United States Patent Office

2,842,498

Patented July 8, 1958

2,842,498

LUBRICATING OIL

Samuel M. Darling, Lyndhurst, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application March 10, 1955
Serial No. 493,558

2 Claims. (Cl. 252—51.5)

The present invention relates to petroleum oils and to a process for the production thereof.

Oils of lubricating viscosity are usually produced from three different types of petroleum crude oils. These are the so-called Pennsylvania crudes, the Coastal crudes, and the Mid-Continent crudes. Pennsylvania crudes are highly paraffinic and oils made therefrom generally require distillation, dewaxing and clay contacting as the only steps in the production of the finished lubricating oils. On the other hand, the Coastal crudes and the Mid-Continent crudes in general, which are hereinafter termed "asphaltic base crudes," contain varying concentrations of asphaltic and aromatic components and, as a result, the production of lubricating oils therefrom almost invariably requires some refining treatment such as acid refining, solvent extraction, or propane deasphalting for the removal of asphaltic, resinous and aromatic type hydrocarbons to improve the stability and oxidation resistance of the resulting oil.

In the production of industrial lubricants such as cutting oils, anti-rust oils, grinding oils, oils for greases, transformer oils, cordage oils, autoclave oils, and solvent oils, as distinguished from oils for lubricating an internal combustion engine, the presence of asphalt and aromatic constituents in the lubricant is not of itself detrimental to the use properties of the lubricant. Oils which fill the needs of industrial lubricants do not require the high viscosity index or the high degree of refining requisite of an oil for use in an internal combustion engine, but the presence of asphaltic or aromatic components does reflect adversely on the saleability of industrial lubricants because unrefined oils are notoriously susceptible to discoloration. Buyers and sellers often include a color specification. Therefore, even in the production from an asphaltic base crude of oils for use as industrial lubricants or as components of industrial lubricants, a step such as acid refining, solvent extraction or propane deasphalting has been considered indispensable.

In a typical refining process for the preparation of lubricating oil from an asphaltic base crude, the crude is first fractionally distilled to recover a distillate boiling in the lubricating oil range. This distillate may then be dewaxed, for example by a conventional chilling and pressing or by solvent dewaxing. The distillate is then separated in a rerun unit into fractions of varying viscosities designated as "neutral stocks," which may or may not be dewaxed depending on whether a dewaxing step is included in the processing. These neutral stocks are stored and then refined by treatment with sulfuric acid to separate the asphaltic and aromatic constituents into the acid phase, followed by treatment with clay to neutralize the oil and remove sulfonates. The resulting acid-refined oils are well known as "conventionally refined" neutral oils. These conventionally refined neutral oils in general have satisfactory color stability, although in some instances color inhibitors may be added as a precautionary measure.

In the process outlined above, the sulfuric acid treatment represents a substantial part of the cost of the total process, because of equipment needs, processing costs, acid requirements and oil lost to the acid phase. It is obvious that the elimination of this step would be desirable from the economic standpoint and, accordingly, it is an object of the present invention to provide a process for producing industrial oils from asphaltic base crudes which avoids the heretofore indispensable step of acid refining, or other equivalent refining step such as solvent extraction, and which for use in industrial applications have the color and other properties of conventionally refined oils.

As discussed above, a combination of distillation, with or without dewaxing steps, applied to an asphaltic base crude leads to the production of "neutral stocks." These waxy or dewaxed neutral stocks, therefore, contain all of the liquid oil components, including asphaltic and aromatic type hydrocarbons, of the original fraction distilled from the crude. In another sense, they may be denfined as "unrefined" oils in the sense that they have not been subjected to acid refining, solvent extraction or equivalent treatment to separate liquid (oil) components by hydrocarbon type. Distillation and dewaxing are not regarded as refining, as the term is generally used, and as it is used here. In physical appearance and properties, the neutral stocks when freshly produced have a sufficiently light color to be saleable and have satisfactory lubricating properties for industrial uses. However, the color of the neutral stocks darkens rapidly with the passage of time. Hence, as explained above, they are not regarded as suitable for use in commercial lubricants without further treatment.

In accordance with the present invention, it has been found that the neutral stocks produced from asphaltic base crudes can be made into oils of good color stability, comparable in quality to the conventionally refined oils that have been made by acid refining, by a combination of steps which comprises (1) contacting a neutral stock with a mineral adsorbent, such as a clay, and (2) adding to the adsorbent-treated neutral stock a minor amount of a compound having the formula:

$$HO—C_6H_4—HC=N—C_3H_6—N=CH—C_6H_4—OH$$

The preferred compounds have the OH group in the ortho position. The C_3H_6 chain may be straight or branched.

