

## UNITED STATES PATENT OFFICE

2,450,633

## COMPOUNDED OIL

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6 Claims. (Cl. 252—33.2)

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This invention relates to lubricants and the like, more particularly, to crankcase lubricants such as those used in the ordinary motor car, in aircraft engines and in Diesel engines.

Crankcase lubricants are required to maintain lubrication of pistons under severe conditions. Temperatures are such and the oxidizing character of the combustion gases (which are hot and under pressure) is such that mineral lubricants decompose forming products which are corrosive and products which foul the piston, interfere with passage of lubricant through the openings in the oil ring and cause sticking of piston rings. In certain types of service, as in heavy Diesel engines, straight mineral lubricants, regardless of selection of crude oil and regardless of the refining procedure, will not stand up under the conditions imposed for a reasonably long period of operation. Added to the effects of lubricant deterioration are deposits formed by the fuel used to operate the engine.

It is now a common practice to add to mineral lubricants one or more agents adapted to stabilize the oil, reduce the amount of deposits on pistons, etc. Seldom is it sufficient, however, to add only one type of addition agent. Thus a strongly detergent addition agent (that is, an addition agent which promotes engine cleanliness) may not adequately stabilize the oil and may allow development of corrosive oxidation products in the oil. Many detergents are corrosive to cadmium-silver bearings and certain of them cause the oil to foam excessively under conditions of violent agitation with air and at low pressures.

It is an object achieved by the present invention to provide a combination of addition agents for lubricating oils and the like which is inexpensive and at the same time effects substantial improvement of the oil.

It is a particular object achieved by the present invention to provide a crankcase lubricant suitable for heavy duty use which combines high detergent qualities, low corrosiveness and reduced foaminess.

These and other objects will be apparent from the following description and the claims.

I have discovered that lubricating oils and the like can be greatly improved by adding thereto

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a salt of a sulfonic acid and a salt of a thiocarbamic acid.

The base oil to which the sulfonic and thiocarbamic salts are added will usually be a petroleum oil of lubricating viscosity. It may range in viscosity from spindle oils to cylinder stocks; it may be from a paraffinic, naphthenic or mixed base crude petroleum; it may be refined by any or several of various methods, may be a distillate or residual oil, etc.

However, the base oil may consist in whole or in part of other oils, such as certain vegetable oils (e. g., castor oil, sperm oil), polymerized olefins, oils synthesized from coal or oxides of carbon, amyl naphthalene, etc.

The sulfonic acid whose salt is added to the base oil (or formed in situ) may be a pure compound but will usually be a mixture, often a complex mixture of sulfonic acids. The so-called "mahogany" acids are preferred. These are high molecular weight, oil-soluble acids formed in the refining of mineral lubricating oils with strong or fuming sulfuric acid to produce medicinal or technical white oil. On heavy treatment of such mineral oil with sulfuric acid two phases are formed, one of which (the lower, heavy layer) is a sludge and the other (the upper layer) consists of the treated oil containing the mahogany acids. The sludge contains the so-called "green" acids, which are water-soluble as distinguished from oil-soluble acids. The mahogany acids may be recovered from the oily phase by various methods. Thus the oily layer may be extracted with aqueous methyl, ethyl or isopropyl alcohol to extract the mahogany acids. Or the oily layer may be neutralized with aqueous alkali and the alkali metal mahogany sulfonates extracted with aqueous methyl, ethyl or isopropyl alcohol or aqueous acetone.

Methods of recovering mahogany acids and their alkali metal salts are well known in the art and further elaboration is not required here except to note that, in connection with the present invention, since the salts of mahogany acids are added to oil, it is not necessary to rid the crude mahogany acids of the oil which they normally contain.

In general, the high molecular weight aliphatic type sulfonic acids are preferred; sulfonic acids of molecular weight above 500 are preferred al-

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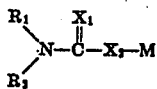
though sulfonic acids of molecular weight of 350 or lower can be used in certain types of service. By "aliphatic type" sulfonic acids is meant sulfonic acids in which at least about 50 per cent by weight of the sulfonic acid consists of aliphatic carbon and hydrogen; it does not mean that the sulfonic acid is necessarily a true aliphatic sulfonic acid wherein the sulfonic group or groups is or are attached only to aliphatic carbon. Thus, besides the mahogany sulfonic acids there may be used benzene, naphthalene and other sulfonic acids in which one or more oil solubilizing, preferably long chain alkyl substituents are attached to the aromatic nucleus. Examples of such aliphatic substituted aromatic sulfonic acids are the salts of cetyl benzene sulfonic acid, cetyl naphthalene sulfonic acid, the sulfonic acids described in Flett, United States Patent No. 2,283,199, and other sulfonic acids prepared from aromatic hydrocarbons containing aliphatic radicals derivable from petroleum.

