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LUBRICATING OILS

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This invention relates to lubricating oils and it comprises an improved lubricating oil to which has been added a small amount, of the order of 0.1 to 1 percent, of the Friedel-Crafts reaction product from a higher fatty acid chloride and a coal tar fraction.

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 materials 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 further discovered that the compounds we add to lubricating oil markedly reduce the pour point of the oil. In some instances we have been able to reduce the pour point of the original oil as much as 60° F. This is a phenomenal pour point lowering and has never hitherto been achieved so far as we are aware by the addition of a so-called "pour point depressor". Moreover, many of the compounds we add increase the viscosity index of the oil, which is highly desirable.

The class of substances coming within the scope of our invention can be broadly defined as the Friedel-Crafts reaction product from a higher fatty acid chloride and a coal tar fraction. This class of substances is broadly new and has been separately described and claimed in the co-pending application of Ralston, Christensen and Bauer filed of even date herewith.

There are many products falling under the generic scope of our invention. They are all obtained by reacting a higher fatty acid chloride with a coal tar fraction, distillate, acid-soluble or

alkali-soluble constituents of coal tar, or fractions or distillates thereof. The exact chemical constitution of our products is uncertain. We do know that none of them are pure chemical compounds. They are all viscous oils or greasy, waxy materials and doubtless consist of a number of substances. In fact, we believe that the marked improvement in lubricating oils achieved by our invention is largely due to the fact that the substances we add are mixtures rather than pure chemical individuals. Our compounds may contain complex ketonic substances, condensed aromatic hydrocarbons of high molecular weight, and possibly many other kinds of organic substances. For this reason we cannot specify our compounds by name but must refer to them by the process by which they are made. We know of no other way of defining them accurately.

We shall now describe many different specific addition agents falling within the generic scope of our invention. It is to be understood of course in each instance from about 0.1 to 1 per cent of these substances, or mixtures thereof, are dissolved in the mineral lubricating oils.

As stated, our addition agents are obtained by reacting a higher fatty acid chloride with a coal tar fraction in the presence of aluminum chloride. Many different higher fatty acid chlorides can be used as starting materials, and by higher fatty acid chlorides we mean to include all those higher fatty acid chlorides derived from fatty acids containing six or more carbon atoms. The higher fatty acid chlorides are made by reacting the corresponding fatty acid with phosphorus pentachloride or other chlorinating agent customarily employed for converting fatty acids to corresponding acid chlorides. All of these acid chlorides have the formula $RCOCl$. Acetyl chloride is the lowest member of the series but we do not prepare our addition agents from this material. We only use acid chlorides derived from fatty acids containing at least six carbon atoms. By definition "higher fatty acid" means an aliphatic carboxylic acid containing at least six carbon atoms. In the practice of our invention we can make addition agents from caproyl chloride, capryl chloride, lauryl chloride, myristyl chloride, palmityl chloride, stearyl chloride, and also the acid chlorides corresponding to arachidic, behenic, carnaubic, cerotic and melissic acids. We can also use higher fatty acid chlorides derived from unsaturated fatty acids such as oleic and linoleic. In most instances we use mixtures of various fatty acids since these are readily obtainable from glycerides occurring in nature.

Likewise in the practice of our invention we can make our addition agents from liquid and solid fractions of coal tar and we generally use those fractions, or distillates, boiling from 200° C. upward. The fractions, distillates, or extracts which we use are generally mixtures of various aromatic and heterocyclic hydrocarbons, phenols, cresols and other substances of complex structure. One of the most desirable materials for addition to lubricating oils is that made from reacting a higher fatty acid chloride with a coal tar distillate known as red wax. Red wax is a coal tar fraction having a boiling range of about 432° C. to 500° C. Many of the coal tar distillates which we use in our invention contain quantities of naphthalene and anthracene admixed with other hydrocarbons, phenols, cresols, and the like and our invention deals particularly with addition agents made from these mixtures and not with pure constituents thereof. As stated above many of the desirable

characteristics in the products which we add to lubricating oils are due to the fact that these products are mixtures of substances and are not pure chemical compounds.

