Patented Dec. 9, 1941 2,265,851

UNITED STATES PATENT OFFICE

2,265,851

COMPOUNDED LUBRICANT

George L. Matheson, Union, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application May 8, 1940, Serial No. 334,012

13 Claims. (Cl. 252—48)

This invention relates to lubricating compositions adapted for service in automotive engines and is particularly concerned with the preparation of Diesel and aircraft lubricants.

Development in the art of preparing lubricants for automotive engines is determined largely by the quality of available mineral oils. For the lubrication of these engines, mineral oils alone are often unsatisfactory because hydrocarbons do not possess the necessary properties under all conditions of engine operation. The incorporation in the higher mineral oil fractions of selected compounds has been found to enhance the lubricating properties of the oil base and impart to the composite properties not possessed by the oil base. Some of the improvements effected in this manner are in regard to oiliness, film formation and tenacity, viscosity-temperature relationship, pour point, physical and chemical stability, color and cast characteristics, and functioning of the lubricant without fouling of the engine system. The present invention is concerned particularly with the improvement in lubricants in regard to clean engine performance.

Engine cleanliness is concerned largely with the condition of the piston assemblies, the rings, slits, grooves, lands, skirts and the like, of crankcases, valve chambers, filters and oil lines, and the prevention of the deposition on these of gummy, varnish-, or sludge-like deposits. The deposits may form as a result of the deterioration of the mineral lubricating oil, or may be partially or wholly formed from fuel residues, water and dirt which find their way into the oil. The deposits, however, are not to be confused with the gums and resins deposited in the engine system by fuels containing, for instance, gum formed by the aging of the hydrocarbons in storage. The fuel deposits are not of the same type or located in the same portions of the engine system. Thus, in the case of the fuels, carburetor jets are choked by gummy material and gum and resinous materials are deposited in the induction system of the engine, as for example on the inlet valve stem, causing the valve to stick in its guide.

In the endeavor to combat the fouling of engine systems many metallic salts have been investigated. The use of metallic salts for this purpose is not to be confused with the uses of soaps to improve viscosity and as thickening agents. When employed to obviate the fouling of the engine system, the metallic salts are necessarily of such a nature, and added in such amounts, as to have little effect on the fluidity of the base oil, otherwise the normal oil circulation system of the engine would be unable to handle the lubricant.

The metallic salts appear to owe their effect at least in part to a detergent action which enables the compounded oil to scour from the engine surfaces such sludges and lacquers as have already been deposited, and also to hold in dispersion such deterioration and degradation products as would tend to deposit from conventional oils with resultant fouling of engine parts. Antioxidant action is not necessary to secure this effect and some of the most active detergents are powerful oxidation promoters. However, not all metallic salts may be employed in improving lubrication in this regard and even among those considered in the prior art as relatively satisfactory, many possess the disadvantage of exerting a corrosive effect on engine parts, particularly on engine bearings of the copper-lead and cadmium-silver type. It is a feature of the present invention that this disadvantage is obviated. In other words, this invention is directed to the preparation of a lubricant which will maintain superior engine cleanliness and which will be generally suitable for a variety of engines.

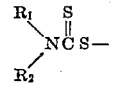
The non-corrosiveness to bearing alloys of the metallic salts of dithiocarbamic acids to which this invention relates is attributed to the peculiar sulfur linkage involved in the molecule. This sulfur appears to exert a pacifying and protecting action upon the alloy which prevents it from being attacked. The action is sufficiently marked that the attack on bearing alloys by ordinarily corrosive materials, such as carboxylic acids and soaps, may be prevented. It is advantageous, therefore, to add a metallic dithiocarbamate to lubricating compositions which are either corrosive per se or become corrosive in use, and to prepare in this manner improved lubricating compositions.

It is important also to observe that the prevention of engine fouling involves a detergent and dispersing action which is not found, to any great degree, in mineral oils per se. Furthermore, this detergent activity is not imparted to mineral oils by any known refining method. In other words, the metallic agents contemplated in this invention impart to the oil blends properties seemingly not obtainable by choice of either crude or refining technique. The metallic agents employed in this invention are not to be considered therefore as substitutes for any conventional refining treatment in the preparation of superior

lubricants, but as the means of imparting to mineral lubricating oils properties inherently lacking in the mineral oils per se.

