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LUBRICATING OIL COMPOSITION

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5 Claims. (Cl. 196—78)

The present invention relates to improved lubricating oils and is more particularly concerned with high-grade oils containing waxy constituents which have at the same time low pour points and also to methods for preparing such oil.

This application is a division of my copending application Serial Number 645,233 filed on December 1, 1932. The nature of the invention will be fully understood from the following description:

Lubricating oils obtained from different crudes vary considerably in their lubricating and other properties. The oils obtained from naphthenic or asphaltic base crudes are characterized among other properties by a naturally low pour point, for example even below 0° F. due to the absence of natural wax. On the other hand, oils derived from wax base crudes of the Appalachian regions and elsewhere are characterized by naturally high pour points, for example above 25°, 30°, 35° or even 75° F. in the heavier grades. It has been the practice for a great many years to simply accept the inherent properties of the oil and when low pour point oils are required they were made from naphthenic or asphaltic base crudes, although for general purposes it was admitted that they were not the equal of the paraffin base oils. In recent years there has been a great demand for low pour point paraffin base oils and methods have been devised for producing them.

One method consisted in the removal of the wax by mechanical means such as cold settling, cold centrifuging or the like, which methods were generally known in the art but heretofore had not been used to produce very low pour point oils, for example oils pouring at —10° F. or —20° F. Another method for producing low pour point oils consisted in the use of pour inhibitors, which substances when present even in minute quantities prevent solidification or congealing of the oil until temperatures far below the normal pour point are reached.

I have discovered a new group of substances of the type of pour inhibitors which can be produced economically from refinery waste products at reasonable cost, but which at the same time are endowed with powerful pour inhibiting properties. I have found that valuable pour inhibitors can be produced from various oils by treatment with aluminum chloride or with other active halides of the same type and especially from cracked oils such as cycle gas oils, distillates from cracked tars and from natural distillate oils especially those derived from naphthenic and asphalt base crudes. It is desirable to use extracts obtained by treatment with solvents of the class of liquid SO_2, furfural, aniline, phenol and the like. I may also use various other similar materials such as coal tars or fractions therefrom, particularly those free from asphaltic or pitch-like mixtures, such as naphthalene, anthracene, carbazol or mixtures of such substances or the hydrogenated or alkylated derivatives of such substances such as tetraline or decaline or ethyl naphthalene, toluene or mixtures of any of these substances. I have also found that these valuable substances can be made from aluminum chloride sludges or residues which are produced in the regular treatment of these oils with aluminum chloride to increase their lubricating value.

With cracked oils derived from all types of crudes, or uncracked oils especially from naphthenic crudes, or coal tar products it is first desirable to remove all tarry or asphaltic constituents and all methods may be used for this purpose, but I have found it generally sufficient to carefully distill the oil and to prevent entrainment of the tarry matter. Cracking coil tars make an excellent source for my inhibitors because of their cheapness and inherent structure. The tar is distilled to a solid residue and the distillate preferably boiling above 700° F. is separately collected. This distillate may have a gravity of between 9° and 15° or 16° A. P. I., for example, when a 12° A. P. I. tar is used. It is quite fluid, has a low pour point and is pale in color. Whatever the source of the oil, whether cracked or uncracked, it is treated with aluminum chloride or equivalent halides, for example zinc chloride, boron fluoride and the like, or with the well known active clay polymerizing agents in proportion of about 2 to 10% by weight. The preferred procedure is somewhat different depending on the amount of the active halide used. If small amounts are used, say 3 to 5% more or less, the major quantity of the valuable inhibitor is obtained in the oily layer but if amounts of say 8 to 10% be used, the solid sludge contains the major quantity of inhibitor and it must be recovered by special methods which will be outlined below.

My procedure may differ considerably depending on the type of oil treated and the conditions of operation, but in general there are two methods by which the inhibitor may be removed. In the one case the conditions are so adjusted that the entire or major quantity of inhibitor is

split from the aluminum catalytic substance and is removed from the oil, while in the other a sludge is separated from the oil and by subsequent steps the inhibitor is removed from the sludge. In some instances a part of the inhibitor may be split off during the first treating steps and consequently removed from the oil while the remainder is precipitated from the sludge and removed from it. Generally it is possible to adjust conditions so that by far the greater quantity of inhibitor is in the oil or in the precipitated sludge.

