

## UNITED STATES PATENT OFFICE

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## LUBRICATING OIL

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5 Claims. (Cl. 252—33)

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This invention has to do with improved oils for the lubrication of internal combustion engines characterized by their ability to minimize or prevent the adherence or formation of lacquers and carbonaceous deposits on pistons and rings to a degree such that even after extended and severe use of the oil in an engine the pistons, rings and other parts will remain remarkably clean and free of deposits from the fuel and lubricant, thereby permitting longer and more efficient operation of the engine.

At the outset we emphasize the distinction between fluid lubricants with which the invention is concerned and solid or substantially non-fluid greases. Since it is by virtue of the use of the present compositions for the lubrication of internal combustion engines that advantage is taken of their improved and novel properties.

It is known that the common tendency of internal combustion engine lubricating oils, particularly under conditions of extended and severe use in an engine, cause or permit the formation on the pistons and in the cylinder of lacquer-like deposits resulting in such conditions as stuck rings. Various oil additives have been used in attempts to prevent or inhibit the formation of such deposits, and with varying degrees of success. As typical, the so-called oxidation inhibitors have been put into the oil to minimize or inhibit the formation of oxidation products responsible for objectionable deposits. Other additives have been used to secure detergency, depression of pour point, film strength, increase of viscosity index, etc.

In the development of the present invention, the problem of preventing or inhibiting the formation of deposits in the cylinder has been approached from standpoints differing fundamentally from past expedients of which we are aware. One major consideration, based on the fact that under conditions of use components of the oil are converted to acidic lacquer-forming compounds by oxidation, is the incorporation in the oil of agents tending to inhibit formation of such compounds and to neutralize them to unobjectionable compounds as they form. This object, generally speaking, is accomplished by providing for effective or active alkalinity in the oil, the quantum of alkalinity being sufficiently great to neutralize whatever acidic compounds that may form in the oil under at least normal life and use. The degree or potential of alkalinity may vary in different oils depending upon their type and intended usage. For example, a heavy duty oil may have substantially greater present or poten-

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tial alkalinity than an oil intended for less severe service. Also the particular alkaline compound or compounds may be varied to best suit the properties and requirements of a lubricant compounded for a particular purpose or service.

The contemplated general class of compounds for imparting alkalinity to the oil are the alkaline earth metal compounds or salts reactive with acidic compounds that may form in the oil. Typical alkaline compounds are the hydroxides and carbonates of the alkali earth metals. Among these, the alkaline compounds (e. g. hydroxide) of barium are preferred for various reasons, including advantages from standpoints of the facility with which predetermined or accurately controllable amounts may be incorporated in the oil, and the degree (as the examples below will show) to which they prevent undesirable lacquer or other carbonaceous deposits from forming.

Maintenance of the alkaline additive in proper and permanent distribution in the oil, apparently as a true colloidal dispersion, is effected by the presence of a dispersing or peptizing agent, preferably a water insoluble alkali earth metal salt or soap of sulphonated hydrocarbons. Most desirably the dispersing agent will consist of salts formed by reacting with oil soluble sulphonic acid compounds (preferably formed in the oil by prior sulphonation), an alkaline compound (e. g. hydroxide or carbonate) of the alkali earth metal to be incorporated in the oil to furnish the described alkalinity. Thus the presence of oil soluble sulphonates acts as a deterrent to the formation of lacquer-like or carbonaceous deposits, as well as to impart detergent characteristics maintaining dispersion in the oil of such compounds when formed, thereby preventing their adherence to pistons and other engine parts. These barium sulphonates also act and are employed as peptizing agents to accomplish the dispersion of the desired free alkalinity in colloidal form in the oil and to so maintain it. Also by "oil soluble" is meant that a substantial quantity can be dissolved in the oil. It is understood that the amount of soap in the oil may be varied to give greater or lesser degree of detergency and varied also to permit colloidal dispersion of greater or lesser amounts of free alkali as demanded by the use of the oil.

