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LUBRICATING OIL COMPOSITION

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The present invention relates to improvements in lubricants and especially to the improvement of lubricating oils principally useful for internal combustion engines operating under severe conditions. The invention will be fully understood from the following description.

Lubricating oils which exhibit improved performance under all types of operating conditions when used for the lubrication of heavy duty gasoline engines and for Diesel engines are coming into greater and greater demand. It has been proposed to add various ingredients to these oils to improve their behavior in such service, and the addition of certain metal-containing organic compounds, such as metallic soaps, metallic phenolates and the like, to mineral lubricating oils results in bringing about greater engine cleanliness and avoidance of ring sticking, varnish formation and carbon deposition. One drawback to the use of such metallic compounds has been that by their use the deterioration of the oil is accelerated somewhat and corrosion of metal parts is promoted. This corrosive action of metallic soaps and the like is inhibited to some extent by the addition of certain other agents. At the same time, a considerable improvement in the condition of engines has resulted in the use of the addition agents described in combination with agents which inhibit their normal corrosive action.

It has been found that some addition agents are not satisfactory when added to high viscosity index oils. Moreover, such metallic detergent agents have often not heretofore been found to be particularly satisfactory when used with oils refined by the use of selective solvents. It has long been the belief that the best results from the use of the metallic detergent agents are obtained when they are used with non-extracted naphthenic oil base stocks.

It is an object of the present invention to provide a lubricating oil base stock which may be blended with the addition agents described above to produce a lubricant which gives unusual engine cleanliness and which has satisfactory non-corrosive characteristics. It is a further object of the invention to provide a base stock which may have been extracted with selective solvents, such as phenol, liquid sulfur dioxide, furfural, etc., until it exhibits a high viscosity index and which is highly suitable for use in blending with the metallic detergent agents hereinbefore described.

It has been found, in accordance with the present invention, that outstanding performance of these additives can be obtained if they are compounded with base stocks characterized by having the property of imparting a dark blue to black stain to a steel surface when the steel, in the form of a bright steel strip, is immersed in

the unblended oil stock for two hours while the oil temperature is maintained at 425° F. Such an oil is obtainable, for example, from paraffinic crudes produced in the Panhandle field. It is not known just what component of the oil causes the production of the stain except that sulfur is involved, since the stain contains sulfur. It is not caused by particularly large quantities of sulfur, since many high sulfur oils do not have this property. It may, therefore, be due to sulfur present in some particular form, or the sulfur may play only a secondary role in causing the staining.

Tests of a variety of samples have shown that the stain producing property is associated with unusual cleanliness of the engine in which they are used. It seems probable that the stain pacifies the metallic surfaces, which normally tend to hasten the deterioration of the metallic compounds added. By the use of an oil base having the characteristics described, the action of any deterioration preventing agent also present is aided and the normal corrosive action of the metallic additive is thereby further pacified. Furthermore, while the use of extracted oils has heretofore resulted in a low degree of engine cleanliness, the results obtained on the use of stain producing base stocks, while slightly poorer in the case of extracted oils than in the case of acid treated oils, are generally still so satisfactory that the extracted oils may advantageously be used in conjunction with the metallic additives.

The use of the stain producing base stock is particularly valuable in the production of oils having high viscosity indices, i. e., over 70, in connection with which the metallic detergent agents may be used without the disadvantages formerly encountered when certain metallic additives were used with such oils.

The metallic addition agents which may be advantageously added to the stain producing lubricating oil base stocks of the present invention comprise particularly the metal salts of hydroxy organic compounds, for example, metallic phenolates, metal alcoholates, metallic aroxy sulfides and metallic enolates, and the metal salts of organic acids, for example, metallic soaps, metallic salts of organo substituted phosphoric and salicylic acids, metallic xanthates, metallic sulfonates, and the like. These compounds may be added alone or preferably in conjunction with certain cooperating compounds, such as the higher alcohols, amines, esters, ketones, ethers, etc. The metallic compounds are preferably added in quantities ranging from 0.05 to 1.5%, the particularly preferred limits being 0.2 to 1.0%.

