Oct. 13, 1936. B. H. SHOEMAKER ET AL 2,057,212

PROCESS FOR STABILIZING MINERAL OILS

Filed Oct. 31, 1932 3 Sheets-Sheet 1

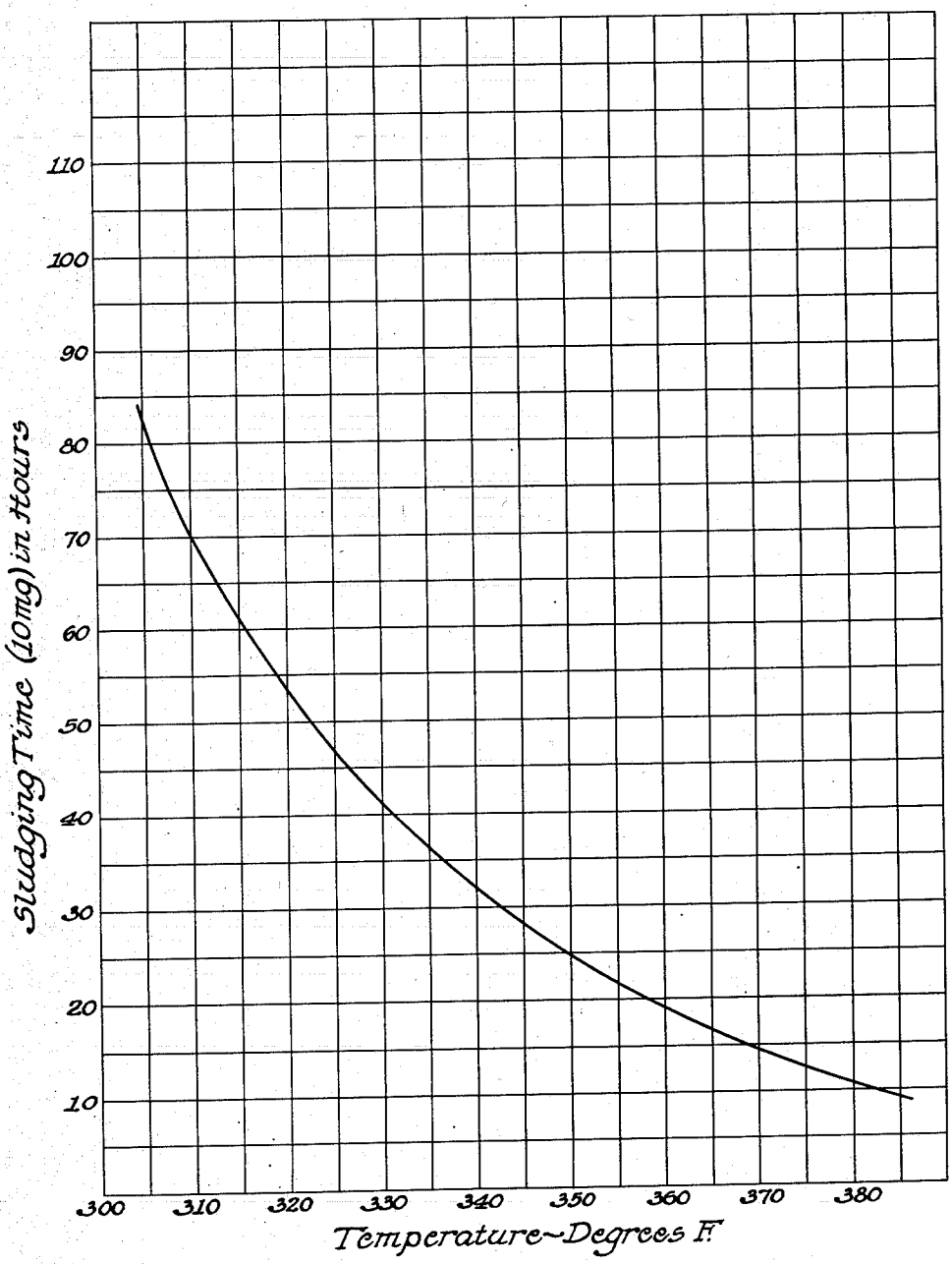


Fig. 1

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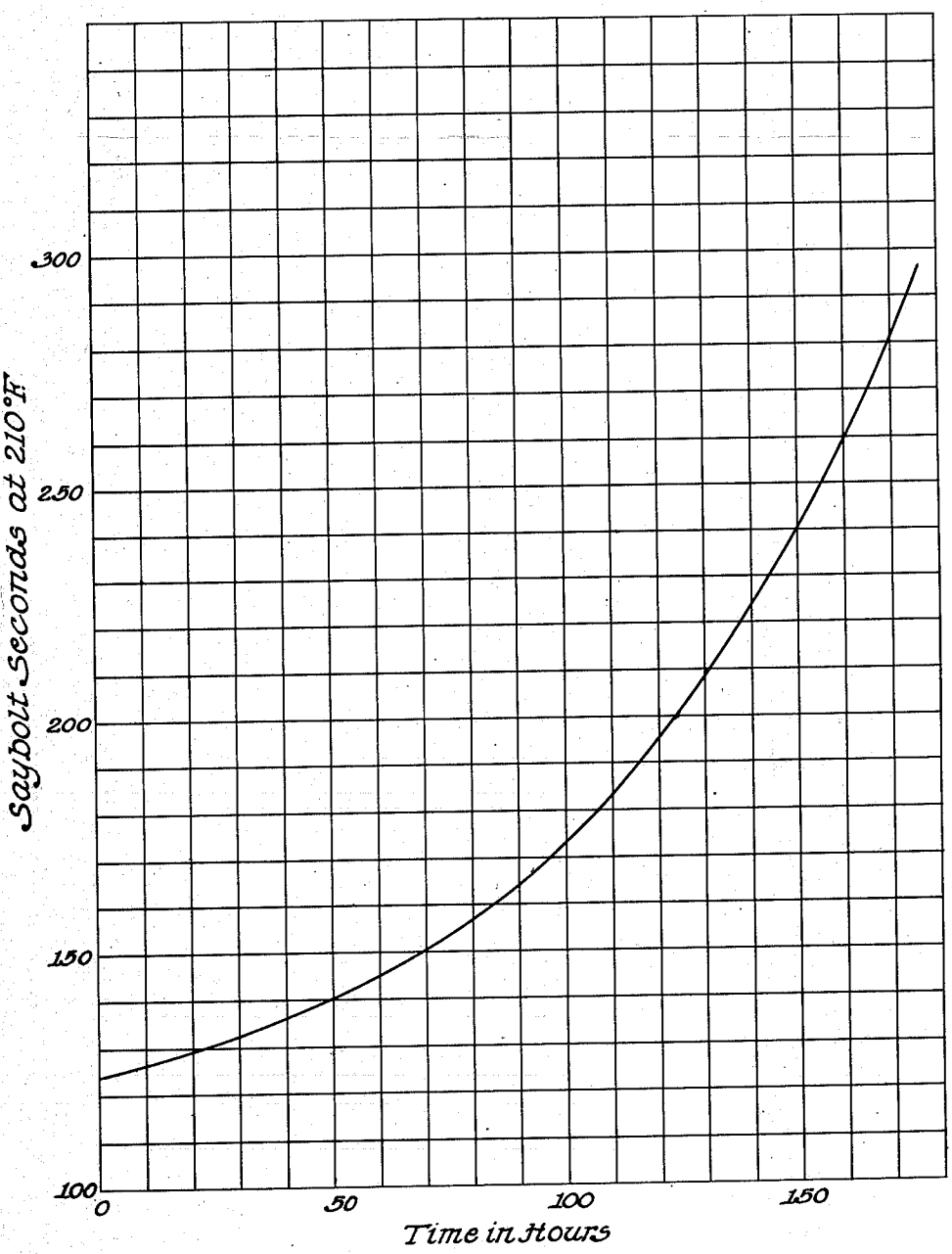