Specifically, the mineral lubricating stocks employed in this invention may be any type of a mineral oil distillate or residue consistent with the service to which the compounded lubricant is to be adapted. It is usual to prepare Diesel lubricants from non-waxy oils or naphthenic base type oils because such oils produce a softer form of carbon which has less tendency to scratch engine parts and does not cause ring sticking to the same extent as paraffinic oils. However, since the metal compounds of this invention reduce the ring sticking tendency of oils, it is possible to employ even highly paraffinic oils for service where they would normally cause excessive ring sticking, if a proper metallic compound is incorporated in the lubricant. The oil should possess such flash point and viscosity characteristics as are normally considered requisite for the service contemplated, since the metal compounds have little effect upon these properties. The base oils employed may be refined by any of the conventional methods such as acid and alkali treating, clay percolation and contacting, and by solvent extraction with such solvents as sulfur dioxide, phenol and the like. Hydrogenated oils as well as synthetic oils prepared, for example, by the condensation of olefins or the reaction of carbon oxides with hydrogen may be employed. The oils chosen will usually range in viscosity from about 40 to 100 seconds Saybolt at 210° F. and of this range, the most frequent need is for oils having a viscosity between 50 and 80 seconds Saybolt at 210° F.

The dithiocarbamate compounds added to these mineral oils have in their molecular structure one or more dithiocarbamate groups which may be represented by the formula



in which N, C and S have the usual significance as representing atoms of nitrogen, carbon and sulfur, R_1 and R_2 representing hydrogen or organic groupings similar or dissimilar in nature, and present in the molecule so that the sum R_1+R_2 contains at least eight carbon atoms in alkyl groups, and the structural relationship indicated by the relative positions and linkages of the respective atoms in the formula. The organic groupings represented by R_1 and R_2 may be alkyl, aryl, alkylaryl, mixture of alkyl and aryl, cycloalkyl and heterocyclic groupings. These groupings may contain inorganic substituents, such as sulfur, oxygen, phosphorus and nitrogen, when special properties are sought. Particularly important to the proper functioning of these compounds is that they possess adequate solubility in the mineral base stock and for this reason it is generally required that the combined R_1 and R_2 groups, when wholly organic, contain a total of at least 8 carbon atoms in alkyl groups. Considerable improvement in this regard is effected by increasing the number of carbon atoms in alkyl groups to 10, 12 and 16 preferably.

The dithiocarbamates which have been found to be especially satisfactory are the salts of the polyvalent metals and of these the derivatives of nickel, cobalt, magnesium, barium and calcium are worthy of special mention. The various metallic derivatives are not equivalents in their effects since the activities of the various compounds are determined to an appreciable extent by the nature of the particular metallic atom present. A relation is noticeable between the effects of the metallic derivatives of closely related elements, such as the elements of the second group of the periodic system of classification of the elements, namely, of calcium, magnesium and barium, and of the metals of the iron subgroup of the eighth group of the periodic system, especially those of nickel and cobalt. In general the magnesium, calcium and barium compounds are the better dispersers of sludge but are the more difficult to obtain in an adequately oil soluble form. Consequently, there are instances in which, despite their lesser effectiveness, it is preferable to use the more soluble nickel and cobalt compounds. No hard and fast rule can be set up in this connection since the nature of the mineral base stocks and the type of service contemplated are important modifying influences.

The derivatives of other metals such as chromium, tin, lead, zinc and aluminum are also of some interest in this connection but are generally inferior to those mentioned in the preceding paragraph. The alkali metal salts are of some value but are generally too difficult to get into oil solution in the quantities required to warrant much consideration. Mixed metal dithiocarbamates may be advantageously employed in many cases. Such mixtures may be merely the physical mixture of the different metallic dithiocarbonate compounds or different dithiocarbamate radicals attached to the same polyvalent metal atom.