I am aware that clay contacting is a widely practiced step in the production of lubricating oils from all types of petroleum crudes and that in many cases it contributes to improved color and color stability of the finished oils. However, its primary function in the usual refining sequence is to remove the remnants of acid and acid sludge remaining after acid refining, or to remove the remnants of solvent remaining after solvent extraction. On the other hand, the function of the clay contacting step in the present invention is to render the oil susceptible to the action of the above-described inhibitor. I do not rely on clay contacting to improve the color of the neutral stock; actually in some cases the clay contacting may darken the color of the oil, but even if darkened, it is rendered susceptible to the inhibitor. The clay treating step of the invention apparently acts upon the neutral stock in some manner to render it vastly more susceptible to the action of the inhibitor.

It is apparent in any case that in the present invention the combination of clay contacting and inhibitor addition leads to results which could not have been predicted from the effects produced by either step alone.

I am also aware that compounds of the above formula are disclosed as color inhibitors for viscous petroleum oils in U. S. Patent No. 2,282,513 to Downing et al.

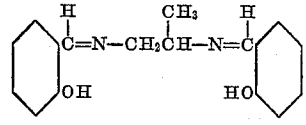
This patent, however, discloses and contemplates the addition of such inhibitors to serve their known function and does not recognize that they can be used as a substitute for acid refining if used in combination with a prior clay treatment. There is no indication from the disclosure of this patent that satisfactory industrial lubricants could be produced from "neutral stocks" from an asphaltic base crude in the manner contemplated by the present invention.

In the first step of the process of the invention, a neutral stock from an asphaltic base crude is contacted with a mineral adsorbent, for example by filtration (percolation) through the adsorbent, as conventionally practiced in the petroleum industry. Alternatively, the adsorbent may be agitated with the oil and then filtered therefrom. In this step of the process the color of the neutral stock may be or may not be improved but the oil is in some way rendered much more susceptible to the action of the inhibitor that is to be later added. In this treatment the amount of mineral adsorbent can advantageously be in the ratio of from about 1 to about 20 lbs. per barrel of neutral stock, preferably from 5 to 10 lbs. per barrel, the temperature from about 175 to 325° F. and the time of contact from about 5 to 60 minutes, depending primarily on the amount of clay and the temperature, shorter times being permitted for higher temperatures and larger amounts of clay.

The mineral absorbent can be any of those natural or synthetic clays that are useful in the preparation of lubricating oils from petroleum crudes. Suitable adsorbent minerals are the members of the group of natural clays which may be acid-activated, and are made from the mineral montmorillonite. They are available under trade names such as "Filtrol" and "Super-Filtrol" lube contact clays, as well as fluid catalysts of the natural clay type available under the trade name "Filtrol D." Also suitable and available from the same supplier is "Neutrol I," a special low-acidity type "Filtrol" clay. Another suitable mineral adsorbent is sold under the trade name "Magnesol," which is a highly adsorptive, synthetic, hydrous magnesium silicate. Other suitable mineral adsorbents are those identified by the trade name "Seasorb" which is a magnesium oxide type clay and MS catalyst which is a synthetic aluminum silicate microsphere cracking catalyst. Another satisfactory clay is known as Cat-lube clay, which is a fluidized natural clay. These clays may be used singly or in admixture or, if desired, treatment with one clay may be followed in sequence by treatment with another clay.

In general, it has been observed that the acidic mineral adsorbents such as "Filtrol," "Super-Filtrol," "Magnesol," and MS catalyst often provide an initial improvement in color; basic clays such as "Seasorb" do not usually give an initial improvement in color but produce a final oil with excellent color stability.

As the second step in the process, there is added to the adsorbent-treated oil a minor amount of a color inhibitor of the formula given hereinabove. A compound of this formula is available under the trade name "Tenamene 60," the active component of which is disalicylal propylene di-imine of the formula:



It is sold as an 80% solution in toluene. The composition has the following physical properties:

Specific gravity (75° F.)	1.07
Viscosity at 100° F. SUS, secs.	80
Freezing point, ° F.	−1
Flash point (closed cup), ° F.	19

The inhibitor can be added to the clay-treated oil in effective concentrations ranging from 0.001 to 1%, preferably from 0.005 to 0.1%, by weight of the oil. Very small amounts within this range are effective and an excess, though not harmful, does not give a corresponding beneficial effect. It can be dissolved in the oil simply by agitation. One convenient method of agitation is air blowing. The order of the steps is critical and cannot be reversed.

