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LUBRICANT

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The present invention relates to improved lubricants and especially to crankcase oils for the lubrication of internal combustion engines, and particularly for high pressure liquid fuel injection engines such as Diesel engines. This application is a continuation in part of application No. 234,899, filed October 14, 1938, now Patent No. 2,233,426, granted March 4, 1941. The invention will be fully understood from the following description.

During the past several years it has been found desirable to add certain polyvalent metal soaps to lubricants, especially such lubricants as are used for automotive engines of the Diesel type. The function of these soaps is complex but the effect is mainly one of maintaining a clean engine condition. The various soaps have peculiarities in behavior depending on the particular metals and to some degree the acid radicals with which they are combined. Certain of the soaps are completely insoluble and others, while soluble, cause gelling of the oil. Still others are capable of giving clean engines, but do not appear to be able to reduce engine wear or perhaps even cause excessive engine wear. Thus the various soaps, while their functions may in some cases overlap, are not equivalents in some certain respects.

It has now been found that certain mixed soap compositions are very much superior to compositions containing a single soap. Of the various soaps to be under consideration here, there appear to be three general groups; the first comprises calcium and magnesium soaps which appear to be interchangeable, although they may be used together if desired. The second type of soap is that of aluminum and the third of nickel. The results produced by these various soaps as stated above overlap to some extent, but nevertheless they do not appear to be full equivalents. Improved results are obtained by using a mixture of soaps from any two of these groups, or by using the three types of soap in combination. Thus either a nickel or an aluminum soap may be used along with either calcium or magnesium and the nickel-aluminum combination is also good. Furthermore, improved results have been obtained by use of three soaps, nickel, aluminum and calcium or magnesium.

It has been stated that the type of acids used is important. Any of the fatty acids may be employed but it is preferable to use predominantly saturated fatty acids with melting points below 50° C. The higher melting acids such as stearic and palmitic are less desirable because their

soaps have a tendency to be less soluble than those of acids having melting points below 50° C., such as capric, lauric and the like. Various mixed acids may be used such as are obtained from the commercial fats or may be made up synthetically, and it is found that if a substantial portion of unsaturated acids be present, say from about 10 to 30%, oil solubility is more readily obtained. Unsaturated acids such as oleic or erucic can also be used alone. Another type of acids that may be employed is that produced by low temperature oxidation of paraffin wax with air, preferably using catalysts. Highly refined oils may be oxidized in the same way, for example, highly solvent extracted oils or hydrogenated oils, but the most suitable product appears to be the so-called oxidized acids which are obtained from sweater oil. This oil is sweated from petroleum waxes and is oxidized catalytically with air at temperatures from about 110 to 160° C.

Naphthenic acids such as those obtained from Venezuelan, Columbian, Gulf Coast, and Roumanian crudes may also be used in making the soaps.

In manufacturing the soaps, the best procedure is to first obtain a soda or potash soap of the particular organic acid or mixture of acids and then prepare the polyvalent metal soap mixture from the soda or potash soap by double decomposition using water soluble salts of the polyvalent metals, for example chlorides or nitrates. In some instances, the polyvalent soaps may be prepared separately and then mixed together, but it is generally preferable to make a mixture of the polyvalent soaps directly by co-precipitation and this is particularly useful when calcium soaps are employed because they have a tendency to be less soluble than the other metal soaps and the co-precipitation method produces materials which are freely soluble.

The amount of the soap may vary somewhat depending on the particular soaps employed and the service in which they are to be used, but the total amount of the polyvalent metal soap varies in general from about $\frac{1}{8}$ to $3\frac{1}{2}\%$ of the oil. The various soaps may be used in equal proportions, but good results are obtained over a fairly large range of variation in proportions. It is preferable to provide that each of the two or more soaps is present in not less than $\frac{1}{8}$ of the total soap. Thus if 3% of the total soap is employed, the mixture may contain from about .3 to 2.7% of the aluminum soap with from 2.7 to .3% of calcium, magnesium or nickel soap.

