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LUBRICATING OIL COMPOSITION

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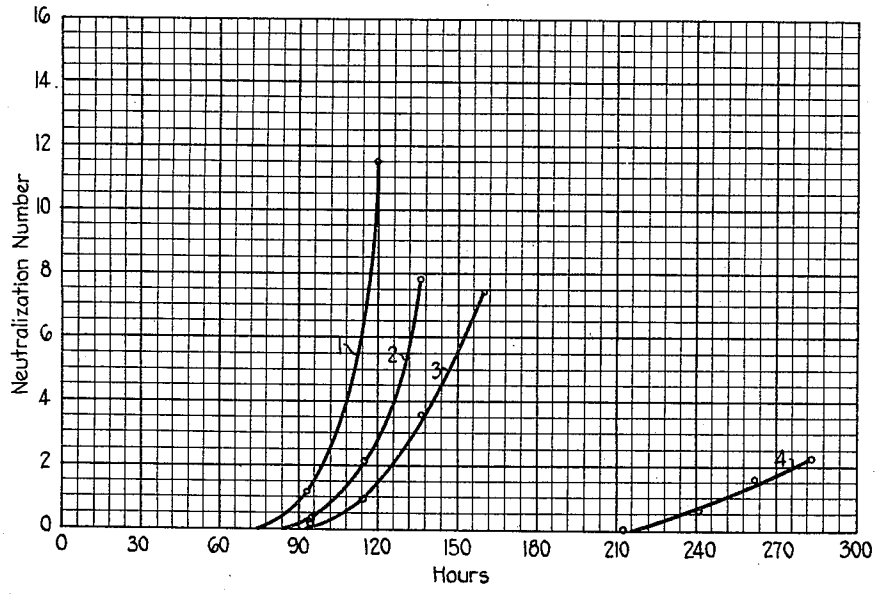


Fig. I

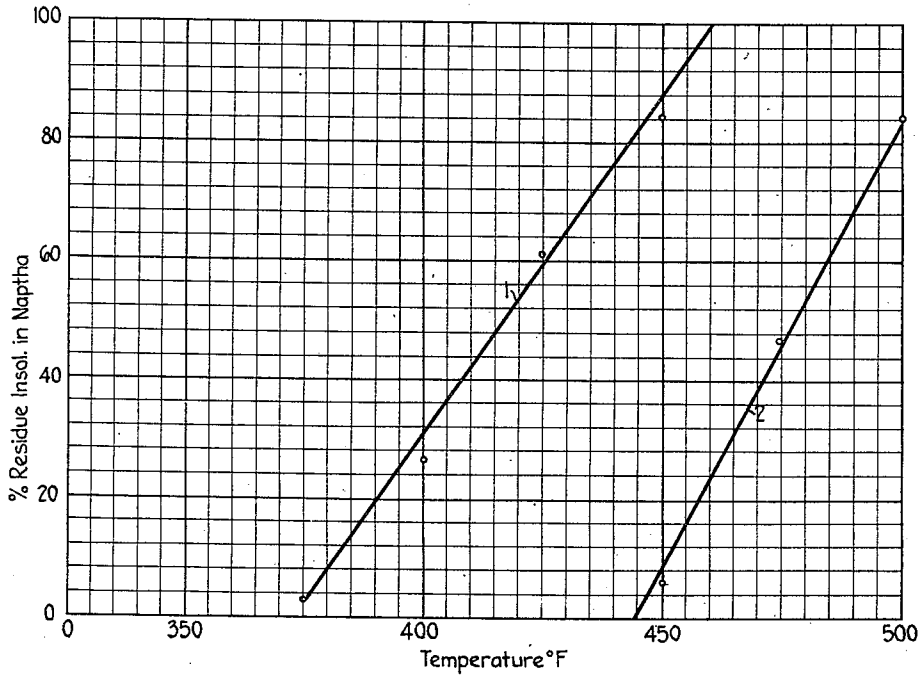


Fig. II

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LUBRICATING OIL COMPOSITION

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6 Claims. (Cl. 196—151)

This invention deals with lubricants which are relatively stable under oxidation conditions and is more particularly concerned with mineral lubricating oils to which a highly cracked hydrocarbon distillate oil has been added.