The lubricating oil base stock for the compositions of the present invention may be any mineral oil base stock having the characteristic of staining a steel surface under the conditions de-

scribed above and may be a fraction resulting from various physical and chemical refining treatments, such as solvent extraction, acid treating, selective precipitation, etc. For the best results, however, the base stock chosen should be one which produces substantially no stain on a copper strip in the conventional A. S. T. M. corrosion test, known as Standard Test D130-30, when conducted for one-half hour at a temperature of 212° F. For the lubrication of medium and high speed Diesel engines it is general practice to use a lubricating oil base stock having a Saybolt viscosity at 210° F. of 45 to 90 seconds, whereas for aviation and similar services this viscosity may extend up to 150 seconds. The viscosity index may vary over a wide range; but, as stated above, the invention is particularly suited to the use of high viscosity index oils, i. e., those having a viscosity index of 70 or above. Oils having a viscosity index as high as 105 or higher are within the scope of the present invention. The oils may be free from other addition agents or they may contain materials for particular purposes, for example, thickeners, sludge dispersing agents, dyes, pour depressants, viscosity index improvers, solvents, oiliness agents, and antioxidants.

In the following examples oil blends made from various types of base stocks have been compared in engine performance tests. These examples are intended as illustrations only and do not limit the scope of the invention in any way.

EXAMPLE 1

Several types of lubricating oil base stocks, obtained from various types of crudes and refined by different methods, were tested for their action on cold rolled steel strips (2" x 1" x 1/8") at a temperature of 425° F. over a period of two hours. The steel strips were immersed in the oil contained in separate glass vessels and in the absence of addition agents. The results of these tests are shown in Table I.

Table I

Oil sample	Type of crude	Method of refining	V. I.	S. A. E. grade	Appearance of steel strip after test
A.....	Coastal naphthenic.....	Acid treated.....	42	30	No stain.
B.....	Panhandle paraffinic.....	Extracted.....	98	20	Black stain.
C.....	Mid-Continent paraffinic.....	do.....	103	20	No stain.
D.....	do.....	do.....	110	20	Do.
E.....	do.....	do.....	95	20	Do.
F.....	Colombian naphthenic.....	do.....	75	20	Do.
G.....	Smackover high natural sulfur naphthenic.....	Acid treated.....	48	30	Very slight stain.
H.....	Pennsylvania paraffinic.....	do.....	99	20	No stain.
J.....	do.....	Extracted.....	107	20	Do.
L.....	Panhandle paraffinic.....	Acid treated.....	90	30	Black stain.
M.....	Mid-Continent paraffinic.....	do.....	88	20	No stain.
N.....	Coastal naphthenic.....	Extracted.....	68	30	Do.

EXAMPLE 2

A number of sixty hour tests in a single cylinder Caterpillar Diesel engine were made under high temperature conditions (140° F. atmospheric temperature, 195° F. oil temperature, 850 R. P. M. engine speed) using various lubricating oils having base stocks selected from those described in Example 1 and having in addition small amounts of metal-containing addition agents of the type hereinbefore described and small amounts of cooperating agents. At the completion of each test the engine was dismantled and the piston rated on a demerit system according to the deposits found on the various parts. The results

are shown in Table II, wherein the letter designations for the base oils refer to the oils having the corresponding designation in Table I.

Table II

Base oil	Additives	Engine demerits ¹
A.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	0.77
B.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	0.56
C.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	1.06
D.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	1.42
E.....	0.5% barium diisobutyl phenoxy sulfide + 0.5% barium diisobutyl phenoxy disulfide + 0.25% stearyl alcohol.	0.77
F.....	0.5% barium diisobutyl phenoxy sulfide + 0.5% barium diisobutyl phenoxy disulfide + 0.25% stearyl alcohol.	0.75
G.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	0.69
H.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	0.90
J.....	1% barium diisobutyl phenoxy sulfide + 0.25% stearyl alcohol.	0.85

¹ Condition of ring slots, grooves, lands and ring sides.

It is obvious that the performance of the various oils varied widely but that the blend in oil B provided definitely the cleanest engine conditions. Oil G, which causes slight staining in the steel strip test, showed up somewhat superior to the remaining oils. It should be noted that in the demerit system the lower the rating the lighter are the engine deposits.

EXAMPLE 3

Several normal temperature tests were made on a single cylinder Caterpillar Diesel engine (70° F. atmospheric temperature, 140° F. oil temperature, 850 R. P. M. engine speed) using various lubricating oils, also having base stocks selected from those tested for staining properties as described in Example 1, and containing various addition

agents. The duration of the tests and the engine demerits observed are indicated in Table III.