Although by far the best results are obtained by incorporating in the oil the described type of alkaline compound together with alkali earth metal sulphonate soap, the quality and lacquer-forming tendencies of internal combustion engine lubricating oils have been materially improved by

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virtue of the presence of the soap itself, with or without other additives such as anti-foam agents and oxidation inhibitors. A probable explanation is that the alkali earth metal soaps serve as efficient dispersing agents preventing deposition of deleterious carbonaceous compounds out of the oil of gummy and resin-forming constituents.

For many purposes it is also desirable to include in the lubricant a suitable oxidation inhibitor such as catechol or any of the phenolic derivatives heretofore used as oxidation inhibitors. In this connection the invention particularly contemplates the use of acidic inhibitors, such as the phenolic derivatives, together with the described alkaline additive. It appears that one result of incorporating both the alkali and acidic inhibitor in the oil is the formation of a reaction product of the alkali and additive (for example an alkali earth metal phenate) which however retains the characteristic function of the alkali alone, in that its metal radical is displaceable out of the compound by reaction with acidic compounds when formed in the oil. The residual inhibitor remains effective with respect to oxidation tendencies.

The superiority of the present lubricants has been established by engine tests under severe conditions and over extended periods of time. Using as a base stock well refined straight mineral oils obtained from crude petroleum, and in which were incorporated the free alkali, dispersing and oxidizing agents as in the examples hereinbelow given, it was found that after continuous runs as long as 200 hours with engine jacket temperatures around 345° F. and crankcase oil temperatures of about 205° F., the piston rings were entirely free, there were no carbon deposits in the slots of the oil ring and substantially no lacquer formation on the pistons or elsewhere in the cylinders. The bearings showed no evidence of corrosion or excessive wear.

In the following, a typical procedure is described for the treatment of lubricating distillates and the incorporation of the free alkali, peptizing or dispersing agent, and such further additives as anti-oxidant and anti-foaming agents, if desired. As illustrative, barium hydroxide is selected as the alkaline additive and barium sulphonates as the dispersing medium, all however with the understanding that other alkaline compounds of alkali earth metals may be similarly employed to advantage.

A lubricating distillate was treated with 25 lb./bbl. of 98% sulphuric acid to reduce the content of unsaturated hydrocarbons, centrifuged for the removal of sludge, then neutralized with caustic soda solution, and the naphtha diluent used to lower the viscosity in the treating operation separated by distillation with steam. The resulting alkaline oil was redistilled under vacuum to separate the stock into various grades of well refined lubricating oil, relatively free of unsaturated constituents. A selected grade is treated for the production of sulphonic acids by efficiently contacting the oil with a sulphonating agent such as concentrated sulphuric acid, fuming sulphuric acid, or even SO<sub>3</sub>. This operation is conducted at a proper temperature which may be around 110° F. in the initial contacting step. The action of concentrated sulphuric acid or oleum on the oil forms sulphonic acids of two general types, namely sulphonic compounds quite soluble in water and relatively insoluble in oil, usually called "green acids," and other sulphonated compounds less soluble in water and soluble in oil, usually termed "mahogany acids."

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After contacting the stock with the sulphonating agent, the mixture of oil, free acid and sludge is centrifuged for the separation of the sludge. The centrifuged acid oil will usually have an acidity ranging from 1.5 to 2.0 mg./KOH/gm., when the oil has been contacted with 18 lb./bbl. of fuming sulphuric acid, containing 15% SO<sub>3</sub>. This acidity is due to mineral acidic compounds such as free sulphuric acid, dissolved sulphur dioxide and the like, and organic material of the nature of sulphonic acids.