Lubricating, transformer, and other refined relatively heavy mineral oils suffer a marked deterioration in use and when exposed to air at elevated temperatures. Generally, such petroleum oils when in use darken in color and eventually may become saturated with and deposit a finely-divided oil-insoluble carbonaceous material, commonly known as sludge. Under some conditions they may deposit a varnish on hot metal surfaces. Such oils, in addition, develop an acidity after some period of use, particularly when used under high temperature conditions. It has been established that the formation of acids is due to oxidation, and it is thought that the formation of sludge may be due to polymerization and/or oxidation. Varnish formation is believed to be caused by similar reactions. The rapidity of this deterioration varies with various oils and depends upon their sources and degree of refinement as well as on the conditions to which they are exposed. In many cases the deterioration appears to be an autocatalytic phenomenon in that products of the reaction serve to speed up or catalyze the further deterioration of the oil itself. In prior attempts to prevent this deterioration of lubricating or transformer oils, use was made of oxidation inhibitors. Such materials are useful for a certain time but soon they themselves are oxidized and lose their effectiveness.

Now, in accordance with our invention, we have found that the addition of certain highly aromatic cracked hydrocarbon oils such as high boiling fractions of coking cycle stock to mineral lubricating oils in suitable quantities produces lubricants which are relatively free from the above disadvantages and of good lubricating qualities.

The coking cycle stock, as herein defined, is a highly aromatic hydrocarbon liquid obtained by operating a liquid phase cracking unit, having a reaction chamber, under conditions to produce coke instead of residual black fuel oil. During such runs, temperatures in the reaction chambers are usually of the order of 865° F. to 895° F. and are thus considerably higher than during fuel oil runs. The vapors leaving the coking chamber are fractionated to remove fixed gases and gasoline and the remaining, relatively heavy, fraction is the coking cycle stock, which is recycled through the heating and cracking zones. When a coking chamber is filled with coke, steam or other suitable convection medium is blown through it. This causes the vaporization of additional extremely aromatic material, which is normally recycled as part of the coking cycle stock. This last material is known as coke blow-down. This blow-down may be an oil or may consist partially or completely of a normally solid non-tacky material, some of which may be in the form of well-defined crystals.

Instead of high boiling coking cycle stock fractions, we may also employ distilled high boiling fractions of fuel oils obtained in vapor phase cracking. In order to be suitable for our purpose, these highly cracked stocks must possess certain properties. As indicated above, they must be high boiling. That is, their initial boiling points should not be below about 500° F. and preferably above 700° F. They also must be highly aromatic. That is, their specific dispersion as measured by the method of von Fuchs and Anderson (Ind. Eng. Chem. 29, 319, March 1937), should be not below 200 and preferably above 250. These highly cracked oils have such a remarkable stabilizing effect that they are effective even without further purification. However, we often do prefer to purify the cracked oils in order to make them even more effective. Such purification may involve removal of olefines or sulfur compounds or other non-hydrocarbon impurities. Thus, we may treat the oil with sulfuric acid, aluminum chloride, clays, and various other treating agents, or we may hydrogenate them under conditions so as not materially to reduce their specific dispersion.

Moreover, the cracked oils may be separated into fractions of various aromaticities, as by solvent extraction or fractional precipitation, or both. For example, the entire coking cycle stock, blow down oil or vapor phase cracked fuel distillates may be dissolved in a solvent for aromatic hydrocarbons, such as furfural, nitrobenzene, phenol, acetone, dichlordiethylether, etc., and sufficient light, straight run naphtha, isopentane or other light paraffin hydrocarbons may be added until a precipitation of the more aromatic portion occurs.

The separation into fractions of different aromaticity may be particularly important when utilizing cracked stocks having specific dispersions in excess of 300. Such stocks frequently contain very highly condensed aromatic bodies, some of which have specific dispersions in excess of 500. These extremely condensed aromatics normally

are solids substantially insoluble in lubricating oils and thus cannot be used in our process to advantage. Their elimination is desirable.

The active compounds of our oils are believed to consist primarily of aromatic hydrocarbons of an intermediate degree of condensation having possibly two, three or four aromatic rings in various close configurations, which rings carry many short alkyl radicals. It is thought that the activity of these aromatic compounds as oxidation retardants is primarily due to their content of many short side chains. As evidence for this assumption, may be cited the fact on the one hand a naphthalene or anthracene, which possesses no side chains, has less anti-oxidant effect, and that on the other hand, diamyl naphthalene or certain highly aromatic extracts of lubricating oils, which are known to consist predominantly of aromatics containing a few fairly long side chains, are also inferior to our additives.

Preferred amounts of the cracked aromatic oils to be added range from about 2–10%, although in most instances amounts within the range of .5–15% may be used.