Table III

Base oil	Additives	Hours	Overall engine demerits
A.....	0.5% cobalt p-ter-amyl phenoxy sulfide+0.2% nickel oleate.	113	1.30
M.....	0.5% cobalt p-ter-amyl phenoxy sulfide+0.2% nickel oleate.	104	1.36
B.....	0.5% cobalt p-ter-amyl phenoxy sulfide+0.2% nickel oleate.	263	1.29

Again the superiority of the oil B blend is manifest, this product maintaining the engine in as

clean a condition for 263 hours as did blends of oils A and M for only 104 to 113 hours.

EXAMPLE 4

Another series of sixty hour tests in a single cylinder Caterpillar Diesel engine were made under severe conditions, using lubricating oils containing additional oil base stocks selected from those described in Example 1. The oils were rated on a demerit system, according to which oil A, previously considered one of the best for Diesel engine service, was taken as the reference oil and given a demerit rating of 100. The other oils were rated in comparison with oil A on a percentage basis, the rating being adjusted to allow for some differences in engine conditions in the various tests. The overall engine demerit ratings thus determined are shown in Table IV. All of the oils tested contained as additives 1% of barium diisobutyl phenoxy sulfide and 0.25% of stearyl alcohol.

Table IV

Base oil	Overall engine demerits (percent of reference)
A	100
N	108
H	118
J	125
L	82
B	89

Here, the blends of the staining oils, L and B, give outstandingly the best performance.

EXAMPLE 5

Base oils A and B, described in Example 1, were each compounded with 0.5% of cobalt p-ter-amyl phenoxy sulfide and 0.2% of nickel oleate and tested in a Hercules model DJBX Diesel engine, each run being made for 84 hours at 1500 R. P. M. under 90% to 95% of full load (210° F. oil temperature, 180° F. water jacket temperature). The oils were given a demerit rating according to the sludge and piston skirt varnish depositions. The ratings are shown in Table V.

Table V

Oil blend	Sludge demerit	Piston skirt demerit
Oil A plus additives	1.83	0.75
Oil B plus additives	1.67	0.58

In this engine also, the blend of the staining oil B performs the better.

The present invention is not to be considered as limited in any way by the various examples described herein, which are given by way of illus-

tration only, but is to be limited in scope solely by the terms of the appended claims.

We claim:

1. A lubricating oil for internal combustion engines comprising a minor proportion of a metal salt of a hydroxy organic compound and a major proportion of a refined mineral lubricating oil base stock capable of imparting a blue to black stain on a bright steel strip which has been immersed in said oil base stock in the absence of addition agents for two hours while the oil temperature is maintained at 425° F.

2. A lubricating oil for internal combustion engines comprising a minor proportion of a metal salt of a hydroxy organic compound and a major proportion of a refined mineral lubricating oil base stock capable of imparting a blue to black stain on a bright steel strip which has been immersed in said oil base stock in the absence of addition agents for two hours while the oil temperature was maintained at 425° F., said oil base stock producing substantially no stain on a copper strip when submitted to the standard A. S. T. M. copper strip corrosion test when conducted for one-half hour at a temperature of 212° F.

3. A lubricating oil according to claim 2 in which the metal salt is a metallic aroxy sulfide.

4. A lubricating oil according to claim 2 in which the metal salt is a metallic phenolate.

5. A lubricating oil according to claim 2 in which the metal salt is barium diisobutyl phenoxy sulfide.

6. A lubricating oil according to claim 2 in which the metal salt is a metallic aroxy sulfide and which contains in addition a small quantity of stearyl alcohol.

7. A lubricating oil according to claim 2 in which the base oil has been refined by solvent extraction.

8. An internal combustion engine lubricating oil composition having as a base oil a refined mineral lubricating oil which imparts substantially no stain to a copper strip in the standard A. S. T. M. copper strip corrosion test when conducted for one-half hour at 212° F. and which imparts a blue to black stain to a bright steel strip which has been immersed in said oil base stock in the absence of addition agents for two hours while the oil temperature is maintained at 425° F., and containing in addition to said oil base stock about 1% of barium diisobutyl phenoxy sulfide and about 0.25% of stearyl alcohol.

9. A lubricating oil according to claim 2 in which the base oil has a viscosity index above 70.

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