Patented Mar. 10, 1936 2,033,543

UNITED STATES PATENT OFFICE

2,033,543

LUBRICATING OILS

Anderson W. Ralston and Carl W. Christensen, Chicago, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois

No Drawing. Application May 4, 1935, Serial No. 19,906

9 Claims. (Cl. 87—9)

This invention relates to lubricating oils and it comprises an improved lubricating oil composed of a hydrocarbon lubricating oil to which has been added a mixed ketone in quantities of the order of 0.1 to 1 percent.

Within recent years efforts have been made to improve mineral lubricating oils by adding various ingredients thereto. In many cases such additions have been made for the purpose of improving that characteristic of the oil commonly referred to as oiliness. These added substances have mostly been fatty acids such as oleic acid, various glycerides, lard, and the like. The property of oiliness has not been clearly defined, but the term has a rather definite meaning to those skilled in the art. Some have defined it as that property which an oil must possess to a sufficient degree to enable the oil to lubricate adequately under all conditions of use. In more practical terms, an oily oil is one which will form a film between bearing surfaces of such strength that the film will withstand rupture under extreme conditions of pressure or temperature. To put it another way, an oily oil is one which has high film strength and as a result will give better engine performance under all conditions of use. At the same time, however, such oils should have low internal friction and should also have the property of clinging to metal surfaces. It used to be considered that viscosity was a good criterion of the oiliness in oil on the theory that the higher the viscosity the stronger would be the oil film. However, it has now been pretty well acknowledged that viscosity alone does not explain oiliness in an oil.

As stated, the prior art has hitherto added small quantities of vegetable oils such as oleic acid to hydrocarbon lubricating oils. Undoubtedly such additions have proved beneficial, in part because of the high "polar" characteristics of the higher fatty acids. That is to say the carboxylic acid group of the fatty acid tends to cling to the metal surfaces of a bearing and thus aids in the development of a persistent film. However, in many instances, the internal friction of the compounded oil has been increased and this is a distinct disadvantage. Many of the added substances hitherto used increase the viscosity of the oil and hence such oils necessarily cause increased power losses in engines lubricated with them. This is because of the internal friction in the oil itself.

Another serious objection to the addition of substances like oleic acid and fats is that these added substances do not have very much resistance to high temperatures. In a gasoline engine the crank-case temperature may on the average be about 210° F. and bearing temperatures may run as high as 400° F. Bearing pressures may occasionally be as high as 600 pounds per square inch which means that a satisfactory oil must have high film strength and heat resistance if it is to function continuously under these conditions.

Substances like oleic acid are not sufficiently heat resistant to operate satisfactorily over long periods of time at the relatively high temperatures in a rapidly rotating bearing. These substances, although they initially contribute oiliness to an oil, tend to break down and decompose at high temperatures. This action may be oxidizing, or it may in part be instituted by the presence of traces of moisture. Fatty esters are readily hydrolyzed at the high operating temperatures in the presence of moisture and free fatty acids thus liberated tend to decompose. All of which means that such substances, although they may initially improve a mineral lubricant very soon lose their effectiveness and actually prove detrimental.

We have now discovered a class of substances which can be added to mineral lubricating oils in small amounts, of the order of 0.1 to 1 percent, and which markedly improve the oiliness of the oil but do not have the many disadvantages unavoidably present in substances hitherto suggested. We have discovered that compounds known as "mixed" ketones satisfy the requirements in this art. These mixed ketones can be generically described as ketones in which aryl or heterocyclic groups, and alkyl groups are linked to a carbonyl. And we have further discovered that of the many substances which can be designated as mixed ketones we find that those in which the alkyl group contains eleven or more carbon atoms are best. In our invention aryl or heterocyclic groups may be varied over a wide range as will be described. Structurally then, the compounds we add to a mineral lubricant oil can be generically illustrated as

$$R-\overset{\overset{O}{\|}}{C}-R'$$

wherein R is a ring compound either of the carbocyclic or heterocyclic series and R' is an alkyl radical containing eleven or more carbon atoms.

The compounds used in our invention are markedly superior to fats and fatty oils or fatty acids. Being ketones they are markedly heat resistant. They are also non-corrosive, even in the presence of much moisture, and they are not easily oxidized. Hence they are chemically stable at the high operating temperatures met with in lubrication. We find that they contribute oiliness to a high degree and thus function to maintain high film strength under all conditions of pressure.