Although nitrogen base and alkali metal sulfonates may be used, polyvalent metal sulfonates are preferred and of the polyvalent metal sulfonates those of the more basic metals, such as magnesium, calcium, strontium and barium are preferred.

Examples of sulfonates that may be used in accordance with the invention are lithium, potassium, sodium, calcium, barium, aluminum, zinc, tin and lead mahogany sulfonates, cetyl benzene sulfonates and cetyl naphthalene sulfonates; the corresponding salts of the sulfonic acids described in Flett, United States Patent No. 2,283,199; the corresponding salts of sulfonic acids prepared from aromatic hydrocarbons containing aliphatic radicals derivable from petroleum; and true aliphatic sulfonates, such as lithium, potassium, sodium, calcium, barium, aluminum, zinc, tin and lead sulfonates derivable from the product of condensing chlorinated petroleum wax with sodium acid sulfite.

A solution of calcium mahogany sulfonate in lubricating oil can be prepared as follows: Take an acid treated oil, preferably at a late stage in the acid treatment and extract the sulfonic acids from the oil by means of ethyl alcohol. Add a petroleum thinner and water to the alcoholic extract and allow the aqueous phase and the petroleum thinner phase to separate; the latter phase will contain the sulfonic acids. Add to the petroleum thinner solution of sulfonic acids, calcium hydroxide in quantity sufficient to neutralize the sulfonic acids and lubricating oil in quantity sufficient to prepare a concentrate of the resultant calcium sulfonate. Filter the mixture and remove the light solvent by distillation, leaving a residue of lubricating oil in which the calcium sulfonate is dissolved.

The thiocarbamates, which form the second component of the compounding of the invention, may be represented generically by the formula

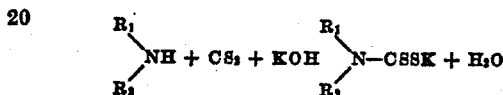


wherein  $R_1$  and  $R_2$  are hydrogen or organic radicals, at least one  $R$  being an organic radical,  $X_1$  and  $X_2$  are oxygen or sulfur, at least one  $X$  being sulfur, and  $M$  is a basic nitrogenous radical or a metal. Where  $M$  is a polyvalent metal, it will be understood that other valences of the metal than that shown will be satisfied by the same or different acid radicals or by an hydroxyl radical.

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The preferred thiocarbamates are the polyvalent metal dithiocarbamates in which  $R_1$  and  $R_2$  are both hydrocarbon or substituted hydrocarbon groups which are sufficiently large (e. g., 4 to 20 carbon atoms each) to impart oil solubility to the dithiocarbamate, or in which  $R_1$  and  $R_2$  are a single bivalent hydrocarbon group as in the "petroleum base" dithiocarbamates discussed hereinbelow. The preferred polyvalent metals are zinc and cadmium. Among other metals that may be used are lithium, sodium, potassium, magnesium, calcium, strontium, barium, aluminum, tin and lead.

The dithiocarbamates may be looked upon as derivatives of amines and carbon disulfide, since the usual method of preparing them is by reacting an amine with carbon disulfide and caustic alkali:



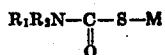
The various polyvalent metal dithiocarbamates may be prepared from the alkali metal dithiocarbamates by double decomposition. The preferred dithiocarbamates may, therefore, be regarded as polyvalent metal dithiocarbamates derived from secondary amines and containing a sufficiently large hydrocarbon group or groups to render the salts oil-soluble. The secondary amine of which the salt is a derivative may be an aliphatic amine (di-alkyl, di-cycloalkyl, mixed alkyl-cycloalkyl, etc.), an aromatic amine or a mixed aliphatic-aromatic amine and it may be an amine such as piperidine or its homologues in which the secondary nitrogen atom is part of a heterocyclic ring.