In order to more fully illustrate the invention, several specific examples, in which parts and percentages are by weight, will be presented. In the examples, the following abbreviations are used for convenience:

N. S.—Neutral stock, i. e., an oil that has been separated from the crude by distillation and not otherwise treated except it may be dewaxed.

O. D.—Optical density.

O. D. D.—Optical density degradation (the difference in or between the initial optical density of an oil at the beginning of a test and its optical density at the end of the test).

CRN—Conventionally refined neutral oil, i. e., an oil that has been acid-treated and then clay contacted (when followed by a number, this is the SUS viscosity at 100° F.).

CTI—Clay treated and inhibited according to the invention (when followed by a number, this is the SUS viscosity at 100° F.).

The tests referred to in the examples are as follows:

OVEN TEST

A 50 ml. sample of the oil to be tested is placed in a 100 ml. beaker in a thermostatically controlled oven at 210° F. for 120 hrs. Optical densities are measured before and after the test.

CATALYZED OVEN TEST

This test is performed in the same manner as the oven test with the exception that the test time is 72 hrs. and thin copper and iron strips are immersed in the oils to catalyze oxidation.

COLOR-HOLD TEST

This test is the same as the oven test except that the time is shortened to 16 hrs.

OPTICAL DENSITY

The Beckmann quartz photoelectric spectrophotometer is the instrument used. The optical density of the sample is measured by the amount of absorption that takes place at 520 mμ. The sample and a reference solvent such as benzene, D. C. naphtha, n-heptane, or iso-octane are placed in 1 cm. liquid type Corex cells, and the absorption of the sample is recorded. The optical density is calculated by the following formula:

$$\text{O. D. color} = 100 \times \frac{A}{b \times \frac{c}{1000}}$$

where

A=absorption of the sample

b=length of optical path

c=conc., ml. of sample per 1000 ml. solution

Example I

There was obtained fresh from the rerun unit of a commercial petroleum refinery a quantity of neutral stock derived from a Mid-Continent crude and having a viscosity of 160 SUS at 100° F. The neutral stock was kept under a nitrogen atmosphere while awaiting further processing in order to prevent deterioration.

The neutral stock behaved as follows in the oven test:

Initial O. D.	Final O. D.	O. D. D.
18.3	>200	>200

Other portions of the same neutral stock were placed with measured amounts of "Super-Filtrol" in flasks and stirred and heated to 260° F. for 15 minutes. The clay-treated portions were then filtered while hot, cooled and stored in an inert atmosphere. The effects of the clay treatment as shown by the oven test are as follows:

Lbs. clay per barrel	Initial O. D.	Final O. D.	O. D. D.
5	22	91	69
10	22	91.9	69.9

To each of the several portions of clay-treated neutral stock there was added a measured amount of "Tenamene 60" which was dissolved with agitation. In this and other tests the amount of "Tenamene 60" is such as to provide the stated amount of the active component. The finished CTI samples gave results in the oven test as follows:

Inhibitor, percent	Amounts of Clay expressed in lbs. clay per barrel of oil	Initial O. D.	Final O. D.	O. D. D.
0.005	5	21.6	51.4	29.8
0.05	5	21.8	44.0	22.2
0.10	5	21.8	49.0	27.2
0.005	10	21.8	46.3	24.5
0.05	10	22.2	46.8	24.6
0.10	10	22.1	46.7	24.6

In order to demonstrate the combined effects of clay-treatment and inhibitor addition, varying amounts of "Tenamene 60" were added to portions of the neutral stock which had not been clay-treated. These inhibited, but not clay-treated, samples gave the following results in the oven test:

Inhibitor, percent	Initial O. D.	Final O. D.	O. D. D.
0.005	19.2	70.4	51.2
0.05	18.5	85.9	67.4
0.10	18.2	84.0	65.8

A study of the results in the several preceding tables vividly demonstrates the advantages of the invention. It can be seen, for example, that treatment with clay at the rate of 5 lbs. per barrel results in an optical density degradation of 69. Doubling the amount of clay serves no advantage. An amount of inhibitor equal to 0.05% in a non-clay-treated sample gives an O. D. D. of 67.4 and doubling this amount of inhibitor gives substantially no advantage. However, the CTI sample which was clay-treated at 5 lbs. per barrel and to which was added 0.05% of inhibitor gave an O. D. D. of only 22.2. This latter figure could not have been predicted from the known results of either treatment alone.