By contacting this acid oil with a desired amount of barium hydroxide (and preferably at elevated temperature to increase reactivity, decrease viscosity, and facilitate removal of water), the barium hydroxide is caused to unite with the mineral acidic material such as free sulphuric acid, to form insoluble barium sulphate. Some of the barium hydroxide unites with the sulphonated organic material to form the barium salts or soaps of these oil soluble acidic compounds. After removal of water this mixture is then subjected to filtration, as, for example, through an inert bed of filtering medium such as "Super-Cel" or finely divided diatomaceous earth or its equivalent. This operation is conducted at elevated temperature and accomplishes the separation of the insoluble barium sulphate and other contaminating elements from the desired oil soluble barium salts of the organic acidic compounds. In conducting this neutralizing step an excess of the alkali is employed, so that the filtered oil is alkaline and contains a desired amount of the oil soluble barium salts we wish to leave in the oil, in addition to an amount of free barium salt. As previously indicated, the barium or other oil soluble alkali salts of the sulphoned hydrocarbons have the property of peptizing so that a considerable amount of free alkali can be dispersed in the oil in colloidal form.

The following gives certain specific examples of base stocks, finished internal combustion engine lubricating oils and the general procedure followed in their preparation.

#### Example 1

(1) Stock was S. A. E. 30 oil which had been previously treated with 25 lb./bbl. of 98% sulphuric acid and neutralized with caustic soda solution. The properties of this oil were as follows:

Grav. (A. P. I.)	20.2
Flash (Cl. O. C.)	445
Fire (Cl. O. C.)	515
Color (U. C.)	2
Vis./100° F. (S. U.)	623.0
Vis./130° F. (S. U.)	251.0
Vis./210° F. (S. U.)	61.8
V. I.	58
Corrosion	Negative
Ash	Nil
Sulphur	2.21 per cent.

(2) This oil was treated with 18 lb./bbl. of 15% fuming sulphuric acid, the oil being first heated to 110° F. before adding the acid. The mixture was then agitated by a mechanical stirrer for 10 minutes and the acid oil then centrifuged and the sludge separated.

(3) The centrifuged acid oil was then treated with 25 grams per liter of barium hydroxide mixed with water, stirring to 275° F. to drive off water used in dissolving the barium hydroxide.

(4) Filtered immediately through a bed of

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"Super-Cel" about one-inch thick, obtaining a bright filtrate free of turbidity.

(5) To this bright filtrate was added 0.5% catechol as an anti-oxidant.

The properties of this finished engine oil were as follows:

Grav. (A. P. I.)	19.8
Flash (Cl. O. C.)	455 °F
Fire (Cl. O. C.)	520 °F
Color (U. C.)	4
Vis./100° F. (S. U.)	646
Vis./130° F. (S. U.)	271.4
Vis./210° F. (S. U.)	64.2
V. I.	67
Corrosion	Negative
Ash	per cent. 1.13
Sulphur	do 1.89
Alkali Neut. No.	1.45

This oil was run in an engine for 150 hours and produced a very clean piston, with rings all free and with hardly any accumulation of deposits or lacquer.

There are several ways of obtaining the desired material, of which the above described procedure is probably the simplest but perhaps not always the most desirable because of the necessity of filtering the total amount of oil employed. Another way of producing the desired salts consists of extracting the centrifuged acid oil with an oil insoluble and water soluble solvent such as a mixture in equal proportions of methyl alcohol and water.

#### Example 2

Grav. (A. P. I.)	20.0
Flash (Cl. O. C.)	320 °F
Fire (Cl. O. C.)	390 °F
Color (U. C.)	2½+
Vis./100° F. (S. U.)	124.2
Vis./130° F. (S. U.)	73.2
Vis./210° F. (S. U.)	39.2
V. I.	34
Ash	Nil
Sulphur	per cent. 2.35
Corrosion	Negative

(1) This oil was treated with 100 lb./bbl. of 15% fuming sulphuric acid in two 50 lb. stages. After the first 50 lb. portion the oil and acid were stirred with a mechanical mixer at 110° F. for ten minutes and the mixture was then centrifuged. The centrifuged acid oil from the first 50 lb. treat was then treated with another 50 lb. of acid following the same procedure.