It is found desirable to use soap mixtures which are substantially free from non-saponaceous ingredients such as free acids, esters, lactones, lactides, and the like and this may be accomplished in various ways, but the best method is by extracting the soap mixtures with oxygen-containing solvents such as alcohols, ketones, and the like in which the polyvalent soaps are relatively insoluble.

In spite of what has been said in the paragraph above, it has been found desirable to add small amounts of certain specific acids to the soap mixtures, but these acids are not of the preferred type used in manufacturing polyvalent soap. The best acid to be added appears to be a good grade of stearic acid, but similar high molecular weight saturated acids may be employed instead. This acid is added to the oil or to the soap mixture after extraction and the amount may vary from about .1 to 1% of the total mixture.

ture was prepared by co-precipitation of the said soaps by addition of aluminum and calcium chlorides to the soda soap of the oxidized sweater oil acids. The blend also contained 5% added free stearic acid.

Each of the three samples described above was subjected to a test over long periods in a Caterpillar single cylinder Diesel engine under comparable running conditions. After each test the pistons were taken down and examined carefully and a demerit rating was assigned to each part depending on its condition, for example, to the rings, slits, and grooves, filter, piston skirt, and liners. In considering these demerit numbers, it should be borne in mind that the lower numbers indicate superior condition. The demerit numbers were then weighted to obtain an overall demerit for the piston as a whole. The amount of oil used was measured as well as the wear on the liner. All of these data are assembled in the following table:

Caterpillar single cylinder engine tests

Eng. No.	Run No.	Hours	Overall piston demerit	Ring edge sharp	Demerits							Oil cons. BHP hrs./gallon	Liner wear per 1,000 hrs.	
					Ring zone cleanliness			Carbon	Skirt and liner	Varnish on skirt	Oil filter		Max.	Av.
					Slits	Grooves	SGLS*							
SAMPLE 1														
C-2---	3	500	1.35	0.17	0.0	3.1	1.72	4.6	0.92	1.0	2	3,290	0.0046	0.0015
		1,000	2.00	0.67	0.5	4.5	2.52	5.0	1.92	0.8	5	3,590	0.0045	0.0016
SAMPLE 2														
C-1---	17	500	2.25	0.17	3.0	4.2	3.03	4.8	3.33	4	4	3,490	0.0028	0.0012
SAMPLE 3														
C-2---	8	500	1.13	0.25	0.0	2.3	1.28	4.4	0.67	0.25	1.0	2,770	0.0036	0.0016
		1,000	1.48	1.00	0.25	3.6	2.01	4.3	0.67	0.00	2.0	3,545	0.0022	0.0009

*Cleanliness of ring slits, grooves, lands, and sides.

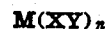
The soaps may be added to any type of mineral oil, that is to say lubricating oils of naphthenic, paraffinic or mixed base crudes, but particularly to the distillates of naphthenic crudes and these compositions are especially desirable for the lubrication of Diesel engines. The oils are preferably well refined having viscosities from 45 to 65 seconds Saybolt at 210° F., and it is preferred that they have pour points of 0° F., or below; whether obtained naturally or by dewaxing or by the use of pour depressants is not important. The essential ingredients of the present composition are the two or more polyvalent soaps of the types mentioned above and the hydrocarbon oil, but other ingredients may be employed such as sludge dispersing agents, oxidation inhibitors, thickening agents, sulfur or phosphorus containing compounds, and the like.