In the attached drawing the effect of the addition of our compounds is clearly illustrated. Two graphs are presented. In Figure I the rate of acid formation in the "Turbine oil stability test" is plotted against time for a 150 viscosity at 100° F., turbine oil to which have been added different coking cycle stocks. The several curves represent the following oils:

Curve	Oil	Addition agent		
		Amount added in percent of turbine oil	Nature	Specific dispersion
		Percent		
1	Turbine oil	None	None	None
2	do	5	Acid-treated coking cycle stock.	201
3	do	10	do	201
4	do	5	do	295

The enormous superiority of the coking cycle stock having the highest specific dispersion represented by curve 4 is self-evident. In Figure 2 is shown the amount of naphtha-insoluble resins formed when heating a sample of a motor oil by a modification of the "General Motors steel plate varnish test." This test is said to be indicative of the tendency of an oil to form varnish in engines at various temperatures. Two curves are shown, one having a conventional S. A. E. 20 motor oil from Mid-Continent crude (curve 1) and the other from the same oil containing 10% of an unrefined blow down oil (curve 2). It will be seen that the addition of the blow down oil permits temperatures of 50° F. to 75° F. higher for equal lacquer formation than the undoped oil.

The "turbine oil stability test" referred to above is a test for oxidation stability. A sample of oil is maintained at a temperature of about 205° F. in the presence of copper, iron and water, while oxygen is passed through it at a rate of about 6 liters per hour. Samples of the oil are withdrawn at intervals, and their neutralization numbers are measured. These values are indicative of the oxidation stabilities of the oils tested.

The "General Motors steel plate varnish test" as referred to above is conducted by submerging a cylindrical receptacle in a heated oil bath maintained at the desired test temperature. A steel plate having a depression on its surface filled with the oil to be tested is then placed in the receptacle for an hour. The amount of residue from the oil sample which is insoluble in naphtha is then measured. The amount of naphtha-insoluble residue in such a test is said to be an indication of the lacquer-forming characteristics of the oil.

Lubricating or electrical oils containing the highly cracked materials described before may be further improved by the addition of pour-point depressors, suitable oxidation inhibitors which prolong the induction period, wax suppressors, blooming agents, extreme pressure agents, wedging agents, reducing agents, corrosion inhibitors, and other compounding ingredients.

The following examples further illustrate our invention.

In the tables below are presented the properties of a turbine oil of approximately 150 viscosity at 100° F. and of a blend of that oil containing 5% by weight of an acid treated coking cycle stock at several periods during the aging by the before-described turbine oil stability test.

EXAMPLE A.—*150 viscosity turbine oil without aromatic addition agent*

	Hours aged					
	0	96	120	144	168	186
Gravity, A. P. I.	31.7	30.6	27.2	23.9		
S. U. vis. at 100° F., sec.	157	185	253	403		
Neutralization number	>.05	1.4	12.1	15.9	Discontinued	
Saponification number	.2	------	15.0	20.8		
Sludge, mg./g. of oil	------	------	4.8	17.6		
Specific dispersion	103.1	------	------	------		

EXAMPLE B.—*150 viscosity turbine oil containing 5% by weight of acid-treated coking cycle stock*

	Hours aged					
	0	96	120	144	168	186
Gravity, A. P. I.	31.7	----	------	------	30.4	28.6
S. U. vis. at 100° F., sec.	147	----	------	147	------	------
Neutralization number	>.05	----	------	.10	.6	4.9
Saponification number	.2	----	------	.22	3.1	12.7
Sludge, mg./g. of oil	------	----	------	------	1.35	------
Specific dispersion	109.2	----	------	------	------	------

The coking cycle stock used in Example B had the following properties: gravity, A. P. I. 16.4; flash, open cup 305° F.; fire, open cup 335° F.; specific dispersion, 201; initial boiling point, 560° F. and an end point of 624° F.

We claim as our invention:

1. A lubricating or electrical oil composition comprising a refined mineral lubricating oil and dissolved therein a small amount of a highly cracked distillate oil free from tar selected from the group consisting of coking cycle stock and cracking coke blow down oil and having an initial boiling point above 500° F. and a specific dispersion above 200 said composition having greater resistance to oxidation than said mineral oil.

2. The composition of claim 1 in which the amount of cracked oil is from .5% to 15%.

3. The composition of claim 1 in which the amount of cracked oil is from 2% to 10%.

4. The composition of claim 1 in which the cracked oil has been treated by a process to remove non-hydrocarbon impurities and olefines.

5. The composition of claim 1 in which the cracked oil is free from substantially oil insoluble solid aromatic hydrocarbons.

6. A lubricating or electrical oil composition comprising a refined mineral lubricating oil and dissolved therein a small amount of a refined highly cracked distillate oil free from tar selected from the group consisting of coking cycle stock and cracking coke blow-down oil and having an initial boiling point above 500° F. and a specific dispersion above 200, said composition having a greater resistance to oxidation than said mineral oil.

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