Fig. 2

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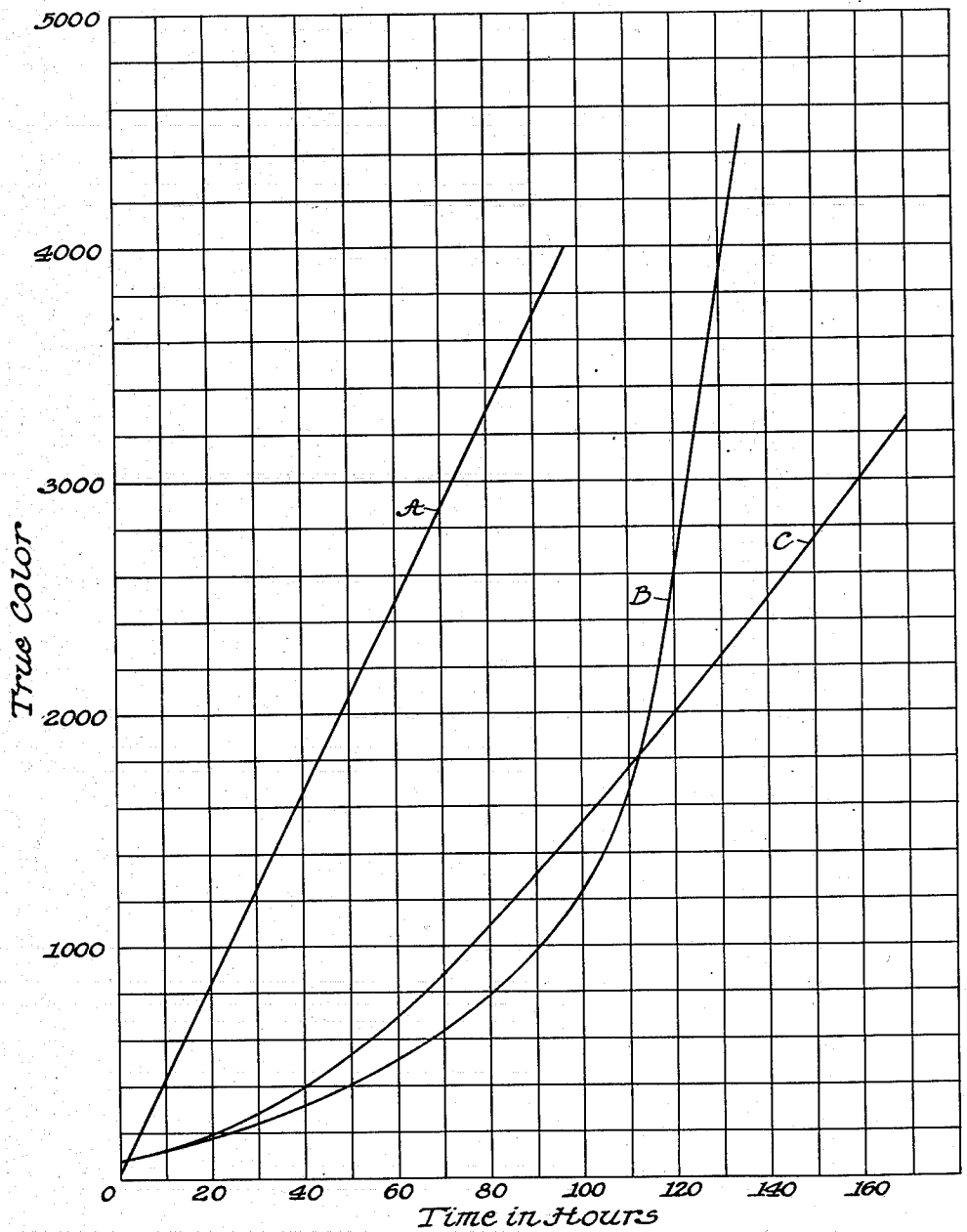


Fig. 3

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UNITED STATES PATENT OFFICE

2,057,212

PROCESS FOR STABILIZING MINERAL OILS

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Application October 31, 1932, Serial No. 640,386

10 Claims. (Cl. 87—9)

This invention relates to the stabilization of mineral oils and it pertains more particularly to a process and composition for preventing sludge and color formation in lubricating oils when used under conditions conducive to deterioration.