Example II

There was obtained fresh from the rerun unit of a commercial petroleum refinery a quantity of neutral stock which had been produced from a Mid-Continent crude. This neutral stock had a viscosity of 110 SUS at 100° F.

Different portions of the same neutral stock were treated with different clays according to a procedure similar to that in Example I, using 15 lbs. of clay per barrel of oil, a contact time of 45 minutes, and a temperature as specified hereinafter. To parts of each portion which was so treated there was added 0.005% of the same inhibitor. The various samples of oil were then tested according to the color-hold test and the oven test. The results of these tests are as follows:

Clay	Temperature, Degrees F.	Inhibited	Color-Hold, O. D. D.	Oven Test, O. D. D.
None		No	8	45
Super-Filtrol	257	No	3.7	52.3
Do	257	Yes	0.6	18.7
Filtrol X-417	317	No	1.3	20.7
Do	317	Yes	0.6	13.4
Filtrol X-466	260	No	1.6	23
Do	260	Yes	1.2	12.6
Neutrol I	230	No	2.5	35.0
Do	230	Yes	1.3	19.8
Magnesol	288	No	2.0	15.8
Do	288	Yes	1.3	9.0
Seasorb 53	290	No	2.8	14.4
Do	290	Yes	0.3	1.2
MS Catalyst	228	No	4.8	50.5
Do	228	Yes	1.5	7.1
Cat-lube Clay	229	No	3.6	112.5
Do	229	Yes	1.2	12.8
Filtrol X-623	260	No	1.4	25.4
Do	260	Yes	0.9	12.5

It can be seen from the preceding results that the combination of clay treatment and inhibitor addition produces a product which fares remarkably well in both tests.

Example III

Samples of representative CTI oils prepared in Example II were held in storage for 55 days and then examined visually for evidence of precipitation of insoluble matter. The results of this observation are as follows:

Clay	Inhibited	Precipitation
Neutrol I	No	Moderate.
Do	Yes	Negligible.
Magnesol	No	Moderate.
Do	Yes	Negligible.
Cat-lube Clay	No	Heavy.
Do	Yes	Trace.
Filtrol X-466	No	Heavy.
Do	Yes	Light.

It can be seen in all cases that the addition of the inhibitor to a clay-treated neutral stock renders the CTI oil comparatively free from precipitation of insolubles on prolonged storage.

Example IV

A quantity of the CTI-110 oil prepared in accordance with the procedure of Example II and containing the 0.005% of the inhibitor, was tested for oxidation stability in the Polyveriform test, according to U. S. Patent No. 2,464,233, for 19 hrs. at 300° F. at a rate of 70 liters of air per hour in the presence of an iron catalyst (ferric ethyl hexoate). The sample tested was a composite of samples in which the clays were Super-Filtrol and Filtrol X-417. The treating time varied from 30 to 45 minutes and the temperature varied from 230 to 280° F. The results of this test in comparison with a typical commercial conventionally refined oil of the same viscosity are as follows:

Oil	Fe Added Expressed as Percent Fe_2O_3	Acid No. of Used Oils	Pentane Insolubles in Used Oils (Percent)
CRN	0.005	2.47	1.13
CRN	0.05	9.02	8.41
CTI	0.005	0.57	0.59
CTI	0.05	7.92	6.25

It can readily be seen that the CTI oil compares favorably with the conventionally refined oil.

Example V

There was obtained quantities of neutral stocks of varying viscosities fresh from the rerun unit of a commercial petroleum refinery processing a Mid-Continent crude.

The neutral stocks were treated by filtration with Super-Filtrol at the rate of 8 lbs. of clay per barrel of oil at a temperature of 260° F. employing a contact time of 45 minutes. These clay-treated neutral stocks were then inhibited with 0.005% of the same inhibitor to produce CTI oils according to the invention using air to agitate the oil and disperse the inhibitor.

These CTI oils were then compared in properties such as pour point, flash point, etc. with a typical conventionally refined neutral oil of the same viscosity from the same refinery. The following table gives the properties of the CTI oils, the specifications for conventionally refined neutral oil.