The oil or other material may be treated with say 2½ to 5% of aluminum chloride for a prolonged period say at least 2½ to 3 hours, although it may be considerably longer, at a polymerizing temperature at which little or no light oil is produced. This temperature may conveniently be at about 400° F. but if lower generally a little longer time is required for polymerization. The polymerization step may be continued for 10 or 12 hours with advantage, but after 2 or 3 hours at the polymerizing temperature, the temperature may be rapidly raised to a point at which splitting occurs rapidly, and in this way the treating time may be made much shorter. This temperature is above about 500 or 600° F. and the heating should be as rapid as possible, for example, it should be completed in 10 to 30 minutes. Temperatures of 625°, 650°, 700° or 750° F. may be attained. If the heating is slow, greater loss is suffered in the form of light oil, and inactive sludge.

The oil may be cooled or allowed to cool and the sludge settled out preferably at a temperature of 200 to 300° F. According to the procedure outlined above, usually where 2½ to 5% of the active halide is used and the oil mixture has been heated to a temperature of 600° F. or above for purposes of breaking the complex, the inhibitor is largely in the oil, but the sludge may contain some and it may be treated for recovery thereof as will be outlined below.

The oily layer generally has a viscosity of from 200 to 300 seconds Saybolt at 100° F. It may be sufficiently clear to give a good grade inhibitor without treatment but it is generally preferred to purify it by clay treatment, or acid, or alkali, or any other suitable means. A typical inspection of the oil at this stage is as follows:

Gravity	16° A. P. I.
Vis. @ 210° F	43 secs. Saybolt
Vis. @ 100° F	215 secs. Saybolt
Flash point	340° F.
Pour	Below 0° F.

The inhibiting substance is now concentrated or removed as a solid and the simplest method is to distill the oil to a solid residue. It is preferable to accomplish this distillation without any destructive action and the temperature should not rise over 650 or 700° F. Generally a high vacuum is used to remove all of the oil. Other well known methods for precipitating the active substance may be used, for example it may be precipitated by the addition of petroleum ether and other light aliphatic solvents, or by other solvents such as alcohols or their mixtures which are capable of mixing with the oil itself but which precipitate the solid inhibitor.

The separation procedure outlined above is preferable for the production of inhibitors for very light colored and the less viscous oils, but in some instances, especially for production of powerful inhibitors from heavy oils of the cylinder oil type, it is found desirable to treat the oil or other material with greater amounts of the polymerizing catalyst. If a greater amount than 5% be used, it is difficult if not impossible to separate all of the inhibitor from the aluminum chloride complex by the means described above. This is especially true if say 8 to 10% of the active halide is used. If the low temperature polymerization step is prolonged for 10 or 12 hours the step of heating to 500 or 550° F. is not required, but as stated above, the polymerization time may be reduced to 3 or 4 hours if temperature is raised to the splitting range for a short time.

The sludge is separated from the bulk of the oil by settling and is then hydrolyzed at a moderate temperature well below the decomposing range, say at 200 or 250° F., preferably with alkali, but water or acid may be used. Such treatment effectively decomposes the complex and the inhibitor may be leached from the solid or semi-solid mass with a suitable solvent such as benzol, toluene, naphthas and the like, and can be removed as a solid by evaporation of the solvent.