Mineral oils, and particularly lubricating oils, when used in internal combustion engines or under conditions where the oil comes in contact with hot surfaces, deteriorate and form sludge, deteriorate in color, form varnish-like products that deposit on the surfaces being lubricated and the viscosity of the oil increases with use. This deterioration of mineral oils is particularly noticeable with oils used to lubricate internal combustion engines. The sludge formed collects on the piston rings and causes them to stick. Also, sludge collects in the oil pumps and oil lines and greatly retards the flow of oil and in some cases plugs up the oil lines and small passages.

The object of our invention is to provide a method for stabilizing mineral oils and particularly lubricating oils against deterioration.

Another object is to provide a method for inhibiting the sludge formation of mineral oils by adding to the oil an inhibiting catalyst.

Another object is to prevent the increase in viscosity of the oil upon continued use.

Another object is to provide a method for preventing color deterioration of the oils.

A further object is to provide a process for preventing the formation of varnish-like products in lubricating oils and the staining of the parts to be lubricated.

In internal combustion engines, it is very important that the lubricating oils be stable as to sludge formation. We have found that motor oils have a great tendency to sludge and deteriorate at the high operating temperatures generally encountered in internal combustion engines such as are used in automobiles and airplanes. At these high temperatures it is common for lubricating oils to decompose and form sludge and coke on the pistons and in the ring grooves of the pistons. This results in sticking of the rings which, in turn, allows more oil to gain access to the cylinder, thereby aggravating the condition, causing excessive oil consumption and loss of compression. The curve in Figure 1 illustrates the tendency of a heavy Mid-Continent lubricating oil to form sludge with increase in temperature. It will be observed that at 320° F. it required about 54 hours for 10 grams of oil to form 10 mg. of sludge, whereas at 360° F. it required only 19 hours to form 10 mg. of sludge. It is very important to note that a relatively small increase in temperature will greatly increase the rate of sludge formed. The sludge stability of the oil with reference to temperature, shown in Figure 1, was determined by heating a quantity of oil to the desired temperature and bubbling air through the sample at the rate of 10 liters per hour. At intervals, 10 grams samples were withdrawn and tested for sludge by the precipitation method described in American Society of Testing Materials Proceedings, volume 24, page 967.

Another undesirable characteristic of lubricating oils is their increase in viscosity upon use. The curve shown in Figure 2 illustrates this property of mineral oils. It will be observed that the Saybolt viscosity increases greatly upon use. The results expressed by the curve in Figure 2 were obtained by maintaining a Pennsylvania oil at 340° F. and bubbling preheated air through the oil at the rate of 100 to 150 liters per hour. It is apparent that when mineral oils are used at elevated temperatures in internal combustion engines, the viscosity increases upon continued use and the oil will become so viscous that a heavy load is put upon the engine, especially when starting. This is particularly noticeable in cold weather.

Another common and undesirable property of mineral oils and particularly those lubricating oils used in contact with hot surfaces, such as in internal combustion engines, is the development of color. Curve A in Figure 3 shows the rate of color formation when a heavy Mid-Continent lubricating oil is heated to 340° F. while air is bubbled into the oil at the rate of 10 liters per hour. Curves B and C show the rate of color formation in the same oil when a small amount of sodium butylate and potassium butylate, respectively, are dissolved in the oil. It is apparent from the curves that a small amount of these alkaline alcoholates are very effective for retarding color formation.

We have found that mineral oils, and particularly lubricating oils, can be stabilized against deterioration as illustrated by sludge formation, increase in viscosity upon use, staining of the surfaces to be lubricated and color formation, by adding to the oil a small quantity of an alkaline alcoholate or mixture of alkaline alcoholates. We have found that the alkali metal alcoholates and alkaline earth metal alcoholates, as well as the thio alcoholates, are particularly suitable for stabilizing mineral oils in this respect. The compounds used for stabilizing these oils have the following general formula:

$$X—B—R \text{ or } X_1=(B—R)_2$$

wherein X is a mono-valent alkaline metal and X_1 is a di-valent alkaline metal, B represents an oxygen or sulfur atom and R represents an alkyl, cyclo-alkyl or aralkyl radical or derivatives thereof. We may use the aliphatic alcoholates, cyclic alcoholates and aralkyl alcoholates, examples of which are the sodium, potassium, lithium, calcium, magnesium, barium and strontium alcoholates of the primary, secondary and tertiary aliphatic alcohols such as methyl alcohol, ethyl alcohol, propyl alcohols, butyl alcohols, amyl alcohols, hexyl alcohols, octyl alcohols and decyl alcohols; primary, secondary and tertiary thio alcohols such as amyl mercaptans, butyl mercaptans, propyl mercaptans, and hexyl mercaptans; cyclic alcohols such as cyclo hexanol, cyclo butanol, hydro phenols, cyclo hexyl mercaptan and the like; primary, secondary and tertiary aralkyl alcohols such as benzyl alcohol, phenyl ethyl alcohol, dibenzyl alcohol, tolyl alcohols and the like; also the alkaline metal derivatives of organic compounds capable of forming the enolic structure, such as acetoacetic ester and ketones, are effective for stabilizing mineral oils. The tautomeric forms of acetoacetic ester are:

$$CH_3—\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5 \qquad CH_3—\overset{O}{\overset{\|}{C}}—CH_2COOC_2H_5$$

The alkaline metal derivatives of the enolic tautomer of the above esters and other compounds such as ketones contain the following characteristic group:

$$—\overset{OR}{\overset{|}{C}}=CH—$$

wherein R represents an alkali metal.

The stabilized oils are prepared by dissolving a small amount of the alcoholates therein. The preferred amounts range from 0.1 to 0.5%, the amount varying with specific materials. However, larger amounts up to 1% may be used if desired.

The following table illustrates the results obtained with a heavy Mid-Continent lubricating oil, having an original true color of 21, when stabilized with alkaline alcoholates at a temperature of 320° F.

Table I

Example	Stabilizer	Percent	True color		Sludging time (hours) 10 mg.
			15 hours	23.5 hours	
1	Control		1435	2000	29
2	C_2H_5ONa	0.2	155	246	37
3	C_4H_9ONa	0.2	123	720	39
4	C_4H_9ONa	0.4		238	49
5	C_4H_9OK	0.2	123	780	
6	$C_5H_{11}ONa$	0.3	115	151	41
7	$C_5H_{11}OK$	0.3	160	475	41
8	$(C_4H_9O)_2Ca$	0.4	520	1230	
9	$(C_4H_9O)_2Ca$	0.3	200		
10	$C_5H_{11}ONa$(cyclo)	0.3	82	117	42
11	C_4H_9S–Na	0.2	255	985	33
12	Na-methyl ethyl ketone	0.2	106		39
13	Na-methyl ethyl ketone	0.3	60	82	44
14	Na-benzylate	0.3	54	70	47
15	Na-butylate(tert)	0.2	200	1065	
16	Li-butylate	0.3	131	240	45
17	Na-decylate	0.4	675	1704	
18	Na-triethylene glycolate	0.3	515		

From the above table it is apparent that the alcoholates of alkaline metals are very effective for preserving color and retarding sludge formation in lubricating oils. It should be noted that the thio alcoholates, as shown in Example 11 are also effective for stabilizing these mineral oils. Also the alcoholate metal derivatives of organic compounds such as ketones and acetoacetic esters, which are capable of forming an enolic structure are effective for stabilizing lubricating oils. It should be noted that these alkaline alcoholates are particularly good color stabilizers. It will be observed that the true color for the unstabilized oil after 15 and 23.5 hours was 1435 and 2000 respectively, whereas the same oils containing a small amount of the alcoholates gained very little in color. Curves C and B in Figure 3 further show the extent of color stabilization over longer periods of time. It will be observed that after 100 hours, the color of the oil is substantially one-third the color of the unstabilized oil. It should be further noted that the alkaline alcoholates derived from the low molecular weight metals such as lithium and sodium, and the high molecular weight alcohols such as butyl amyl and cyclo hexyl alcohols, are particularly effective for stabilizing the oils against sludge formation.

The following table further shows the effectiveness of the alcoholates for inhibiting sludge formation in lubricating oils. The particular oil used was a heavy Mid-Continent lubricating oil which had been treated with 2 lbs. of sulphuric acid per gallon of oil.