We shall now describe our invention with specific reference to preparing products from many different coal tar fractions, and the addition thereof to lubricating oils. In order to keep our disclosure within reasonable bounds we shall restrict our specific examples to addition agents made from stearyl chloride. This acid chloride can be made from stearic acid readily. It is to be understood, however, that all of the higher fatty acid chlorides enumerated above can be used instead of stearyl chloride.

We shall now refer to products obtained by reacting so-called "crude tower bottoms" with stearyl chloride. These crude tower bottoms have a boiling point range of about 230° C. to 375° C. They are obtained by distilling coal tar and condensing a fraction having this boiling point range. The exact composition of the crude tower bottoms is not known but they contain anthracene, naphthalene, and probably many other substances.

We first prepare a mixture of about 35 parts by weight of the tower bottoms, 73 parts by weight of stearyl chloride, and 258 parts by weight of carbon disulphide. To this mixture we add, at room temperature, 67 parts by weight of aluminum chloride over a period of three hours. The mixture is then refluxed for about two hours at 46° C. and then poured upon a mixture of ice and hydrochloric acid. The mixture is then steam-distilled, this resulting in the hydrolysis of a complex aluminum compound probably analogous to the usual type of compound obtained in the Friedel-Crafts synthesis. When the hydrolysis is complete the product obtained will appear as a reddish-brown, free-flowing oil floating on the surface of the aqueous mixture of aluminum chloride. Hydrolysis should be continued until this oily reaction product is substantially free of aluminum.

The chemical composition of this reaction product is not clearly understood. It probably contains ketonic compounds derived from anthracene and stearyl chloride. But since phenols and cresols are also present in the initial coal tar fraction it is apparent that the final reaction products are probably quite complex.

We now add from 0.1 to 1 per cent of this reaction product to a lubricating oil to be improved. When added to an SAE number 30 mid-continent lubricating oil the pour point of the oil is reduced from 20° F. to 15° F. the oiliness of the oil is markedly increased.

We can vary the ratio of coal tar fraction starting material to stearyl chloride over rather wide limits. Instead of starting with these crude tower bottoms we can start with various fractions thereof. For example, 35 parts by weight of the fraction boiling range 315° C. to 330° C., and 73 parts by weight of stearyl chloride will give Friedel-Crafts reaction product which, when added to a lubricating oil, so that the oil contains 0.5 percent thereof, will reduce the pour point from 20° F. to 5° F. That fraction of crude tower bottoms, boiling range 230° C. to 345° C., will give a pour point lowering in the same oil of 20° F.

We shall presently tabulate the results obtained from many other coal tar fractions, distillates and extracts. It is to be understood, of course, that in each instance stearyl chloride is reacted with the coal tar fraction in the presence of a

solvent such as carbon disulphide and an aluminum chloride catalyst. In general the quantity of aluminum chloride is about the same as the amount of stearyl chloride or other higher fatty acid chloride used. The amount of solvent, such as carbon disulphide, can be varied over wide limits and should of course be enough to insure solution of the reacting constituents. Any skilled chemist familiar with the Friedel-Crafts reaction will understand its requirements. In conformity with the usual practice in the Friedel-Crafts synthesis the first reaction product (complex aluminum compound) is hydrolyzed to remove aluminum and the final reaction product (viscous oil or waxy solid) is removed and then added to the lubricating oil.

The table which follows tabulates results obtained when 0.5 percent of reaction product is added to a number 30 SAE Mid-Continent oil. The pour point of the original oil was 20° F. and the table gives the pour point lowering observed. In each instance the addition compound was made from 73 parts of stearyl chloride, and except where otherwise noted, the quantity of coal tar fraction starting material was 35 parts by weight. For example, the table gives data for crude red wax in three different quantities, one being 35 parts by weight, another 70 parts and a third 140 parts. Likewise the amount of aluminum chloride is constant throughout and is about equal to the weight of stearyl chloride.