EXAMPLE 1

Lubricating oils are made from naphthenic lubricating distillate having a viscosity of about 55 seconds at 210° F. Sample I contained 1% of an aluminum soap of an oxidized sweater oil acid and .5% of free stearic acid. Sample 2 contained 1% of a calcium soap of the same oxidized sweater acids and .5% of naphthenic acid which was used to solubilize the calcium sweater oil acids soap. Sample 3 contained .75% of a mixture of aluminum and calcium sweater oil acids soaps in equal proportions. This mix-

From the above data it is clear that the oil containing both the calcium and the aluminum soap, Sample 3, is much superior to either of the blends in which the single soaps are used. The overall demerit rating is much better and only in one comparison is it inferior to either of the other samples. This is in respect to the sharpness of the ring edge, but it is clear that this is not of very great importance and is much overshadowed by the improved condition of the slits, grooves, etc., the decrease in the varnish and the improved filter condition.

It has now also been found that in addition to the metal soaps of natural and synthetic fatty acids and naphthenic acid as disclosed in the parent application referred to, it is possible to use a large number of other polyvalent, oil-soluble metal salts. Broadly these metal compounds may be considered as having the general formula



where M is a metal in one of the two groups of the alkaline earth metals and aluminum; X is either oxygen or sulfur, and Y is an organic radical, the letter n representing the valency of the metal M. Some of the classes of metal salts which come within the general scope of this invention but were not disclosed in the parent application are the phenolates, thio-phenolates, as well as alkylated derivatives of either of them, sulfide derivatives of phenolates, thio-phenolates and alkylated derivatives thereof; alcoholates,

carbamates and thio carbamates, xanthates and enolates. In the case of salts of the alkyl phenol sulfides, the metal M in the above formula may also represent nickel. It is particularly preferred to use alkylated and/or sulfide derivatives of the phenolates and thio-phenolates because these compounds not only possess superior oil-solubility but also are less corrosive to bearings of the lead, bronze and cadmium-silver type. In addition they frequently impart superior lubricant action and give lower demerit ratings in engine tests.

It has also been found that the salts of varium may be properly included along with calcium and magnesium salts in the general field of alkaline earth metal salts as far as this invention is concerned.

It has been found that the metal compounds of this invention are particularly applicable in Diesel lubricants comprising a major proportion of a refined mineral oil having a viscosity of 40 to 75 seconds Saybolt at 210° F. and preferably having a pour point of 30° F. or lower.

By the use of the metal salts according to this invention such small amounts of metal compounds are used, and particularly when used in a mineral oil of a sufficiently low viscosity and low pour point to be suitable for a Diesel lubricant, that no substantial thickening is effected by the incorporation of the metal salt. For instance, the increase in viscosity is in most cases less than 10% of the Saybolt viscosity at 210° F.

Although as stated previously the total amount of metal compounds to be used should be between the approximate limits of 0.1 to 3.5% by weight of the mineral oil used, it is normally preferred to maintain the total amount of metal compounds added between the approximate limits of 0.2 and 1.5%. Larger quantities of the additive usually fail to confer enough additional benefit to justify the additional cost. Also although it is desired that in a mixture of the several different types of metal compounds, each type should be present in an amount corresponding to at least 0.1 of the total amount of the metal compounds present, it is ordinarily preferred for practical operation that each type of metal compound be present in at least 1/4 the amount of the total compound used. Equal proportions or a ratio of 1 to 2 are in most cases satisfactory for practical operation.

For the sake of illustration, a number of specific examples of the metal compound falling within the scope of this invention are listed herewith. (Under the first group listed, namely the phenolates, corresponding compounds are given for all of the four different metals, namely calcium, magnesium, barium and aluminum, but in the rest of the classes, to avoid unnecessary permutations, only the calcium compound is given as representative of the various metals.)