Specification Tests	100 SUS			75 SUS			65 SUS		
	CRN Spec.	CTI	Typical CRN	CRN Spec.	CTI	Typical CRN	CRN Spec.	CTI	Typical CRN
Gravity, ° API	27.5–28.5	27.7	28.0	28.5–29.5	28.8	29.2	29.5–30.5	29.7	31.0
Pour, ° F.	25 Max.	25.0	30.0	25 Max.	25	25	25 Max.	15	35
Flash, ° F.	350 Min.	370	350	330 Min.	360	330	305 Min.	345	315
Fire, ° F.	390 Min.	415	400	365 Min.	405	370	340 Min.	385	360
Color, ASTM	1½–2½	2+	2	1½–2½	2−	1½+	1½–2½	1½+	1½+
Vis. SUS at 100	98–105	103	100	75–80	79.54	79	60–65	67.2	61
Acid No.	0.05 Max.	0.038	0.06	0.05 Max.	0.027	0.04	0.05 Max.	0.022	0.06
Carbon Residue	0.07 Max.	0.07	0.07	0.07 Max.	0.07	0.08	0.05 Max.	0.07	Trace

Example VI

The samples of CTI oils prepared in Example V were placed in tank storage for 41 days. The following table shows the optical densities at the start and end of the storage period and the changes during the period. All three of the oils show very little change thus proving to be satisfactory.

	Initial	O. D. Final	O. D. D.
CTI–100	15.4	14.8	−0.6
CTI–75	8.1	7.6	−0.5
CTI–65	7.5	7.3	−0.2

Example VII

Other samples of the CTI oils prepared in Example V were stored in indirect light in glass bottles for 38 days. All three of the CTI oils proved to be color stable under these conditions. The CTI–100 oil showed an O. D. D. of only 2.6, the CTI–75 an O. D. D. of only 3.5, and the CTI–65 an O. D. D. of only 2.7.

Example VIII

The CRN–100 and CTI–100 oils of Example V were tested in the catalyzed oven test. The results are as follows:

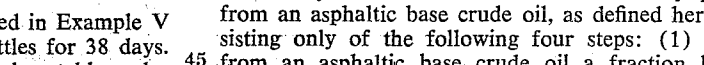
	CTI	CRN
Final Color (O. D.)	42	200.
Sludge	none	heavy.
Copper Strip Appearance	slight discoloration.	moderate discoloration.
Iron Strip Appearance	bright	bright.

It is evident that the CTI oil compares very favorably in this test with the CRN oil and is actually superior.

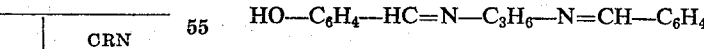
The elimination of acid-treating of oils from Mid-Continent crude to provide oils as good as or superior to conventionally refined oils by the combination of steps disclosed represents a saving of acid-treating capital and operating costs, acid costs and oil loss in the acid-treating. CTI oils were formulated in greases, cutting oils, grinding oils, soluble oils, anti-rust oils and similar industrial lubricants and compared with identical products formulated with CRN oils. In every instance, the products made with the CTI oil met all of the specifications previously set on the basis of CRN oils and the products proved acceptable in service.

I claim:

1. A process for producing a petroleum lubricating oil having color stability comparable to that of a conventionally refined oil of the same viscosity produced from an asphaltic base crude oil, as defined herein, consisting only of the following three steps: (1) distilling from an asphaltic base crude oil, a fraction having a lubricating oil viscosity which would normally deteriorate in color upon storage unless additionally refined; (2) contacting said lubricating oil distillate with about 1 to 20 pounds of mineral adsorbent per barrel of oil; and (3) then adding to the lubricating oil produced in step (2) from 0.001 to 1% by weight of a compound of the formula:



2. A process for producting a petroleum lubricating oil having color stability comparable to that of a conventionally refined oil of the same viscosity produced from an asphaltic base crude oil, as defined herein, consisting only of the following four steps: (1) distilling from an asphaltic base crude oil a fraction having a lubricating oil viscosity which would normally deteriorate in color upon storage unless additionally refined; (2) de-waxing said lubricating oil distillate; (3) contacting said de-waxed lubricating oil distillate with about 1 to 20 pounds of mineral adsorbent per barrel of oil; and (4) then adding to the lubricating oil produced in step (3) from 0.001 to 1% by weight of a compound of the formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,282,513	Downing et al.	May 12, 1942
2,596,942	Robertson et al.	May 13, 1952
2,679,471	Ayers et al.	May 25, 1954

OTHER REFERENCES

"Motor Oils" by Georgi, Reinhold Pub. Co., N. Y., 1950, pages 120–123.