In addition to the inclusion in the thiocarbamic acid radical of organic groups having a sufficient number of carbon atoms in alkyl groups to insure the requisite oil solubility, the choice of a metal which is not too difficult to solubilize, and the choice of a mineral oil base of high solvency, the incorporation of the metallic salt in the oil as a stable addition may be assisted by the use of certain compounds which serve as coupling agents. To some extent, these make possible the use of combinations which would otherwise separate in storage or in service. The coupling agents should be solvents for both the oil and the metal salt, they should be sufficiently high-boiling as not to evaporate quickly in the engine at service temperature and they should exert no deleterious influence upon engine performance. Esters, ketones, and other stable oxygen-containing materials and their halogenated derivatives, halogenated hydrocarbons, and similar materials may be used for coupling, providing they possess a boiling point of at least 300° F. and preferably of 400° F. or higher. The amounts in which these compounds are employed is usually between 0.5% and 1.0% by weight of the mineral oil base.

Particularly useful as coupling agents are the higher saturated aliphatic alcohols: octyl, lauryl, cetyl, stearyl; and the corresponding olefinic, branched-chain, cyclic and aromatic alcohols. The optimum results are obtained by the use of cetyl and higher alcohols. The effect is seemingly not merely one of solubilizing but the alcohol appears to enter into a loose molecular arrangement with the metal salt to provide particularly enhanced performance in engine service.

The compositions may also include other types of compounds to convey and/or enhance other desirable properties of the blended lubricants. Such compounds may be added for purposes of

improving the viscosity, lowering the pour point or improving the color and cast characteristics. The additional use of such materials is within the scope of the invention since these materials are added as accessories and are not of the nature of essential constituents so far as the present invention is concerned.

The amounts in which the dithiocarbamate compounds are added depend upon the expected uses of the compounded lubricants and the particular compound employed. In general, the dithiocarbamates are employed in proportions between 0.2% and 5% by weight of the oil and of this range particularly effective action has been noted when using amounts between 0.25% and 1.0%. Quantities of thiocarbamates below 0.20% also affect the performance of oils markedly in laboratory tests, but for improving the detergent properties of crankcase lubricating oils, such amounts are of limited value. Conversely, the concentrations of 0.25% or over, and particularly of 1% or thereabout, provide compositions valuable for cleaning out already fouled engines. The fouled engine may be operated on such a detergent oil for 5 minutes to one hour, and then flushed, though far superior results are obtained if the operation is continued for several days to obtain the full benefit of the detergent. The detergent oil should then be drawn from the crankcase and it discharges with it, much of the material which had been deposited in the fouled engine. When the metallic derivatives, especially those of lead, are added in amounts of 5–10%, extreme pressure characteristics are imparted to the lubricating compositions. In all cases, the amount and the nature of the additives are adjusted so as to effect only slight change in fluidity of the oil base.

The preparation of metallic dithiocarbamate compounds is illustrated by the preparation of nickel dicyclo-hexyl dithiocarbamate. 362 grams (2 mols) of dicyclohexyl amine, 152 grams (2 mols) of carbon disulfide, 83 grams (about 2 mols) caustic soda and 400 cc. of water were mixed in a two-liter flask. The reaction which occurred was very slightly noticeable. About 200 cc. of acetone were added, and as a result a homogeneous mixture was formed and the reaction immediately became more pronounced with the evolution of heat. The mixture was allowed to stand for about 45 minutes, and upon cooling the dithiocarbamate compound crystallized out. Due to the difficulties in filtering, the product was allowed to dry in the air. The yield of the sodium dicyclohexyl dithiocarbamate was 580 grams of a light yellow crystalline product, theoretical yield being 582 grams. 291 grams (1 mol) of the above product was then dissolved in ethyl alcohol and 0.5 mol of crystalline nickel chloride ($NiCl_2.6H_2O$) added. The nickel dicyclohexyl dithiocarbamate crystallized out. The material was dissolved in chloroform, and from the chloroform solution the nickel salt was obtained by evaporation. 200 grams of the nickel dicyclohexyl dithiocarbamate was recovered.

Another example of preparation of a metallic derivative of a disubstituted dithiocarbamate compound is the preparation of nickel di-n-butyl dithiocarbamate (molecular weight 466.7). This compound was prepared by mixing 68.1 grams of sodium di-n-butyl dithiocarbamate (0.3 mol), prepared similarly to the sodium dicyclohexyl dithiocarbamate above, in 200 cc. of water, to 45 grams (0.15 molecules) of nickel nitrate dissolved in 100 cc. of water. A precipitate of the nickel di-n-butyl dithiocarbamate was formed which was separated, washed with water and then with 95% ethyl alcohol.