Illustrative examples of thiocarbamates that may be used in accordance with the invention are calcium, lead, zinc and cadmium dibutyl dithiocarbamates; zinc methyl octyl dithiocarbamate; zinc dicetyl dithiocarbamate; zinc diamyl thiolcarbamate; zinc diamyl thionocarbamate; zinc monocetyl dithiocarbamate; zinc butyl amyphenyl dithiocarbamate; calcium di-(cyclohexylphenyl) dithiocarbamate; calcium, zinc, cadmium and potassium "petroleum base" dithiocarbamates; zinc dibenzyl dithiocarbamate; zinc di-(cetylphenyl) dithiocarbamate; and zinc di-(amylpiperidyl) dithiocarbamate.

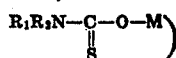
General methods of preparing thiocarbamates are available in the literature. The best method presently available for preparing dithiocarbamates is that method in which a primary or secondary amine is allowed to react with carbon disulfide and aqueous or alcoholic caustic soda or caustic potash, producing an alkali metal dithiocarbamate. This may be recovered by crystallization, but since the polyvalent metal salts are preferred, it will be the usual practice to add an aqueous solution of a water-soluble polyvalent metal salt, such as calcium chloride or zinc sulfate, to the reaction mixture (diluted with water if necessary) containing the alkali metal dithiocarbamate, thereby precipitating the desired polyvalent metal dithiocarbamate. This may be purified by crystallization from a suitable solvent, such as a light hydrocarbon thinner. Alternatively, to an aqueous solution of alkali metal of dithiocarbamate may be added petroleum thinner and to the mixture may be added an aqueous solution of a polyvalent metal salt, thus precipitating polyvalent metal dithiocarbamate from aqueous

solution and forming a solution of the same in petroleum thinner.

General methods of preparing monothiocarbamates (which are of two types: thiolcarbamates,



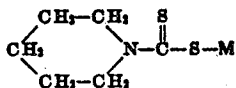
and thionocarbamates,



are available in the literature; e. g., thiolcarbamates from amines and COS.

The preparation of "petroleum base" dithiocarbamates is described in detail in Miller and Rutherford application, Serial No. 441,964, filed May 6, 1942 (now Patent No. 2,363,012, dated November 21, 1944). Briefly stated, the "petroleum base" dithiocarbamates are prepared by extracting the nitrogen bases from nitrogen-containing cracked naphtha or the like, reducing the bases and reacting the reduced bases with carbon disulfide and caustic alkali to produce the alkali metal "petroleum base" dithiocarbamates, from which the polyvalent metal "petroleum base" dithiocarbamates can be prepared by double decomposition.

From the properties and reactions of the reduced, cracked petroleum nitrogen bases from which the aforesaid "petroleum base" dithiocarbamates are derived, it is believed that they are complex mixtures predominating in piperidine derivatives, also containing tetrahydro-quinoline (reduced nitrogen ring) and/or its derivatives. These bases contain alkyl substituents, such as methyl, ethyl and propyl substituents, on the carbon portion of the ring. The dithiocarbamates produced from these bases, that is, the aforesaid "petroleum base" dithiocarbamates, are, therefore, believed to be a mixture of compounds of the formula



wherein M is a metal and one or more of the hydrogen atoms are substituted by short alkyl groups (about C<sub>1</sub> to C<sub>5</sub>) and/or by a condensed benzene ring.

Although the "petroleum base" dithiocarbamates are believed to be principally piperidine and tetrahydroquinoline derivatives, with one or more hydrocarbon substituents on the carbon part of the ring, dithiocarbamates derived from other ring type amines, such as trimethylene imine, tetramethylene imine and hexamethylene imine, preferably containing one or more alkyl substituents on the carbon part of the ring, may also be used according to the invention.

The sulfonates hereinabove described may be used in oil in proportions of 0.1 per cent or less to 5 per cent or more, about 0.5 to 1.5 per cent being preferred, and the thiocarbamates may be used in oil in proportions of 0.1 per cent or less to 2 per cent or more, about 0.5 to 1.5 per cent being preferred. All percentages so stated are by weight based on finished oil. Concentrates of sulfonate and thiocarbamate in oil may be prepared for later blending with more oil to produce the finished lubricant; for example, concentrates containing 10 to 50 per cent of sulfonate and 10 to 50 per cent of thiocarbamate, such percentages being by weight based on total concentrate.