Before tabulating the data we obtain, a description of the various coal tar fractions in the table will be helpful. The "crude tower bottoms" have already been described above. The fractionated crude tower bottoms are distillation cuts made from tower bottoms and having the boiling point ranges (B. P. R.) indicated. The alkali-washed tower bottoms are the residue obtained after washing the tower bottoms with several portions of 20 percent caustic soda solution until no further substances can be extracted with alkali from the tower bottoms. The alkali washings from crude tower bottoms are the alkali-soluble materials in the alkaline solution used for extraction. These were recovered by neutralizing the alkaline extraction liquors with an acid to liberate the alkali-soluble constituents. The neutralized solution is advantageously extracted with ether to remove any alkali-soluble constituents not thrown out on neutralization, the ether is then evaporated, and the alkali-soluble constituents reacted with stearyl chloride.

In a similar manner the tower bottoms were washed with 40 percent sulphuric acid solution to obtain the acid-washed tower bottoms, and the acid-soluble constituents were recovered from the acid washings by neutralizing and ether extraction. The acid- and alkali-washed tower bottoms are the residue of washing the tower bottoms with both acid and alkali.

Crude red wax is the product obtained when coal tar pitch is distilled. Crude red wax is that distillate having a boiling point range of about 432° C. to 500° C. In a further example this material was also acid washed and the product after acid extraction reacted with stearyl chloride as indicated in the table. The coal tar overheated distillate was a fraction of the red wax with a boiling range of 450° C. to 500° C.

The light coal tar bases were obtained from commercial sources and are substances obtained from coal tar by extraction with sulphuric acid. These bases have a boiling point range of from about 100° C. to 355° C., 80 percent of which boils

substantially over 200° C. The heavy coal tar bases are products similarly obtained from coal tar by extraction with sulphuric acid and over 95 percent has a boiling point range of 239° C. to 391° C.

The crude anthracene was a coal tar distillate containing approximately 40 percent anthracene, the remainder being naphthalene, methyl naphthalene, carbazol, fluorene, phenanthrene and other substances. The crude anthracene "product purified" was also crude anthracene-stearyl chloride reaction product which was fractionated by distillation in order to remove unreacted anthracene and naphthalene. Approximately 10 percent of the crude material was distilled off, the remainder being used for addition to the oil. The acid-washed crude anthracene was, as its name implies, the residue from washing crude anthracene with sulphuric acid and then reacting with stearyl chloride.

Three other coal tar distillates are described, these being three cuts from material boiling from 300° C. to 500° C. The creosote oil residues are material commercially obtainable by that name on the market and were made by extracting coal tar with an alkali, neutralization of the extract and isolation of the creosote therein.

Although we specifically mention creosote oil residue from coal tar we can use such residues from wood tar and petroleum oil. The fractionated creosote oil residue was a particular fraction of the residue boiling point range from 200° C. to 250° C. at 10 mm.

The table follows.

Coal tar fraction starting material	Character of reaction product	Pour point lowering °F.
Crude tower bottoms.....	Heavy reddish-brown free-flowing oil.	5
Fractionated crude tower bottoms fraction B. P. R. 315-330° C.	Dark viscous brown oil.	15
Fractionated crude tower bottoms fraction B. P. R. 330-345° C.	Dark brown grease	20
Alkali washed tower bottoms....	Greenish brown viscous oil.	15
Acid washed tower bottoms.....	Light reddish-brown grease.	5
Acid washings from crude tower bottoms.	Brown waxy solid.	20
Acid and alkali washed tower bottoms.	Dark red, waxy oil.	.5
Crude red wax.....	Hard dark red solid.	10
Crude red wax (70 parts).....	Soft red wax.....	35
Crude red wax (140 parts).....	Reddish brown oil.	25
Acid washed red wax.....	Dark red wax.....	5
Coal tar overhead distillate B. P. R. 450-500° C. (70 parts).	Heavy dark red oil.	35
Light coal tar bases.....	Dark red greasy solid.	10
Heavy coal tar bases.....	do.....	40
Heavy coal tar bases (70 parts)...	Dark brown soft waxy solid.	15
Heavy coal tar bases (140 parts)...	Dark brown waxy solid.	10
Crude anthracene.....	Red, waxy material	20
Crude anthracene product "purified."	do.....	35
Acid washed crude anthracene..	Dark red oil.....	5
Coal tar distillate B. P. R. 300-375° C.	Red free-flowing oil.	10
Coal tar distillate B. P. R. 300-375° C. (70 parts).	Free flowing oil.....	5
Coal tar distillate B. P. R. 400-500° C. (70 parts).	Red viscous oil.....	30
Creosote oil residue (50 parts)...	Brown viscous oil.	30
Fractionated creosote oil residue B. P. R. 200-250° C. at 10 mm. (50 parts).	Reddish brown oil.	10

