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LUBRICATING OILS CONTAINING METAL DERIVATIVES OF CYCLIC IMIDES

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1

The present invention relates to improved lubricants for internal combustion engines. More particularly it relates to mineral lubricating oils containing small amounts of metal imides.

Mineral lubricating oils employed as crankcase lubricants in internal combustion engines tend to oxidize at the high temperatures to which they are subjected in this type of service with the formation of gums and sludges, which clog the oil feed lines and form varnish-like deposits on the surfaces of rings, pistons, cylinders and other engine parts. Such deposits decrease the efficiency of operation of the engine and eventually lead to piston sticking and scoring of the cylinder walls.

It is common practice to add to crankcase oils small amounts of so-called "detergents," which have the property of reducing this formation of sludges and varnishes. Various types of metal organic compounds are known to be effective for this purpose, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. For example, Davis et al. in U. S. Patent No. 2,335,261 disclose that polyvalent metal salts of high molecular weight fatty acids such as wax acids and alkylated aromatic acids such as alkylated benzoic and phthalic acids are effective for this purpose. The metal phenates, particularly the polyvalent metal phenates, are disclosed for example by Gardiner et al. in U. S. Patents No. 2,228,661 and No. 2,347,152.

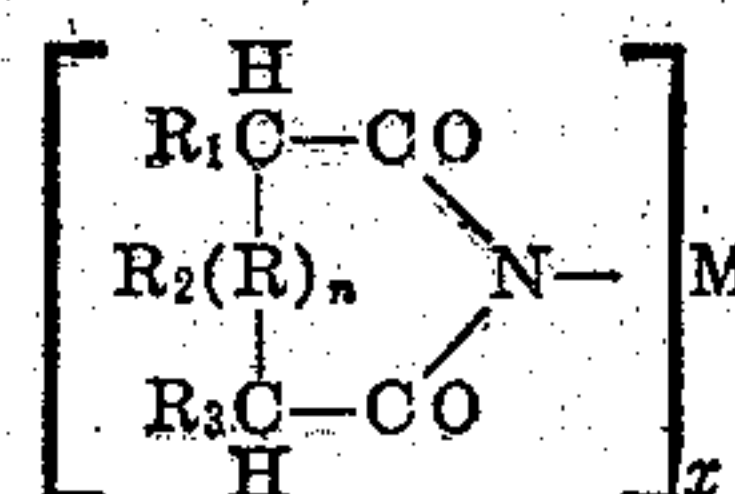
However, compounds of the above type have the disadvantage that they are unstable in the presence of water, so that they hydrolyze with the formation of water soluble metal compounds or sludges as well as objectionable corrosive materials. The detergent compounds thus become destroyed or removed from the lubricating composition when the latter becomes contaminated with water, such as may occur in handling and in storage.

In accordance with our invention lubricating oils having superior detergency and stability, suitable for use as crankcase oils in automotive, diesel and airplane engines, are produced by adding to mineral lubricating oils small amounts of compounds of the class consisting of oil-soluble metal cyclic imides derived from aliphatic dicarboxylic acids. Suitable compounds of this type are metal derivatives of stable cyclic imides,

2

particularly those obtained from succinic and glutaric acids, having aliphatic substituent groups of sufficient size to impart oil solubility to the molecule. We have found that compounds of this class wherein a metal is linked directly to a nitrogen atom positioned between two acyl groups possess excellent detergency and anti-sludging properties in mineral lubricating oils, and are furthermore characterized by a remarkable stability and resistance to hydrolysis as compared with the corresponding compounds containing the metal-oxygen linkage which have been employed heretofore in lubricating oils to promote engine cleanliness. They are particularly valuable for use in producing lubricating oils to meet the severe requirements of airplane engine oils.

The preferred compounds employed as lubricating oil additives according to our invention may be represented by the general formula



wherein M is a metal, x is an integer equal to the valency of the metal, R is a methylene group, n is 1 or 0, and R_1 , R_2 and R_3 are members of the group consisting of hydrogen and aliphatic hydrocarbon groups, at least one of them being an alkenyl or alkyl group containing from about 15 to about 30 carbon atoms, and most suitably from about 18 to 25 carbon atoms. M of the formula may be any alkali metal, alkaline earth metal or other metal capable of forming compounds of this type, as for example sodium, potassium, lithium, calcium, barium, strontium, magnesium, aluminum, tin, zinc, cobalt, nickel, titanium or manganese. It is preferably a polyvalent metal. The bivalent metals, particularly zinc and magnesium, are especially suitable.