The sulfonates, such as calcium mahogany sul-

fonate, have been heretofore proposed as motor oil detergents. They are, however, unduly corrosive toward hard alloy bearings such as cadmium-silver and copper-lead bearings and they do not satisfactorily inhibit gum formation and deposition in piston ring slots, etc. I have found that the sulfonates, such as calcium mahogany sulfonate, are considerably improved in these respects by the use of thiocarbamates, such as zinc "petroleum base" dithiocarbamates and zinc dibutyl dithiocarbamate.

The following specific examples will serve to illustrate the advantages obtainable by and the preferred manner of practicing the invention.

**Example 1—Lauson engine tests.**—Various oils were subjected to test as crankcase lubricants in single cylinder Lauson gasoline engines of the kind described in Farrington et al. U. S. Patent No. 2,325,597. Engines were operated at 1200 revolutions per minute, 375° F. jacket temperature, 300° F. oil temperature and for 60 hours. After each run the engine was disassembled, inspected, cleaned and reassembled.

The manner of testing may be illustrated as follows: Assume that three oils designated as I, II and III are under investigation. These oils are tested in the same engine; also tested in the same engine is a "reference oil," which is a standard, commercially available heavy duty lubricant containing as compounding agents a metal phenate and a metal organo phosphate. The first run in the engine is with reference oil, then oils I, II and III are tested in that order, and, finally, the reference oil is again tested.

It is now known that an engine changes its characteristics during operation; thus an engine that has been run 60 hours will not, even though disassembled, cleaned and reassembled, give the same performance with a fresh quantity of the same lubricant. To avoid as much as possible errors in comparing oils due to the aforesaid change of engine characteristics, the following plan was used.

Suppose the "piston discoloration number" (PD No.), which is a form of rating crankcase lubricants explained in detail hereinbelow, of the reference oil when first tested is 200, the PD Nos. of oils I, II and III are 150, 175 and 200, respectively, and the PD No. of reference oil when last run is 250. An interpolated reference oil PD No. is calculated for each of the oils I, II and III. It is assumed, since the same engine gave a PD No. of 200 before oils I, II and III were run and a PD No. 250 afterwards, or a difference of 50 PD No. units, that if at the time oil I was actually tested the reference oil had been used, the PD No. of reference oil would have been 200 plus one fourth of 50 or 212.5; similarly, that the PD Nos. of reference oil if used at the times oils II and III were used would have been 225 and 237.5, respectively. From these interpolated PD Nos. of reference oil and from the actual PD Nos. of oils I, II and III are calculated PD No. differences, each of these being the difference between the actual PD No. and the corresponding interpolated PD No., the difference being positive if the actual PD No. is greater, negative if it is smaller than the interpolated PD No.

This manner of rating oils is more accurate than a manner of rating which simply compares actual PD Nos., for it corrects in part at least for changed characteristics of the same engine and it makes more reliable the comparison of PD Nos. obtained in different engines,

"PD No.," an abbreviation of "piston discoloration number," hereinabove and hereinbelow referred to, is arrived at in this manner: The engine is run as described for 60 hours. Then it is disassembled. The piston skirt is inspected visually. To a piston skirt which is completely black is assigned a PD No. of 800; to one which is completely clean is assigned a PD No. of zero; to those intermediate completely black and completely clean are assigned PD Nos. in proportion to the carbonaceous deposits. Actually, further refinements were employed in arriving at PD Nos. hereinbelow disclosed, but since the same method was used in every case it is unnecessary to describe these refinements.

Results obtained with various oils are set forth in Table I below.

ute to the more water-soluble, less oil-soluble character of the sulfonate.

**Example 2—Full scale engine tests.**—Tests were carried out in two types of full scale engine using as crankcase lubricants the preferred oils of the invention. The said engines and the conditions of operation were as follows: One engine, preferred to herein as the "L-1" engine, was a single cylinder, 5 $\frac{3}{4}$ " bore Diesel engine; it was run for 480 hours at 1000 revolutions per minute, at a load of 19.8 brake horse power, oil temperature of 145°–150° F., jacket temperature of 175°–180° F., oil change at 120 hour intervals. The other engine, herein referred to as the "L-3" engine, was a 4 cylinder, 4 $\frac{1}{4}$ " bore Diesel engine which was run for 120 hours at 1400 revolutions per minute, BHP of 37, oil temperature of 210°–