Moreover the compounds of our invention have a beneficial effect on viscosity. Many compounds hitherto added to mineral lubricating oils

for increasing oiliness actually increase the viscosity of the oil and lower its viscosity index. In contrast thereto many of the compounds which we add to a lubricating oil raise the viscosity index several points. For example, stearophenone is one very advantageous substance to add to an oil in the practice of our invention. When we add 1 percent of stearophenone to a number 30 (SAE) Mid-Continent lubricating oil the viscosity index is increased from 86.7 to 92. At 100° F. the viscosity (Saybolt) is 493 seconds whereas the untreated oil has a viscosity of 514 seconds. At 210° F. both the compounded oil and the untreated oil have the same viscosity. Hence it is apparent that the addition of the aralkyl ketone has decreased the viscosity at 100° F. and thus increased the viscosity index. This is a marked advantage because it means that oiliness is increased without increasing the internal friction in the oil. As stated almost all substances hitherto added to oils for increasing oiliness have increased internal friction whereas, in our invention, the internal friction is either decreased or remains substantially unchanged. Such a result has long been desired.

In addition, many of the substances which we use for increasing oiliness pronouncedly lower the cloud point of the mineral lubricating oil. In the example given above the original oil has a cloud point of 52° F. The addition of 0.1 percent of stearophenone lowers the cloud point to 30° F.

We shall now describe numerous examples of compounds falling within the generic disclosure given above. It is to be understood of course that these compounds are simply admixed and blended in the mineral lubricating oil in proportion of from about 0.1 to 1 percent based on the weight of the oil. This quantity can be increased somewhat but to no substantial advantage. All of the compounds we add are, of course, soluble in lubricating oil, and it is to be understood that we can treat lubricating oils from any source and of any viscosity. We can add our improving substances to mixed lubricating oils and to lubricating oils composed of both mineral and vegetable oils such as castor oil, but in the ordinary practice of our invention the ketones are generally added to an ordinary mineral lubricating oil. We do not however wish to be restricted to lubricants composed entirely of mineral oils.

We shall now describe our invention with reference to the treatment of a Mid-Continent lubricating oil having an (SAE) viscosity of 30 it being understood however that this is merely illustrative and not limiting.

There are many mixed ketones we can use. If the generic formula for our compounds be written as

$$R-\overset{\overset{O}{\|}}{C}-R'$$

R′ can be any alkyl group having eleven or more carbon atoms. It can also be a substituted alkyl group. Thus R′ can be undecyl $C_{11}H_{23}$, tridecyl $C_{13}H_{27}$, pentadecyl $C_{15}H_{33}$, and heptacecyl $C_{17}H_{35}$.

R can be any one of a number of closed ring radicals. The following are examples thereof; phenyl, xylyl, tolyl, anisyl and chlorphenyl, these being typical examples of phenyl and substituted phenyl radicals. R can also be phenoxyphenyl, diphenyl, naphthyl and anthracyl or substitution products thereof, as further examples of carbocylic ring compounds. R can also be furyl, fluoryl, carbazoyl, dibenzofuryl, thiophenyl and dibenzothiophenyl, as examples of heterocyclic radicals.

We shall now give examples of many compounds falling under our generic invention.

In the following table, from 0.1 to 1 percent of various aralkyl ketones are added to a No. 30 Mid-Continent lubricating oil which has a cloud point of 52° F., a pour point of 20° F. a Saybolt viscosity at 100° F. of 514 seconds and at 210° F. of 62 seconds, and a viscosity index of 86.7.