Phenolates

Calcium phenolate, $\text{Ca}(\text{OC}_6\text{H}_5)_2$
Magnesium phenolate, $\text{Mg}(\text{OC}_6\text{H}_5)_2$
Barium phenolate, $\text{Ba}(\text{OC}_6\text{H}_5)_2$
Aluminum phenolate, $\text{Al}(\text{OC}_6\text{H}_5)_3$

Thio-phenolates

Calcium thio-phenolate, $\text{Ca}(\text{SC}_6\text{H}_5)_2$

Mixed oxy- and thio-phenolates

Calcium oxy-thio-phenolate, $\text{Ca}(\text{OC}_6\text{H}_5)_2\text{SC}_6\text{H}_5$

Alkylated phenolates

Calcium di-tertiary butyl phenolate,
 $\text{Ca}(\text{OC}_6\text{H}_4\text{-t-C}_3\text{H}_7)_2$

Alkylated thio-phenolates

Calcium tertiary amyl thio-phenolate,
 $\text{Ca}(\text{SC}_6\text{H}_4\text{-t-C}_5\text{H}_{11})_2$

Sulfide phenolates

10 Calcium phenolate sulfide, $\text{Ca}(\text{O-C}_6\text{H}_4)_2\text{S}$

Alkylated phenolate sulfides

Calcium tertiary amyl phenolate sulfide,
 $\text{Ca}(\text{O-C}_6\text{H}_3\text{-t-C}_5\text{H}_{11})_2\text{S}$

15 Calcium tertiary amyl phenolate disulfide,
 $\text{Ca}(\text{O-C}_6\text{H}_3\text{-t-C}_5\text{H}_{11})_2\text{S}_2$

Thio-phenolate sulfides

Calcium thio-phenolate sulfide, $\text{Ca}(\text{S-C}_6\text{H}_4)_2\text{S}$

20 Alkylated thio-phenolate sulfides

Calcium tertiary amyl thio-phenolate sulfide,
 $\text{Ca}[\text{S-C}_6\text{H}_3(\text{t-C}_5\text{H}_{11})]_2\text{S}$

Alcoholates

25 Calcium methylate, $\text{Ca}(\text{O-CH}_3)_2$

Calcium ethylate, $\text{Ca}(\text{O-C}_2\text{H}_5)_2$

Calcium propylate, $\text{Ca}(\text{O-C}_3\text{H}_7)_2$

Calcium isopropylate, $\text{Ca}(\text{O-i-C}_3\text{H}_7)_2$

Calcium hexylate, $\text{Ca}(\text{O-C}_6\text{H}_{13})_2$

30 Calcium octylate, $\text{Ca}(\text{O-C}_8\text{H}_{17})_2$

Calcium octadecylate, $\text{Ca}(\text{O-C}_{18}\text{H}_{37})_2$

Calcium methylate octadecylate,
 $\text{Ca}(\text{O-CH}_3)\text{O-C}_{18}\text{H}_{33}$

Thio alcoholates

35 Calcium thio-hexylate, $\text{Ca}(\text{S-C}_6\text{H}_{13})_2$

Carbamates

Calcium carbamates of the general formula
40 $\text{Ca}(\text{OOC-NR}_2)_2$, in which R is a hydrocarbon radical preferably an alkyl group having at least 4 carbon atoms such as butyl or octyl, or a cyclic hydrocarbon group such as cycloalkyl, aryl, etc.

Thio-carbamates

45 Calcium di-butyl mono-thio carbamates,
 $\text{Ca}[\text{S-OC-N(C}_4\text{H}_9)_2]_2$

Di-thio carbamates

50 Calcium di-butyl di-thio carbamate,
 $\text{Ca}[\text{S-SC-N(C}_4\text{H}_9)_2]_2$

Xanthates

Calcium amyl xanthate, $\text{Ca}(\text{S-CS-OC}_5\text{H}_{11})_2$

55 Thio-xanthates

Calcium amyl thio-xanthate, $\text{Ca}(\text{S-CS-SC}_5\text{H}_{11})_2$

Phosphites

60 Calcium di-octyl phosphite, $\text{Ca}[\text{OP}(\text{OC}_8\text{H}_{17})_2]_2$

Thio-phosphites

Calcium di-octyl thio-phosphite,
 $\text{Ca}[\text{SP}(\text{OC}_8\text{H}_{17})_2]_2$