Table I

| No. | Base Oil | Sulfonate Additive                         | Conc., millimols per Kilogram of Oil | Dithiocarbamate Additive            | Conc., millimols per Kilogram of Oil | PD No. Difference |
|-----|----------|--------------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|-------------------|
| 1   | A        | Ca mahogany sulfonate I                    | 7                                    | Zn "petroleum base" dithiocarbamate | 20                                   | -105              |
| 2   | B        | do                                         | 14                                   | do                                  | 20                                   | -115              |
| 3   | A        | do                                         | 7                                    | Zn dibutyl dithiocarbamate          | 20                                   | 0                 |
| 4   | A        | Ba mahogany sulfonate I                    | 14                                   | Zn "petroleum base" dithiocarbamate | 20                                   | -150              |
| 5   | A        | Ca "petroleum alkylated" phenol sulfonate  | 15                                   | do                                  | 20                                   | -30               |
| 6   | A        | Ca "petroleum sludge" sulfonate            | 14                                   | do                                  | 20                                   | +215              |
| 7   | A        | Ca tetra-amyI benzene sulfonate            | 14                                   | do                                  | 20                                   | +75               |
| 8   | A        | Ca mahogany sulfonate II                   | 14                                   | do                                  | 20                                   | -265              |
| 9   | A        | Ca "petroleum alkylated" benzene sulfonate | 14                                   | do                                  | 20                                   | -245              |
| 10  | A        |                                            | (1)                                  |                                     |                                      | +400 to +500      |

<sup>1</sup> No Compounding.

In Table I above, base oil A designates an SAE 30 grade blended oil, a blend of solvent treated California naphthenic base oil and California paraffinic base oil. Base oil B designates a straight SAE 30 grade California paraffinic base oil. The concentrations are expressed as millimols of metal per kilogram of compounded oil; thus, 7 millimols of Ca mahogany sulfonate I and 20 millimols of zinc "petroleum base" dithiocarbamate mean 0.007 and 0.020 gram mols of calcium (in form of sulfonate) and zinc (in form of dithiocarbamate) per kilogram of oil.

The calcium mahogany sulfonate I was the calcium salt of a mahogany acid obtained in the sulfuric acid treatment of a blend of asphaltic and paraffinic base oils to produce white oil; calcium mahogany sulfonate II was the calcium salt of a mahogany acid obtained in the sulfuric acid treatment of a paraffinic base oil to produce white oil; the calcium "petroleum alkylated" benzene and phenol sulfonates were the calcium salts of sulfonic acids produced from benzene and phenol, respectively, that had been alkylated with chlorinated white oil; and the calcium "petroleum sludge" sulfonate was the calcium salt of a sulfonated phenol extract of petroleum, said sulfonated extract being of more water-soluble and less oil-soluble character than mahogany sulfonic acids.

It is apparent from Table I that the sulfonate-dithiocarbamate compounding greatly improved the base oil and in most cases yielded a much lower PD No. than the reference oil. It is significant that the calcium "petroleum sludge" sulfonate-zinc "petroleum base" dithiocarbamate compounding made a poor showing compared with the reference oil, although a much better showing than the base oil. This result we attrib-

214° F., jacket temperature of 198°–202° F., no oil change.

Results are given in Table II below.

Table II

|                                                  | Oil A        | Oil B       | Reference Oil |
|--------------------------------------------------|--------------|-------------|---------------|
| <b>L-1 Test:</b>                                 |              |             |               |
| Piston Ring Sticking                             | None         | None        | None          |
| Ring Belt Deposits                               | Moderate     | Moderate    | Moderate      |
| Piston Skirt Deposits PD No.                     | 5            | 10          | 10            |
| Top Ring Groove Deposits                         | Thin to Med. | Med to Hvy. | Med to Hvy.   |
| Oil Ring Clogging, percent.                      | 0            | 0           | 0             |
| Cylinder wear $\frac{1}{4}$ " from Cylinder Top. | 0.0010"      | 0.0010"     | 0.0010"       |
| <b>L-3 Test:</b>                                 |              |             |               |
| Piston Ring Sticking                             | None         | None        | None          |
| Ring Belt Deposits                               | Excep. Clean | Light       | Moderate      |
| Copper Lead Vrg.                                 | 37           | 21          | 26            |
| Wt. Loss, Mgs./Whole Brg.                        |              |             |               |

Oil A consisted of base oil A of Table I, 1.4% Ca mahogany sulfonate and 1% zinc "petroleum base" dithiocarbamate. Oil B differed from oil A only in that it contained half as much sulfonate. The reference oil was the same as described in Example 1.