As suitable examples of the above class of compounds may be mentioned magnesium docosenyl succinimide, calcium docosenyl glutarimide, zinc- α -methyl- β -pentadecenyl succinimide, cobaltous nondecenyl glutarimide, calcium penta-cosenyl succinimide, titanous α -propyl- β -eicosenyl succinimide, and so forth.

The above described imide derivatives may be employed in varying amounts depending upon the characteristics of the lubricating oil and the conditions under which it is to be employed.

3

Even in very small amounts, as about 0.01 per cent by weight, they impart substantial improvement in the detergency characteristics of mineral lubricating oils. Ordinarily they are employed in crankcase oils in amounts within the range of from about 0.5 to about 5 per cent by weight, and preferably with the range of from about 0.5 to about 3 per cent by weight of the composition.

The metal imides of this invention are formed by treating aliphatic substituted succinimides and glutarimides with metal compounds under conditions such that the hydrogen atom of the imido group is replaced by metal. The aliphatic substituted succinimides and glutarimides may conveniently be obtained by reacting the anhydrides of maleic, glutaric, citraconic, homomesaconic, or itaconic acids, or homologues thereof, with unsaturated aliphatic hydrocarbons, and then converting the aliphatic-substituted anhydrides obtained to the corresponding imides by treating with ammonia. Alkenyl substituted anhydrides, which are obtained when olefinic anhydrides are reacted with olefin polymers, may be hydrogenated if desired either before or after conversion to the imides to obtain the corresponding alkyl substituted compounds.

In forming the polyvalent metal salts the imide may be treated directly with a suitable compound of the polyvalent metal or the imide may be first treated with an alkali metal compound and the alkali metal imide derivative then converted to the polyvalent metal derivative by double decomposition with a suitable polyvalent metal compound.

The following examples illustrate the preparation of these metal imide derivatives by each of the above methods.

EXAMPLE 1

The magnesium derivative of an alkenyl succinimide was prepared by the following procedure: An alkenyl succinic anhydride was first prepared by heating together at 225° C. for 24 hours a mixture of 300 grams of maleic anhydride and 960 grams of butylene polymer. The latter had a boiling point at 1 mm. Hg of 100–140° C. and a molecular weight corresponding to 21–22 carbon atoms per molecule. The reaction product was distilled at 1 mm. Hg and the fraction boiling at 170–230° C. converted to the imide directly by passing ammonia into it for 2½ hours while the temperature was increased gradually from 100° C. to 240° C. and the heating then continued for ½ hour longer without the introduction of ammonia. The product was taken up in ether and washed free of excess ammonia, the ether stripped out and the product dried by adding toluene and again stripping to remove the toluene and water. 405 grams of the alkenyl succinimide thus obtained were dissolved in toluene and a solution of magnesium methylate obtained by dissolving 12.4 grams of magnesium metal in dry methanol added. The mixture was heated under reflux for 18 hours and the solvent stripped off. 417 grams of product were obtained analyzing 3.10% magnesium and 3.44% of nitrogen, as compared with the theoretical values 3.00% and 3.48%, respectively, for magnesium alkenyl (C₂₁) succinimide.

EXAMPLE 2

The zinc derivative of an alkenyl succinimide was prepared as follows. An alkenyl succinimide was prepared as described in Example 1, employing in the alkylation of the maleic anhydride a

4

propylene polymer having a molecular weight corresponding to 21 carbon atoms per molecule. 324 grams of the alkenyl succinimide thus obtained were added to a solution of sodium methylate obtained by dissolving 19.2 grams of sodium metal in methanol, and the reaction mixture refluxed for two hours. 52 grams of zinc chloride dissolved in methanol were then added and the mass stirred for four hours, the alcohol stripped out and the residue taken up in ether and washed with water until the wash water was free of chlorine. The ether was then stripped out and the product dried by adding toluene and again stripping. 338 grams of product were obtained which analyzed 9.82% of ash as compared with the theoretical value of 9.63% of zinc oxide for zinc alkenyl (C₂₁) succinimide.

The compounds obtained as described in the above examples were oil-soluble and water-stable and possessed outstanding properties with regard to detergency and anti-sludging properties in lubricating oils. Table I below shows test data obtained on the magnesium alkenyl succinimide obtained as described in Example 1.