65 Phosphates

Calcium di-octyl phosphate,
 $\text{Ca}[\text{OP-O}(\text{OC}_8\text{H}_{17})_2]_2$

Thio-phosphates

70 Calcium di-octyl di-thio-phosphate,
 $\text{Ca}[\text{SP-S}(\text{OC}_8\text{H}_{17})_2]_2$

Enolates

Calcium enolate hexyl ester of aceto-acetic acid,
75 $\text{Ca}[\text{OC}(\text{CH}_3)=\text{CH-CO-O-C}_6\text{H}_{13}]_2$

Many of the compounds listed are only sparingly oil soluble and can consequently only be employed with the assistance of a mutual solvent such as, for instance, stearic acid, stearyl alcohol, dibutyl phthalate, tricresyl phosphate, or other high boiling compound. It is therefore generally preferred so to alter their structure by alkylation as to obtain sufficient inherent oil solubility to render the use of mutual solvents unnecessary. Where compounds contain a sulfur group it is usually sufficient to have the equivalent of two alkyl chains of at least 4 to 5 carbon atoms present as exemplified by:

Calcium tertiary amyl phenolate sulfide,
 $\text{Ca}(\text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{tC}_5\text{H}_{11})_2\text{S}$

When sulfur groups are absent even more carbons in alkyl chains are required and the equivalent of two alkyl chains of at least 8 carbons appears essential, as in:

Calcium octyl phenolate, $\text{Ca}(\text{OC}_8\text{H}_7 \cdot \text{C}_8\text{H}_{17})_2$
 Calcium di-butyl phosphite, $\text{Ca}(\text{OP} \cdot (\text{C}_4\text{H}_9)_2)_2$

It is obvious that as the solvent power of an oil varies with its crude source the exact minimum requirements, as given above will also vary.

In the various compounds discussed above, which involve sulfur as one constituent, it is understood that the corresponding selenium or tellurium compounds could also be used.

For further illustration the following additional examples are given of lubricants prepared according to this invention and comprising combinations of various metal salts.

EXAMPLE 2

To the same mineral oil described in Example 1, metallic salts of tertiary amyl phenol sulfide were added. Sample 1 contained 1% of the nickel salt, sample 2 contained 1% of the barium salt, and sample 3 contained 0.5% of each.

Samples 1 and 2 were run in a single cylinder Caterpillar Diesel engine for 60 hours under comparable operating conditions. The same sample 2, and sample 3, were run in a second similar single cylinder Caterpillar Diesel engine, also under comparable operating conditions, though not identical with those employed in the first engine.

After each test the engine was dismantled, examined and rated following the procedure described in Example 1. The results are assembled in the following table:

Caterpillar single cylinder engine tests

Engine No.	Run No.	Sample No.	Metal used	Rings stuck	Engine demerits				
					Heat groove	Ring grooves and sides		Piston skirt varnish	Oil filter
						#1 and #2	#3 and #4		
1	35J	1	1.0% nickel salt	0	7.0	13.5	15.0	0.75	3.0
1	35K	2	1.0% barium salt	0	2.0	16.0	13.0	0.75	2.0
2	19F	2	1.0% barium salt	1	7.5	11.5	28.5	1.25	2.0
2	19J	3	0.5% nickel salt+0.5% barium salt	0	6.0	9.0	16.0	1.0	1.5

From the above data it is apparent that in No. 1 engine the oil containing 1.0% of the barium salt (sample 2) performed better than that with 1.0% of the nickel salt (sample 1), and that the oil blended with the mixture of 0.5% of each (sample 3) performed better than the 1.0% barium salt composition (sample 2). It may be

concluded therefore that the use of the two additives in combination give results superior to those obtainable with either alone.