The solid recovered varies in color from yellow to dark red or brown, depending on the source of the oil and the method with which is is made or recovered. That recovered by my first method from the oil is generally of better color than that obtained from sludge by alkali, or other hydrolyzing agents, but the latter is more powerful especially in dark colored heavy oils. The solid generally has a molecular weight in the neighborhood of 350, although this may vary. It is soluble in chloroform, aromatic hydrocarbons such as benzol and toluol and in hydrocarbon oils such as heavy naphthas, kerosene, gas oil and lubricating oils, but it is only partially soluble in hot petroleum ether, alcohols, ketones and the like. These latter solvents appear to dissolve inert constituents leaving an even more powerful inhibitor undissolved. For example, the solid residue left from a distillation under high vacuum may be dissolved to the extent of about 85% with acetone. The 15% remaining is a very active inhibitor, many times more powerful than the unextracted solid. The solid inhibitor appears to be a hydrocarbon, for example an ultimate analysis shows the following results:

	Per cent
Carbon	91.72
Hydrogen	6.79

In a particular case the balance was sulphur, but in other similar tests it was found that the carbon-hydrogen ratio did not vary much although the amount of sulphur varied considerably. The oil itself may be washed and purified in any known method, for example with sulphuric acid or alkalis, or with clay but ordinarily only the clay treatment is necessary.

As indicated above, my product may be produced from the sludges obtained in the ordinary treatment of oils with aluminum chloride. The sludge is removed in the ordinary manner by settling without the addition of water or acid or alkali to hydrolyze the mass and it is rapidly heated to a temperature of about 500 or 600° F. or above. The sludge may be heated alone, but it is preferred to add an oil thereto in order to prevent the baking of the solid material on the walls of the heating vessel and to insure uniform heating. Gas oils are usually satisfactory for this purpose. The sludge may be stirred into the oil during heating and after the elevated tem-

perature has been reached it is allowed to settle out as before. If preferred the alkali splitting method may be used as outlined before, or both methods may be used in combination.

The following examples are given to illustrate the method by which my inhibitor is produced and its effect on different wax-containing oils:

A 10% gravity A. P. I. cracking coil tar is reduced to a solid residue by distillation under vacuum and the distillate boiling above 700° F. at atmospheric pressure is collected. To this distillate 5% by weight of anhydrous aluminum chloride is added and the mass is stirred for about 3½ hours at 400° to 425° F. At the end of this time, the oil is rapidly heated to 625° F., the heating being accomplished in about 20 minutes, and then the mixture is allowed to cool naturally. Light oil production occurs almost exclusively during the 20 minute heating period and it is allowed to distill off and is separately collected. When the oil temperature has dropped to about 300° F. it is found that the sludge has settled into a dense layer and the clear oil layer is decanted. This oil amounts to 37% of the original distillate treated. It is treated with clay at 250° F. and is then allowed to cool to room temperature.

The oil recovered above (37% of the original distillate) is now distilled under high vacuum, care being taken to prevent a temperature rise over about 625° F., a red-colored solid is removed from the still. This material has a molecular weight of approximately 350 and a carbon-hydrogen ratio of .135. The following table shows the effect of this substance on various wax-containing oils:

	Viscosity Saybolt sec.	Concentration of inhibitor	Original pour	Reduced pour
			°F.	°F.
Spindle oil	140 at 100° F.	.5%	30	−5
Hydrogenated oil	350 at 100° F.	.05% dewaxed to	0	−20
Engine oil	52 at 210° F.	.5%	30	−5
Cylinder oil	131 at 210° F.	.5%	95	75
Do	131 at 210° F.	1.0%	95	45
Heavy cyl. oil	153 at 210° F.	.5%	35	15

The solid obtained above contains inert materials as well as active constituents. When extracted with acetone 85% or thereabouts dissolved leaving 15% of an insoluble residue. This residue is an extremely powerful inhibitor approximately 8 to 10 times as powerful as the unextracted solid. It may be added in much smaller quantities to produce a given depression or, if added in equal quantities, produces a considerably greater depression. In the use of my pour inhibitors the solid may be added directly to the lubricating oil and stirred into it until completely dissolved, or it may be dissolved in high concentration in a relatively small quantity of the oil and then added to the bulk. It may be dissolved in an aromatic oil, for example benzol or toluol and added to the lubricating oil and in this case the oil may be heated to remove the benzol or toluol.

