil	21
Cr, ppm	Nil	3
Zn, wt.%	0.111	0.116
Ca, wt.%	0.098	0.105
Mg, wt.%	0.133	0.14

The analysis was carried out by atomic adsorption.

Table 1 shows that the initial copper to barium ratio was 1.6 to 1.0. Thus, the copper due to wear in the used oil can be calculated as follows:

$$105 - 1.6 \times 62 = 6$$

While the above has illustrated the invention applied to copper and barium, the invention can be applied to other primary metals other than copper such as chromium, iron, lead, using either barium as the secondary or tracer metal, or other tracer metals such as potassium, tungsten or lithium can be used.

Claims

1. A method of determining the source of a first metal in engine oil after use, wherein the first metal may be present both as a component of an additive in fresh oil and as a result of engine wear, which method comprises the addition to said oil of a second and different metal whose sole source in used oil is as a component of an additive in fresh oil, and determining, from the amount of the second metal in used oil and the known predetermined ratio of the first metal and the second metal in fresh oil, the amount of the first metal in the used oil due to wear.
2. A method according to claim 1, wherein the first metal is copper, iron, lead or chromium.
3. A method according to claim 2, wherein the first metal is copper.
4. A method according to any of claims 1 to 3, wherein the second metal is barium, potassium, lithium or tungsten.
5. A method according to claim 4, wherein the second metal is barium.
6. A method according to claims 3 and 5, wherein the first metal is added as copper oleate and the second metal is added as a neutral barium alkaryl sulfonate.
7. A method according to claim 6, wherein copper oleate is added to said oil in an amount equivalent to 5 to 500 ppm copper and barium sulfonate is added in an amount of 10 to 300 ppm barium.

Patentansprüche

1. Verfahren zur Bestimmung der Herkunft eines ersten Metalls in einem Motoröl nach dessen Verwendung, wobei das erste Metall sowohl als Komponente eines Additivs zum frischen Öl als auch als Ergebnis von Motorabrieb vorhanden sein kann, bei dem dem Öl ein anderes zweites Metall, dessen einzige Quelle in dem verwendeten Öl diejenige einer Komponente eines Additivs zum frischen Öl ist, zugesetzt und aus der Menge des zweiten Metalls in dem verwendeten Öl und dem bekannten vorbestimmten Verhältnis des ersten Metalls zu dem zweiten Metall im frischen Öl die Menge des ersten Metalls in dem verwendeten Öl aufgrund von Abrieb bestimmt wird.

2. Verfahren nach Anspruch 1, bei dem das erste Metall Kupfer, Eisen, Blei oder Chrom ist.

3. Verfahren nach Anspruch 2, bei dem das erste Metall Kupfer ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem das zweite Metall Barium, Kalium, Lithium oder Wolfram ist.

5. Verfahren nach Anspruch 4, bei dem das zweite Metall Barium ist.

6. Verfahren nach den Ansprüchen 3 und 5, bei dem das erste Metall als Kupferoleat und das zweite Metall als neutrales Barium-Alkarylsulfonat zugesetzt werden.

7. Verfahren nach Anspruch 6, bei dem Kupferoleat dem Öl in einer 5 bis 500 ppm Kupfer äquivalenten Menge und Bariumsulfonat in einer Menge von 10 bis 300 ppm Barium zugesetzt werden.

Revendications

1. Procédé de détermination de l'origine d'un premier métal dans une huile moteur après utilisation, dans lequel le premier métal peut être présent à la fois comme constituant d'un additif présent dans une huile neuve et en résultat de l'usure du moteur, procédé qui consiste à ajouter à ladite huile un second métal, différent, dont la seule origine dans l'huile usagée est son utilisation comme constituant d'un additif dans l'huile neuve, et à déterminer, à partir de la quantité du second métal dans l'huile usagée et du rapport prédéterminé connu du premier métal au second métal dans l'huile neuve, la quantité du premier métal dans l'huile usagée due à une usure.

2. Procédé suivant la revendication 1, dans lequel le premier métal est le cuivre, le fer, le plomb ou le chrome.

3. Procédé suivant la revendication 2, dans lequel le premier métal est le cuivre.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le second métal est le baryum, le potassium, le lithium ou le tungstène.

5. Procédé suivant la revendication 4, dans lequel le second métal est le baryum.

6. Procédé suivant les revendications 3 et 5, dans lequel le premier métal est ajouté sous forme d'oléate de cuivre et le second métal est ajouté sous forme d'un alkarylsulfonate de baryum neutre.

7. Procédé suivant la revendication 6, dans lequel l'oléate de cuivre est ajouté à l'huile en une quantité correspondant à une quantité de 5 à 500 ppm de cuivre et le sulfonate de baryum est ajouté en une quantité correspondant à une quantité de 10 à 300 ppm de baryum.