EXAMPLE 3

To the above uncompounded mineral oil 0.5% of the nickel salt of tertiary amyl phenol sulfide and 0.5% of the calcium salt of the enol form of the hexyl ester of aceto acetic acid was added. The resulting blend was a clear, fluid oil not appreciably different from the original mineral oil in appearance. When mixed with carbon black, the latter settled only very slowly indicating that the composition possessed dispersing ability not characteristic of the mineral oil alone.

It has been pointed out above that many of these compounds, particularly those containing sulfur, are non-corrosive to such bearing metals as the lead bronzes and the cadmium-silver alloys. Others, however, lack this desirable property and are therefore used most advantageously in conjunction with such known corrosion preventions as sulfur compounds and sulfurized oils, anti-oxidants (particularly phenols) metal deactivators (particularly organic phosphites), etc. For greater oiliness and lubricity, oiliness agents may be included; thickeners, viscosity-index improving agents, pour depressors and dyes may all be present in the finished lubricating composition.

This invention is not to be limited by any specific examples which have been presented herein solely for the purpose of illustration, but only by the following claims, in which it is desired to claim all novelty inherent in the invention.

I claim:

1. An improved lubricating composition comprising a mineral lubricating oil and small amounts of polyvalent metal salts selected from each of the groups consisting of aluminum, and alkaline earth metal salts, the total amounts of such metal salts amounting to from 0.1% to 3.5% by weight of the oil and the amount of each type of metal salt being at least one-tenth of the total metal salt present.

2. Lubricant according to claim 1 in which the various metal salts used have the general formula

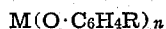


in which M represents the metal, X represents oxygen, sulfur, selenium or tellurium, and Y represents an organic radical, the subscript n representing a numeral corresponding to valence of metal M.

3. Lubricant according to claim 1 in which the metal salts used are compounds containing an organic radical selected from the group consisting of alkyl, aryl, alkylated aryl, carbamyl, xan-

thyl, thio-xanthyl, enolyl, acyl and thio-acyl, phosphyl and thio-phosphyl.

4. Lubricant according to claim 1 in which at least one of the metal compounds has the formula



in which M is the metal and R is an alkyl group sufficiently large to make the compound soluble in mineral oil.

5. An improved lubricant for Diesel engines comprising a major proportion of a refined mineral oil having a viscosity of about 40 to 75 seconds Saybolt at 210° F., and a pour point at least as low as 0° F. and containing 0.1 to 3.5% of polyvalent metal salts, at least 1/4 of the total amount of metal salts present being selected from each of the groups consisting of aluminum, and alkaline earth metal salt.

6. An improved lubricant for Diesel engines comprising essentially mineral oil having a viscosity of 40 to 75 seconds Saybolt at 210° F., and a pour point at least as low as 30° F. into which has been dissolved from 0.1 to 3.5% by weight of oil-soluble polyvalent metal salts having the general formula



in which M is the metal and R is an oil-solubility-imparting alkyl group, said metal salts being selected from at least two of the groups consist-

ing of aluminum, nickel and alkaline earth metal salts, the amount of each type of salt present being at least 1/4 of the total amount of metal salt present.

7. A lubricating composition comprising a major proportion of a mineral lubricating oil and a small amount each of a nickel alkyl phenolate sulfide and barium alkyl phenolate sulfide.

8. Lubricant according to claim 6 in which the said lubricant contains one of said salts of aluminum and one of said salts of an alkaline earth metal.

9. Lubricant according to claim 6 in which the said lubricant contains one of said salts of nickel and one of said salts of an alkaline earth metal.

10. An improved lubricating composition comprising a mineral lubricating oil and small amounts of polyvalent metal salts selected from at least two of the groups consisting of aluminum, nickel and alkaline earth metal salts, the said nickel salt being, in each instance in which it is used, a compound having the general formula $Ni(OC_6H_3R)_2S$, in which R is an oil-solubility-imparting alkyl group, the total amounts of such metal salts amounting to from 0.1% to 3.5% by weight of the oil and the amount of each type of metal salt being at least one-tenth of the total metal salt present.

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