Table II

	Sludge time in hours required to form 10 mg. of sludge
Control	92
0.2% $NaOC_4H_9$	205
0.2% KOC_4H_9	128

We have found it particularly desirable to add small quantities of an alcoholate to oils for seasonal storage to inhibit color and sludge formation. As indicated by the above tables, it is apparent that the alcoholates are very effective for inhibiting the deterioration of the oil.

As pointed out hereinbefore in connection with Figure 2, the viscosity of the oil greatly increases as the oil is used and we find that the presence of a small amount of alcoholates will retard this increase in viscosity upon use.

The term "stabilize" is used in our application in a generic sense to include the preserving of the oil against deterioration in any of the foregoing respects, such as sludge formation, color formation, increase in viscosity and the formation of varnish-like products. The alkaline compounds used in our invention are not reducing agents and their stabilizing action cannot be explained by the theory upon which the action of antioxidants is explained. However, it is thought that the deterioration of mineral oils is accompanied by the formation of intermediate acidic products, and the alkaline derivatives of compounds containing the alcoholate structure retard the formation of these intermediate acidic products and thereby stabilize the mineral oils against deterioration. Our invention is not limited to the specific alcoholates disclosed above, but it includes the alkaline metal derivatives of other alcohols such as isopropyl, secondary butyl, isobutyl alcohols, isoamyl alcohols, secondary amyl alcohols, hexyl mercaptans and the like.

While we have described our invention with

reference to certain oils and compounds, the scope of our invention is not limited thereby except insofar as set forth in the claims.

We claim:

1. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon lubricating oil and from 0.1 to 0.5% of an alkali metal alcoholate having the following formula:

$$X—B—R$$

wherein X represents a mono-valent alkali metal, B represents an oxygen or sulfur atom, and R represents an alkyl, cyclo-alkyl, or aralkyl radical.

2. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and a small proportion of an oil-soluble alkaline metal alcoholate.

3. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and from 0.1 to 0.5% of an alkali metal alcoholate dispersed therein, said alcoholate having the following formula:

$$X—B—R$$

wherein X represents a mono-valent alkali metal, B represents an oxygen atom, and R represents an alkyl radical containing at least 3 carbon atoms, a cyclo-alkyl or aralkyl radical.

4. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and from 0.1 to 0.5% of an oil-soluble alkali metal alcoholate having the general formula:

$$X—B—R$$

wherein X represents a sodium atom, B represents an oxygen atom, and R represents an alkyl radical containing at least 4 carbon atoms.

5. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and a small proportion of an oil-soluble alkali alcoholate selected from the group consisting of sodium propylates, sodium butylates, potassium butylates, sodium amylates, potassium amylates, lithium butylates, and the sodium derivatives of butyl mercaptan.

6. A sludge-resistant mineral lubricating oil comprising a viscous mineral oil and from 0.1 to 0.5% of an alkali metal alcoholate selected from the group consisting of sodium propylate, sodium butylate, potassium butylate, sodium amylate, and potassium amylate.

7. A sludge-resistant hydrocarbon lubricating oil comprising a viscous hydrocarbon mineral oil and a small proportion of an alkali metal alcoholate selected from the group consisting of sodium propylate, sodium butylate, potassium butylate, sodium amylate, potassium amylate, lithium butylate, and sodium derivatives of butyl mercaptan.

8. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and a small proportion of an oil-soluble alkali metal derivative of the enolic form of an aliphatic ketone.

9. A sludge-resistant mineral lubricating oil comprising a viscous hydrocarbon mineral oil and a small proportion of an oil-soluble alkali metal derivative of the enolic form of an aliphatic ketone, said alkali metal derivative containing the following group

$$—C(OR)=CH—$$

wherein R represents an alkali metal.

10. A sludge-resistant lubricating oil comprising a viscous mineral oil having incorporated therein a small proportion of an oil-soluble alkaline alcoholate of the following formula:

$$X_1=(B—R)_2$$

wherein X_1 represents a divalent alkaline metal, B represents an oxygen or sulfur atom, and R represents an alkyl, cyclo-alkyl or aralkyl radical.

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