Table I

Additive	Carbon Black Dispersion	High Temperature Deposits Test—Deposits, mg.	Water Stability Test—Additive Removal, Percent
None (Base oil).....	2	618	—
1% Mg alkyl (C ₂₁) phenolate.....	6	218; 230 (304) ¹	85
1% Mg alkenyl (C ₂₁) succinimide.....	14	186; 176	25

¹ A different base oil giving only 304 mg. of deposit₀ was used in this test.

The water stability test of the above table is carried out in the following manner: 200 grams of oil containing additive and 200 grams of distilled water are stirred together for 15 minutes at room temperature by means of a Mixmaster running at 700 R. P. M. The emulsion is then centrifuged and an ash determination made on the clarified oil. The per cent of additive removed is calculated from the difference between the ash content of this washed sample and that of the original oil.

The carbon black dispersion test of the foregoing table is a bench test designed to show the detergency characteristics of an oil. The test is carried out in the following manner: A 100 ml. portion of a suspension prepared by thoroughly mixing 1 gram of carbon black into a solution consisting of 150 grams of the test oil and 150 grams of kerosine is placed in a centrifuge tube and centrifuged at 2000–2100 R. P. M. for 5 minutes. About 35 ml. of the centrifuged suspension is immediately poured from the top of the centrifuge tube and a 5 ml. portion of this taken and diluted to 60 ml. with kerosine in a tall bottle or Nessler tube. The sample thus prepared is compared visually with a series of graduated standards containing various amounts of carbon black suspended in a similarly diluted oil of the same character as the test oil. The dispersion value of the test oil is expressed in terms of arbitrary numbers assigned to these standards on the basis of the relative amounts of suspended carbon which they contain. This test measures specifically the ability of an oil to hold in suspension or dispersion carbon black, which may be considered comparable to blow-by carbon in an internal combustion engine, and it

also provides a generally good indication of the oil ring sludging character of an oil in service.

The high temperature deposits test of the table is also a bench test wherein an aluminum cylinder one inch in diameter and three inches long is repeatedly dipped into a beaker containing a sample of the test oil maintained at 525° F. for a period of 20 hours. The deposit remaining on the test specimen after washing with pentane and drying is determined.

As shown in Table I, the magnesium alkenyl succinimide was highly effective in dispersing carbon black and in reducing varnish-formation in a mineral lubricating oil at high temperatures. It was markedly superior in these tests indicating the ability of an oil to maintain engine cleanliness in comparison with magnesium alkyl phenolate, which is considered to be one of the most effective compounds employed for this purpose at the present time. In addition the compound of our invention has a satisfactory degree of water-stability, equal to over three times that of the phenolate. The improved water-stability of this compound is in agreement with tests performed on another typical compound of this class wherein barium alkenyl succinimide was heated for an hour in sulfuric acid without substantial change.

The detergency characteristics of compounds prepared as described in Examples 1 and 2 were further determined by means of the C. F. R. high speed engine test, which is a test for determining the ability of an oil to reduce engine deposits under severe operating conditions. This test is carried out with a standard C. F. R. single cylinder internal combustion engine operating under the following conditions:

Compression ratio -- 6.5:1.
Speed, R. P. M. ---- 1800.
Air/fuel ratio ----- 13:1.
Jacket temperature . 285° F.
Oil in temperature . 185° F.
Oil out temperature 200° F.
Fuel ----- 100 octane (minimum)
aviation type contain-
ing 4 cc. TEL/gal.

Duration of run ---- 50 hours.

At the termination of each run, electrical measurements are taken of the piston skirt deposit with respect to the extent or percentage of surface area of the piston skirt which is covered by the lacquer deposit as well as the average thickness of the deposit. The carbonaceous deposits in the piston ring grooves are also carefully scraped off and weighed. Extensive laboratory testing has shown that a crank case lubricating oil which will markedly reduce the tough black lacquer deposit on the piston skirt and the carbonaceous deposits occurring in the ring belt area, can be expected to reduce deposits at all points where high temperatures are encountered. The tests listed are therefore an accurate indication of the engine cleanliness of the oil compositions under test.