The product obtained was dissolved in a solvent extracted high viscosity index lubricating oil of S. A. E. 40 characteristics in the amount of 0.25% and was run for 14 hours in a single cylinder C. F. R. gasoline engine operated at 1200 R. P. M. with a cooling jacket temperature of 390° F. At the conclusion of the run, the engine was dismantled and the engine parts, especially the piston, were carefully examined. Each part of the piston was given a demerit rating depending upon its condition: wear, cleanliness, presence of gum and/or carbonaceous deposits being evaluated. The data were tabulated and by a correlation in which the relative importance of each demerit was considered, the overall rating of the engine condition was obtained. The lowest demerit rating is best. In comparison with the uncompounded oil the following data were obtained.

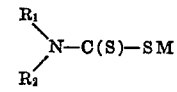
	Base oil	Blended oil
Overall demerit	4.27	0.78
Rings stuck	3	0
Degrees of ring sticking	855	0
Ring zone cleanliness demerit	5.33	0.33
Carbon on underside of piston, gs	4.0	0.5
Piston skirt varnish demerit	5.0	0.0

It is apparent that the engine condition was materially benefited in every respect by the presence of the additive. Ring sticking was completely eliminated, deposition of varnish on the piston skirt was stopped in its entirety, and the accumulation of carbon on the piston underside was retarded materially.

The above description and illustrative examples of the preparation and application of the compositions of the invention are presented for purposes of explanation, but not of limitation, of the invention. Modifications and variations can be made therein without exceeding the scope of the invention. It is intended to claim broadly all the novelty inherent in the invention and to be limited only by the following claims or their equivalents.

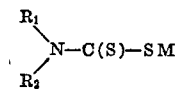
What is claimed is:

1. A lubricating composition comprising a mineral lubricating oil and a dithiocarbamate compound of formula



in which R_1 and R_2 are organic groupings of which R_1+R_2 contains at least eight carbon atoms in alkyl groups and M is a metal selected from the class consisting of alkaline earth metals and metals of the iron sub-group of the periodic system.

2. A lubricating composition comprising a mineral lubricating oil, a dithiocarbamate compound of formula



in which R_1 and R_2 are organic groupings of which R_1+R_2 contains at least eight carbon atoms in alkyl groups and M is a metal selected from the class consisting of alkaline earth metals and metals of the iron sub-group of the periodic system, and a coupling agent.

3. A lubricating composition according to claim 2 in which the coupling agent is a higher alcohol.

4. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5% of an oil soluble salt of a dithiocarbamic acid and a metal of the iron sub-group of the eighth group of the periodic system.

5. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5.0% of an oil soluble salt of a dithiocarbamic acid and an alkaline earth metal.

6. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5.0% of an oil soluble nickel dithiocarbamate.

7. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5.0% of nickel di-n-butyl dithiocarbamate.

8. A lubricating composition comprising a mineral lubricating oil and 0.25% of nickel di-n-butyl dithiocarbamate.

9. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5% of a calcium salt of a dithiocarbamic acid.

10. A lubricating composition comprising a mineral lubricating oil and from 0.2% to 5.0% of a barium salt of a dithiocarbamic acid.

11. The method of cleansing and lubricating automotive engines which consists in charging to said engines a lubricant comprising a mineral hydrocarbon oil and having incorporated therein a derivative of a dithiocarbamic acid and a metal selected from the class consisting of alkaline earth metals and metals of the iron sub-group of the periodic system in amount and potency sufficient to obviate the formation of varnish and sludge deposits and to remove any such deposits already present.

12. Method of lubricating engines with a composition according to claim 5 in which the dithiocarbamate compound is a derivative of a dialkyl dithiocarbamic acid.

13. Method of lubricating automotive engines with a composition according to claim 4 in which the dithiocarbamate compound is the nickel salt of di-n-butyl dithiocarbamic acid.

GEORGE L. MATHESON.