(2) The centrifuged acid oil was then extracted with 4% by volume of a mixture of 50% methyl alcohol and 50% water in the following manner:

The centrifuged acid oil and alcohol mixture was heated to 150° F. while stirring and then allowed to settle until there was a sharp line between the extracted oil and the alcohol extract. The alcohol extract was then drawn off and measured and titrated for total acidity. From this total acidity the acidity of the centrifuged acid oil was figured and from this acidity was calculated the theoretical amount of barium hydroxide to use to just neutralize it. The theoretical amount of barium hydroxide in just enough boiling water to substantially dissolve it was then added to the alcohol extract and stirred mechanically while heating to 150° F. This produced thick soaps containing alcohol and water. Some of this alcohol and water could then be poured from the soaps. To these soaps was then added extracted oil from the same treat. The amount

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of extracted oil which was added was 66% of the amount of alcohol extract used at the start of the treat. To this was added enough more barium hydroxide mixed with water to make the total amount 2½ times the theoretical amount to neutralize the centrifuged acid oil. This mixture was then brought to 275° F. to flash off the water and then immediately filtered through a bed of "Super-Cel," which produced a bright filtrate. 4.51% of this bright filtrate was then added to an S. A. E. 30 oil to produce an alkali neutralization number of approximately 3.0 and an ash content of approximately 1.5%. To this was added 0.05% "Resorcinol" as an anti-oxidant. This was the finished engine oil, the properties of which were as follows:

Grav. (A. P. I.)	18.6
Flash (Cl. O. C.)	450 °F
Fire (Cl. O. C.)	505 °F
Color (U. C.)	4-
Vis./100° F. (S. U.)	562
Vis./130° F. (S. U.)	232
Vis./210° F. (S. U.)	59.5
V. I.	58
Reaction	Alkaline
Sulphur	per cent. 2.06
Ash	do 1.09
Alkali Neut. No.	2.80
Corrosion	Negative

This oil was run in an engine for 150 hours and showed very little carbonaceous deposit back of the piston rings, none in the slots of the oil ring and substantially no lacquer either on the piston wall or underneath.

#### Example 3

For producing the extracted soaps, an S. A. E. 10-W oil was used. This oil had been previously treated with 25 lb./bbl. of 98% sulphuric acid and neutralized with caustic soda solution. The properties of this treated oil were as follows:

Grav. (A. P. I.)	20.0
Flash (Cl. O. C.)	320 °F
Fire (Cl. O. C.)	390 °F
Color (U. S.)	2½+
Vis./100° F. (S. U.)	124.2
Vis./130° F. (S. U.)	73.2
Vis./210° F. (S. U.)	39.2
V. I.	34
Ash	Nil
Sulphur	per cent. 2.35
Corrosion	Negative

(1) This oil was treated with 100 lb./bbl. of 15% fuming sulphuric acid in two 50 lb. portions. After the first 50 lb. portion the oil and acid mixture was stirred with a mechanical mixer at 110° F. for ten minutes and then centrifuged. The centrifuged acid oil from the first 50 lb. treat was then treated with another 50 lb. of acid following the same procedure.

(2) The centrifuged acid oil was then neutralized with 15% by volume of a mixture of 50% methyl alcohol and 50% water, plus 1¼ times the theoretical amount of barium hydroxide necessary to just neutralize it. The alcohol and water mixture and the barium hydroxide were all mixed together. This mixture was stirred to 145° F. and allowed to settle for one hour. This separated in three layers, the alcohol and water; the extracted oil; and the soaps (containing some of the extracted oil). The soaps were drawn from the bottom of the receptacle and enough additional barium hydroxide was added so that the total

amount in the soaps would be  $2\frac{1}{2}$  times theoretical amount to neutralize it. Extracted oil was also added to this mixture to insure easy filtering. The amount of extracted oil was approximately 66 $\frac{2}{3}$ % of the amount of soaps. This mixture was brought to a temperature of 275° F. to flash off the water left in the soaps and then filtered through a bed of "Super-Cel" producing a bright filtrate. 6.32% of this bright filtrate was added to an S. A. E. 30 oil, plus 0.05% "Resorcinol" as an antioxidant. This was the finished oil, the properties of which were as follows:

Grav. (A. P. I.)	18.9
Flash (Cl. O. C.)	425 °F
Fire (Cl. O. C.)	505 °F
Color (U. C.)	4
Vis./100° F. (S. U.)	547
Vis./130° F. (S. U.)	223
Vis./210° F. (S. U.)	58.6
V.I.	55
Reaction	Alkaline
Sulphur	per cent. 2.09
Ash	do 1.21
Corrosion	Negative
Alkali Neut. No.	2.87

This oil was run in an engine for 150 hours and the piston showed very little carbonaceous deposit back of the top ring, none back of the second ring or oil ring. Oil ring slots were clean and there was no lacquer on piston walls or underneath.