Table 1

Percent added	Material added	Cloud point	Pour point	Saybolt viscosity time in seconds		Viscosity index
				100° F.	210° F.	
		°F.	°F.			
.1	Phenylheptadecyl ketone	42	20	512	64	96.5
.5	do	32	20	500	64	90.2
1.0	do	30	20	493	62	92.0
.1	Phenoxyphenyl heptadecyl ketone	38	15	510	63	92.4
.5	do	32	15	507	62	88.4
1.0	do	30	20	499	62	90.3
.1	Xylyl heptadecyl ketone	38	20	513	63	91.7
.5	do	30	20	506	62	88.7
1.0	do	34	20	498	62	92.0
.1	Dimethyl aniline stearoyl chloride	30	15	517	63	90.7
.5	do	26	15	507	62	88.3
1.0	do	46	25	506	61	83.3
.1	Furyl heptadecyl ketone	34	20	514	63	91.5
.5	do	34	20	509	62	88.0
1.0	do	38	15	506	62	88.9
.1	Anthracyl heptadecyl ketone	22	15	521	62	84.8
.5	do	Too dark	−15	522	62	84.6
1.0	do	Too dark	−15	530	62	82.5
.1	Alkyl phenone (lard fatty acids)	34	20	514	63	91.4
.5	do	36	20	508	62	88.1
1.0	do	36	20	497	61	85.7
.1	Naphthyl heptadecyl ketone	36	20	518	63	90.5
.5	do	34	20	504	62	89.3
1.0	do	34	20	501	62	90.0
.1	Anisyl heptadecyl ketone	34	20	519	62	85.2
.5	do	32	20	510	62	87.8
1.0	do	28	20	506	62	88.2
.1	Biphenyl heptadecyl ketone	34	15	513	63	92.0
.5	do	32	15	506	62	88.8
1.0	do	32	5	498	62	92.0
	Control (taken after tests completed)	53	20	514	62	86.7

The compound from dimethyl aniline and stearoyl chloride is probably a mixture of ketones which can be generically described as dimethyl aminophenyl heptadecyl ketones. The aralkyl phenones (lard fatty acids) were made by reacting acid chlorides obtained from lard fatty acids with benzene in the presence of aluminum chloride as will be explained. It is a mixture of ketones in which oleyl phenone probably predominates. Anthracyl heptadecyl ketone colors the oil somewhat when used in percentages of 0.5 and 1.0 which makes the cloud point determination difficult. These amounts do not however deleteriously affect oiliness and they actually reduce the pour point markedly.

It is to be noted that most of the above compounds tabulated increase the viscosity index. In some instances the index is slightly reduced but the reduction is markedly less than that commonly met with when adding many of the substances hitherto used for increasing oiliness.

It is of course obvious that we can use mixtures of ketones and thus obtain the desirable advantages of individual substances. For example we can add a mixture of phenyl heptadecyl ketone and anthracyl heptadecyl ketone in this way obtaining the advantageous increase in viscosity index contributed by phenyl heptadecyl and the marked reduction in pour point contributed by anthracyl heptadecyl ketone. Both of these compounds markedly increase oiliness in the oils.

Curiously, in some instances, impure ketones work better. This may be due to the fact that the impure ketone really contains a mixture of ketonic compounds and this effect is especially noticeable in the case of the anthracyl ketones. One of the best ketonic substances to add is that obtained from reacting anthracene oil or fractions thereof with higher fatty acid chlorides by the Friedel-Craft's synthesis as will be explained. This gives us a mixture of ketones which are difficult to isolate separately but which markedly contribute oiliness to the lubricating oil.

In Table 2 which follows we describe the effect of adding various other "mixed" ketones among which are ketones in which the alkyl radical is undecyl. This table also shows the effect of ketones in which the aryl group is substituted by chlorine and by methoxy. The character of the lubricating oil treated is indicated at the bottom of the table. It was a Number 30 Mid-Continent lubricating oil.

In the above table, cloud points and pour points were not determined in every instance. In the case of dibenzofuryl heptadecyl ketone it is to be noted that 0.5 percent thereof lowers the viscosity index somewhat. When using this substance we therefore find it best to keep the quantity at about 0.1 percent. Many of the ketones given above are not ordinarily used in the commercial practice of our invention because they are more expensive than substances like stearophenone and the anthracyl derivatives, but we have described these compounds to illustrate the generic characteristics of our invention.

Many of these mixed ketones or aralkyl ketones are new materials and, in copending applications, we have so claimed them as new compounds. All of these aralkyl ketones can be made by a simple Friedel-Craft's synthesis. This can be illustrated in connection with the preparation of diphenyl tridecyl ketone. Thirty-five grams of diphenyl are admixed with fifty grams of myristyl chloride and 100 cubic centimeters of carbon disulfide. This mixture is cooled in an ice bath and then to it fifty grams of aluminum chloride are slowly added with stirring until there is no further evolution of hydrochloric acid. Then dilute hydrochloric acid solution is added and the contents of the mixture steam-distilled. This removes disulfide. The ketone can then be decanted from the aqueous solution of aluminum chloride and crystallized from carbon tetrachloride.