The following table gives the results obtained in the above test on an oil containing small amounts of our compounds as compared with the base oil alone, which was a highly refined residual lubricating oil from a paraffin base crude employed as an airplane engine lubricating oil. The magnesium alkenyl succinimide of the table is that prepared as described in Example 1. The zinc alkenyl succinimide was prepared as described in Example 2 except that a propylene

polymer averaging 19.3 carbon atoms per molecule was used in the alkylation step.

Table II

C. F. R. HIGH SPEED ENGINE TESTS

Additive	Piston Skirt Deposit	
	Percent Covered	Thickness In. $\times 10^{-4}$
None (Base oil)-----	80	2.0
1% Mg alkenyl succinimide + 0.5% Zn alkenyl succinimide-----	0.0	0.0

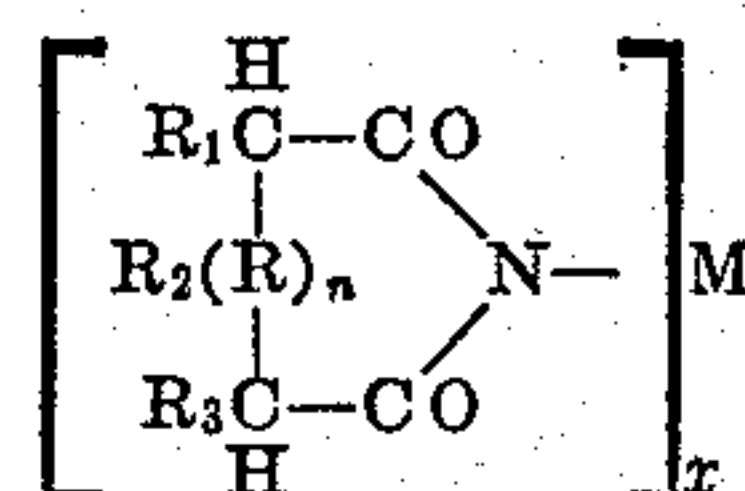
The data given in Table II show the outstanding properties of our compounds in reducing engine deposits in an actual engine test. In this test an oil was produced by the use of small amounts of typical compounds of our invention which gave zero engine deposits after 50 hours of severe operating conditions corresponding to those encountered in airplane engine lubrication, as compared with heavy varnish deposits covering 80 per cent of the piston skirt obtained with the uninhibited base oil under the same conditions.

Lubricating compositions containing the additives of our invention may also contain other additives such as are ordinarily employed in lubricants, such as oxidation inhibitors, pour point depressors, viscosity index improvers, corrosion inhibitors, and so forth, as well as other detergents such as metal phenates, sulfonates and other metal salts.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricant consisting essentially of a refined mineral lubricating oil and a small amount sufficient to improve the detergency thereof of a compound of the general formula



wherein M is a polyvalent metal, x is an integer equal to the valency of the metal, R is a methylene group, n is 1 or 0, and R_1 , R_2 and R_3 are members of the group consisting of hydrogen and aliphatic hydrocarbon groups, at least one of them being an aliphatic hydrocarbon group containing from about 15 to about 30 carbon atoms.

2. The lubricant according to claim 1 wherein the metal is a divalent metal.

3. A lubricant consisting essentially of a refined mineral lubricating oil and about 0.1 to about 5 per cent by weight of the magnesium salt of a succinimide substituted on one of its methylene groups by an aliphatic hydrocarbon group containing from about 15 to 30 carbon atoms.

4. A lubricant consisting essentially of a refined mineral lubricating oil and about 0.1 to about 5 per cent by weight of the zinc salt of a succinimide substituted on one of its methylene groups by an aliphatic hydrocarbon group containing from about 15 to 30 carbon atoms.

5. A lubricant consisting essentially of a refined mineral lubricating oil containing about 0.5 to 3.0 per cent by weight of magnesium alkenyl

(C₁₅₋₃₀) succinimide and about 0.5 to 2.0 per cent by weight of zinc alkenyl (C₁₅₋₃₀) succinimide.

6. A lubricant consisting essentially of a refined mineral lubricating oil containing from about 0.1 to about 5 per cent by weight of a mixture consisting of a magnesium salt of a succinimide substituted on one of its methylene groups by an aliphatic hydrocarbon group containing from about 15 to about 30 carbon atoms and a zinc salt of a succinimide substituted on one of its methylene groups by an aliphatic hydrocarbon group containing from about 15 to about 30 carbon atoms.

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