We have previously indicated that for the preparation of a lubricant according to the described procedures, the quantity of free alkali to be dispersed in the oil may vary in accordance with the type of the oil and its expected service. In general, the free alkali content of compositions within a preferred scope may be identified in terms of the alkali neut. no., which may range between substantially 0.50 and 3.0, and an ash content of from about 0.30 to 1.50. As commonly used in the industry, (see A. S. T. M. Designation: D663-46T) the expression "alkali neut. no." or "alkali neutralization number," is understood to mean the alkali equivalent in terms of KOH, and herein is used to designate the inorganic alkali present in the oil in terms of KOH equivalency, i. e. milligrams of KOH per gram of oil.

Comparative tests made in the same engines under the same conditions using the same lubricating oil but containing no additive produced pistons heavily coated with lacquer, voluminous carbonaceous deposits in the oil slots and stuck compression rings, and after only 48 hours' running.

Where the claims define the lubricating oil as "consisting essentially of" the defined compositions, it is to be understood that such terminology does not preclude the presence of any of various substances such as anti-oxidation agents, anti-corrosion agents, pour control agents, or other additives, so long as the defined components retain essentially their identities and described functions.

We claim:

1. An internal combustion engine compounded

lubricating oil consisting essentially of a lubricating grade hydrocarbon oil containing a permanent dispersion of an alkaline inorganic compound of the group consisting of the hydroxides and carbonates of an alkali earth metal, and an oil soluble mahogany sulfonate in sufficient quantity to serve as a dispersing agent for said compound, said compounded oil having an alkali neutralization number as herein defined between 0.50 and 3.0.

2. An internal combustion engine compounded lubricating oil consisting essentially of a lubricating grade hydrocarbon oil containing a permanent dispersion of an alkaline inorganic compound of the group consisting of the hydroxides and carbonates of an alkali earth metal, and an oil soluble mahogany sulfonate of said metal in sufficient quantity to serve as a dispersing agent for said alkaline compound, said compounded oil having an alkali neutralization number as herein defined between 0.50 and 3.0.

3. An internal combustion engine compounded lubricating oil consisting essentially of a lubricating grade hydrocarbon oil to which has been added a permanent dispersion of an alkaline inorganic compound of the group consisting of the hydroxides and carbonates of an alkali earth metal, and an oil soluble mahogany sulfonate of said metal derived by sulfonation of part of said oil and in sufficient quantity to serve as a dispersing agent for said alkaline compound, said compounded oil having an alkali neutralization number as herein defined between 0.50 and 3.0.

4. An internal combustion engine compounded lubricating oil consisting essentially of a lubricating grade hydrocarbon oil containing a permanent dispersion of a small quantity sufficient to all remain in suspension in the oil of barium hydroxide, and barium oil-soluble mahogany sulfonate in sufficient quantity to serve as dispersing agents for the barium hydroxide, said compounded oil having an alkali neutralization number as herein defined between 0.50 and 3.0.

5. An internal combustion engine compounded lubricating oil consisting essentially of a lubricating grade hydrocarbon oil containing a permanent dispersion of a small quantity sufficient to all remain in suspension in the oil of barium carbonate, and barium oil-soluble mahogany sulfonate in sufficient quantity to serve as dispersing agents for the barium hydroxide, said compounded oil having an alkali neutralization number as herein defined between 0.50 and 3.0.

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ILO S. DELLINGER.

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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. 2,485,861

October 25, 1949

SUMNER E. CAMPBELL ET AL.

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

Column 4, line 38, for "sulphoned" read *sulphonated*;  
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 April, A. D. 1950.

[SEAL]

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