As a second example a 12° A. P. I. distillate is obtained from a 8° A. P. I. cracking coil tar and is heated at about 400° F. for 3 hours with constant stirring with 10% of anhydrous aluminum chloride. The oil was then heated rapidly to 650° F. and the sludge settled and separated by decanting the oil. The sludge is then warmed to 250° F. and flake caustic is added to effect neutralization or hydrolysis of the chloride. The pasty mass is cooled and thoroughly extracted with kerosene which on distillation leaves the inhibitor as a reddish solid. It is darker in color than the inhibitor secured in the prior example but is more active especially in respect to heavy oils. When added in proportion of 1% to the cylinder oil (131 viscosity @ 210° F.) mentioned in the previous example, it is observed that the original pour point of 95° F. is reduced to 20° F.

As a third example, naphthalene and anthracene are mixed with aluminum chloride in ratio of 1:1:1 and heated for 1 hour at 250° F. The complex was broken in this instance by addition of sulphuric acid using as a diluent an aromatic oil obtained by the extraction of petroleum with liquid sulphur dioxide. The oily layer is separated from the acid layer and is filtered and washed with water. It is then reduced by fire and steam distillation to 500° F. The solid inhibitor is secured as a bottoms. When added to an oil having a pour point of 30° F. in concentration of .5% it is noted that the pour is reduced to 15° F. In similar tests anthracene green oil and naphthalene were used in admixture to produce an inhibitor.

My inhibitors induce pour depressions of from 30 to 50° F. or even more, and in the case of high pour oils it is often desirable to partially dewax and then to add the inhibitor to the oil. In this way smaller quantities of the inhibitor are required.

I claim:

1. A lubricating oil of low pour point comprising a blend of a wax containing petroleum lubricating oil with a minor proportion of a pour inhibiting agent prepared by adding to a refractory distillate from a cracking-process tar boiling above 700° F. about 5% by weight of anhydrous aluminum chloride, heating the mass to a temperature between 400° F. and 425° F. and maintaining it at this temperature for about 3 hours, then rapidly heating the mass to between 625° F. and 700° F. for about 20 minutes, allowing the mass to cool to about 300° F., separating the oily layer from the sludge, distilling the oily layer under vacuum at a temperature below about 625° F. and recovering the red colored solid residue from the still.

2. A lubricating oil of low pour point comprising a blend of a wax containing petroleum lubricating oil with a minor proportion of a pour inhibiting agent prepared by treating a refractory distillate from a cracking-process tar boiling above 700° F. at atmospheric pressure with anhydrous aluminum chloride at temperature around 400° F. for a prolonged period, then rapidly heating the mass to about 700° F. for about 20 minutes, separating the sludge of aluminum chloride complex from the liquid products, vacuum distilling the liquid products at temperatures up to about 500° F. to obtain a red colored solid residue.

3. A lubricating oil according to claim 2 in which the red colored solid residue is extracted

with acetone and the undissolved material recovered.

4. An improved method for producing wax modifying agents having pour point depressant properties which comprises distilling a cracking-coil tar under vacuum to a solid residue, collecting the distillate which boils above 700° F. at atmospheric pressure, adding to this distillate about 5% by weight of anhydrous aluminum chloride, heating the mass to a temperature between 400° F. and 425° F. and maintaining it at this temperature for about 3 hours, then rapidly heating the mass to between about 625° F. and 700° F. for about 20 minutes, allowing the mass to cool to about 300° F., separating the oily layer from the sludge by decantation, neutralizing the sludge with caustic, extracting the neutralized sludge with a solvent and recovering the pour inhibitor from the extract as a residue after removing the solvent from the extract by distillation.

5. An improved method for producing wax modifying agents having pour point depressant properties which comprises distilling a cracking-process tar under vacuum to a solid residue, collecting the distillate which boils about 700° F. at atmospheric pressure, adding to this distillate about 5% by weight of anhydrous aluminum chloride, heating the mass to a temperature between 400° F. and 425° F. and maintaining it at this temperature for about 3 hours, then rapidly heating the mass to between about 625° F. and 700° F. for about 20 minutes, allowing the mass to cool to about 300° F., separating the oily layer from the sludge by decantation, neutralizing the sludge with sodium hydroxide, extracting the neutralized sludge with acetone and recovering the pour inhibitor as a residue after removing the acetone by distillation.

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