All of the many aralkyl ketones described herein can be made by this general procedure as will be apparent to those skilled in the art.

Thus when we wish to make the corresponding anthracyl compound we start with anthracyl or fractions of anthracyl oil. When we wish to make the corresponding furyl compound we start with furane.

In the appended claims we generically define radicals of the carbocyclic series and heterocyclic series, as closed ring radicals, and we generically define our alkyl radicals as those comprising the alkyl residue of a fatty acid containing at least twelve carbon atoms. To illustrate, $C_{17}H_{35}COOH$ is the formula of stearic acid and $C_{17}H_{35}$ is the alkyl residue of said acid.

As stated, many of the ketones which we use are new materials. In our copending applications we have described and claimed them as such. In our copending application Serial Number 17,873, filed April 23, 1935, we have claimed the

Table 2

Percent added	Material added	Cloud point	Pour point	Saybolt viscosity time in seconds		Viscosity index
				100° F.	210° F.	
		°F.	°F.			
.1	Fluoryl heptadecyl ketone			511	62	87.3
.5	do	38	10	511	62	87.3
.1	Dibenzofuryl heptadecyl ketone			514	62	86.7
.5	do	44	20	538	61	74.8
1.0	do			524	61	78.5
.1	p-Biphenyl undecyl ketone			516	62	86.1
.5	do	32	20	506	62	88.7
.1	Phenyl undecyl ketone			516	62	86.1
.5	do	32	20	511	62	87.3
.1	p-Chlorphenyl undecyl ketone			507	62	88.5
.5	do	32	20	503	61.5	87.0
.1	p-Methoxyphenyl heptadecyl ketone			520	61.5	82.5
.5	do	32	20	517	61.5	83.1
.1	p-Methoxyphenyl undecyl ketone			517	61.5	83.1
.5	do	34	20	512	61.5	84.5
	Control	42	20	518	62	86.2

mixed phenoxy phenyl alkyl ketones, in our copending application Serial Number 17,874, filed April 23, 1935, we have claimed the mixed diphenyl alkyl ketones, in our copending application Serial Number 17,875, filed April 23, 1935, we have claimed the mixed furyl alkyl ketones, and in our application Serial Number 48,940, filed November 8, 1935 as a division of Serial Number 17,875, we have claimed the benzofuryl alkyl ketones.

Having thus described our invention, what we claim is:

1. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a ketone having the structural formula

$$R-\underset{O}{C}-R'$$

wherein R is a closed ring radical and R' is an alkyl radical having at least eleven carbon atoms.

2. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a ketone having the structural formula

$$R-\underset{O}{C}-R'$$

wherein R is an aryl radical and R' is an alkyl radical having at least eleven carbon atoms.

3. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a ketone having the structural formula

$$R-\underset{O}{C}-R'$$

wherein R is an aryl radical and R' is the alkyl residue of a fatty acid containing at least twelve carbon atoms.

4. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a ketone having the structural formula

$$R-\underset{O}{C}-R'$$

wherein R is a radical chosen from the group consisting of phenyl, naphthyl, diphenyl, anthracyl, furyl, fluoryl, thiophenyl, carbozoyl and dibenzofuryl, and R' is an alkyl residue of a higher fatty acid containing at least twelve carbon atoms.

5. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a ketone having the structural formula

$$R-\underset{O}{C}-R'$$

wherein R is a radical chosen from the group consisting of phenyl, naphthyl, diphenyl, anthracyl, furyl, fluoryl, thiophenyl, carbozoyl and dibenzofuryl, and R' is an alkyl radical containing at least eleven carbon atoms.

6. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a mixed phenyl alkyl ketone wherein the alkyl radical contains at least eleven carbon atoms.

7. A lubricating oil comprising a mineral lubricating oil containing a small amount, of the order of 0.1 to 1.0 percent, of a mixed anthracyl alkyl ketone wherein the alkyl radical contains at least eleven carbon atoms.

8. The lubricating oil as in claim 6 wherein the ketone is a phenyl heptadecyl ketone.

9. The lubricating oil as in claim 7 wherein the ketone is an anthracyl heptadecyl ketone.

ANDERSON W. RALSTON.
CARL W. CHRISTENSEN.