Some of the products we add to mineral oils are highly colored and tend to discolor the oil. This is not ordinarily objectionable but we can

obviate the disadvantage by treating the addition products with a decolorizing agent such as the decolorizing carbons, silica gel, and clay used for this purpose. Likewise we can add our
5 addition agents to a lubricating oil and then subject the treated oil to a decolorizing material.

The above data is primarily directed to the improvement of a number 30 SAE Mid-Continent oil. We have treated many other oils from other
10 sources and obtained similar improvements. For example, the addition of 5 percent of product made from crude red wax (70 parts) to a lubricating oil known as Atlantic red lowers the pour point of the oil 45° F. The addition of product
15 made from the coal tar overhead distillate boiling point range 450–500° C. to Atlantic red shows a pour point lowering of 60° F.

In appended claims we advantageously define the product which we add to lubricating oils as
20 being the Friedel-Crafts reaction product from a higher fatty acid chloride and a coal tar fraction. To those skilled in the art this means a material made by reacting a higher fatty acid chloride with a coal tar fraction in the presence
25 of aluminum chloride, hydrolizing the first reaction product containing aluminum, and isolating the final or Friedel-Crafts reaction product. We have already stated above what we mean by higher fatty acid chlorides. By coal tar fractions
30 we mean those distillates obtained by distilling coal tar or by extracting coal tar with acids or bases.

Having thus described our invention, what we claim is:

- 35 1. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a coal tar fraction and a fatty acid chloride having at least six carbon atoms.
- 40 2. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a coal tar distillate and a fatty acid chloride having at least six carbon atoms.
- 45 3. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a coal tar fraction chosen from the group consisting of alkali-soluble and acid-soluble portions of coal tar and a fatty acid chloride having
50 at least six carbon atoms.

4. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and the coal tar fraction "red wax".

5. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from heavy coal tar bases and a fatty acid chloride having at least six carbon atoms.

6. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from crude anthracene and a fatty acid chloride having at least six carbon atoms.

7. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a coal tar fraction the major portion of which boils above 200° C. and a fatty acid chloride having at least six carbon atoms.

8. A lubricating oil comprising a mineral lubricating oil and a small amount, of the order of 0.1 to 1 percent, of a Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and a coal tar distillate, the major portion of which boils above 200° C.

9. The oil as in claim 1 wherein the chloride is stearyl chloride.

10. The oil as in claim 2 wherein the chloride is stearyl chloride.

11. The oil as in claim 3 wherein the chloride is stearyl chloride.

12. The oil as in claim 4 wherein the chloride is stearyl chloride.

13. The oil as in claim 5 wherein the chloride is stearyl chloride.

14. The oil as in claim 6 wherein the chloride is stearyl chloride.

15. The oil as in claim 7 wherein the chloride is stearyl chloride.

16. The oil as in claim 8 wherein the chloride is stearyl chloride.

17. The process of improving lubricating oils which comprises adding a small amount of a Friedel-Crafts reaction product from a coal tar fraction and a fatty acid chloride having at least six carbon atoms, to the oil.

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