The same three oils were also subjected to a foaming test in which oil is pumped from the crankcase of a 1 $\frac{1}{2}$  horsepower Wisconsin single cylinder air-cooled gasoline engine to an evacuated flask where the height of foam is measured, thence back to the crankcase. From data observed in this test a "foam index" is calculated. This foam index measures both the foaminess of an oil at an absolute pressure of 5" mercury and the extent to which the pressure can be reduced before foaming becomes universal throughout the body of oil in the flask. Results, both in height

of foam and foam index, are given in Table III below.

Table III

|                                                               | Oil A | Oil B | Reference Oil |
|---------------------------------------------------------------|-------|-------|---------------|
| Height of foam in inches at 5" mercury absolute pressure..... | 2.0   | 1.8   | 3.5           |
| Foam index.....                                               | 8.0   | 7.2   | 35+           |

Further examples of compounded oils of the invention are as follows:

| Base Oil                     | Sulfonate                          | Thiocarbamate                           |
|------------------------------|------------------------------------|-----------------------------------------|
| SAE 30 naphthenic oil.....   | 1% Ba mahogany sulfonate.....      | 1% Zn "petroleum base" dithiocarbamate. |
| SAE 30 paraffinic oil.....   | 1% Ca mahogany sulfonate.....      | 1% Ca "petroleum base" dithiocarbamate. |
| SAE 30 mixed base oil.....   | 1% Ca octyl benzene sulfonate..... | 1% Ba dibutyl dithiocarbamate.          |
| SAE 30 Pennsylvania oil..... | 1% Ca mahogany sulfonate.....      | 1% Cd "petroleum base" dithiocarbamate. |

Besides the ingredients indicated, the finished oils of the invention may contain other ingredients, such as extreme pressure agents, blooming agents, pour point inhibitors, etc. The invention is particularly concerned with liquid lubricating oils, more particularly with crankcase lubricating oils; however, the employment of the compounding agents of the invention in other lubricants, in transformer oils, in greases, etc., is contemplated.

I claim:

1. A petroleum lubricating oil comprising a major proportion of a petroleum oil of lubricating viscosity, about 0.1 to 5 per cent by weight based on finished oil of an alkaline earth metal mahogany sulfonate and about 0.1 to 2 per cent by weight based on finished oil of zinc "petroleum base" dithiocarbamate.

2. A petroleum lubricating oil comprising a major proportion of petroleum oil of lubricating viscosity, about 0.1 to 5 per cent by weight based on finished oil of an oil-soluble calcium higher alkaryl sulfonate of above about 500 molecular weight and of the aliphatic type in which at least 50% by weight of the sulphonic acid consists of aliphatic carbon and hydrogen and about 0.1 to

2 per cent by weight based on finished oil of zinc dibutyl dithiocarbamate.

3. A petroleum lubricating oil comprising a major proportion of petroleum oil of lubricating viscosity, about 0.1 to 5 per cent by weight based on finished oil of calcium mahogany sulfonate and about 0.1 to 2 per cent by weight based on finished oil of zinc dibutyl dithiocarbamate.

4. A petroleum lubricating oil comprising a major proportion of a petroleum oil of lubricating viscosity, about 0.1 to 5% by weight based on finished oil of an oil-soluble alkaline earth metal

high molecular weight aliphatic type alkaryl sulfonate and about 0.1 to 2% by weight based on finished oil of an oil-soluble zinc dithiocarbamate.

5. The petroleum lubricating oil of claim 4 wherein the alkaline earth metal is calcium.

6. A petroleum lubricating oil comprising a major proportion of a petroleum oil of lubricating viscosity, about 0.1 to 5% by weight based on finished oil of calcium mahogany sulfonate and about 0.1 to 2% by weight based on finished oil of zinc "petroleum base" dithiocarbamate.

JAMES O. CLAYTON.

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The following references are of record in the file of this patent:

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**Certificate of Correction**

Patent No. 2,450,633.

October 5, 1948.

**JAMES O. CLAYTON**

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 10, lines 20 and 21, claim 4, strike out "high molecular weight aliphatic type alkaryl sulfonate" and insert instead *higher alkaryl sulfonate of above about 500 molecular weight and of the aliphatic type in which at least 50% by weight of the sulphonic acid consists of aliphatic carbon and hydrogen;*

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of January, A. D. 1949.

[SEAL]

**THOMAS F. MURPHY,***Assistant Commissioner of Patents.*