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PROCESS FOR REFINING HYDROCARBON OILS

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Our invention relates to the refining, improvement and purification of mineral oils by oxidizing them and then treating them to remove the oxidized materials. One application of our invention consists in the treatment of mineral oils whose original properties have been unfavorably altered by exposure to vitiation and contamination with extraneous materials and/or partial decomposition or oxidation in service. More specifically, our invention may be applied to the improvement of lubricating or transformer oils whose lubricating or insulating characteristics have been adversely affected through usage.

It is among the objects of our invention to provide a process for improving the lubricating and/or insulating properties of hydrocarbon oil by removing impurities from hydrocarbon oils, such as asphaltic and carbonaceous substances, coloring matter, water and various other decomposition or oxidation products formed when the oil is deliberately oxidized or similarly changed as result of use. Another object of our invention is to provide a process for removing depreciated, coloring, and other foreign material from contaminated, oxidized or partially decomposed oils by the action of chemical compounds that possess preferential affinity for the noxious substances present, whereby several desirable improvements can be effected simultaneously which heretofore have necessitated the use of a multiplicity of steps. It is a further object to provide a process of the type described which will not only remove the impurities which have been acquired by the oil during service, but will also remove certain non-paraffinic constituents from the oil, thereby leaving the oil more paraffinic, improving its temperature-viscosity characteristics (i. e. raise its viscosity index) and improve its stability against oxidation to a degree to yield an oil which is often superior to the original unused oil.

Our invention finds special application in the recovery of crankcase drainings from internal combustion engines, such as gasoline, gas and Diesel engines.

When oil is used in crankcases of internal combustion engines it is exposed to air and moisture at elevated temperatures, resulting in a darkening of the oil and an increase in the content of asphaltic and carbonaceous matter. Moreover, organic acids and other oxygenated organic substances are produced in the crankcase. Low boiling diluents, such as water, gasoline, kerosene and stove or solar oil, which are either present in the engine fuel or are formed as a result of the combustion of the fuel in the engine cylinder, are also introduced into engine lubricating oil during service. Similar oxidation and decomposition reactions are encountered in connection with transformer oils and other oils which are exposed to oxidizing conditions, resulting in the

formation of oxygenated organic compounds, such as alcohols, acids, aldehydes and ketones.

In accordance with our invention we treat the oxidized or used oil with selective solvents which are particularly effective in dissolving the noxious materials. We have found that the oxygenated substances can be dissolved in most selective solvents of the type used in extracting mineral oils to produce highly paraffinic oils, and their removal offers no special or new difficulties. These oxidized bodies which are asphaltic in nature and which are not highly oxygenated are, however, not readily soluble in most selective solvents. These oxidized bodies of low oxygen content, moreover, predominate among the noxious materials which are acquired by the oil during service. It follows from the above circumstances that high solubility of the asphaltic material in the deteriorated oil is a primary requisite for such a solvent. Thus, while liquid sulfur dioxide, "Chlorex" (β, β' -dichloroethyl ether), furfural, crotonaldehyde and other similar solvents are useful for extracting hydrocarbon oils obtained from crude oils to produce high viscosity index or highly paraffinic oils, they are not suited for the regeneration of deteriorated oils because of their low solvent power for the particular impurities encountered in the latter case.

We have discovered that the following classes of solvents are suitable for refining oxidized oils:

Hydroxy-aromatic compounds, such as phenol, cresylic acid, o-xyleneol, carvacrol, as well as their halogen derivatives such as p-chlorophenol.

Nitrogen ring compounds, such as pyrrole, pyridine, picoline, quinoline, iso-quinoline and quinaldine.

Aromatic aldehydes such as benzaldehyde, tolu-aldehyde, isopropyl benzaldehyde, trimethyl benzaldehyde, as well as hydroxy substituted aldehydes, such as o-hydroxy benzaldehyde (salicylaldehyde) and 3,4-hydroxy benzaldehyde.

Amino-aromatic compounds such as aniline, o-toluidine, o-xylidine and naphthylamines, as well as secondary and tertiary amines containing at least one aromatic radical, which are liquid at the temperature of treatment, such as diphenyl amine, methyl aniline and dimethyl aniline.

Nitro-aromatic compounds, such as nitrobenzene and nitrotoluene.

The solvents may be used separately or in mixtures with other solvents or diluents which may or may not fall within the above classes.

In treating the oxidized or the used oils we may use any suitable method of the type commonly used in extracting lubricating oils, which may consist of simply admixing the oil and the solvent, as by agitation, permitting the mixture to stratify, and separating the two phases, as by decantation or centrifuging. Most of the solvent will be in the lower stratum, and will con-

tain the noxious materials, while the lighter phase will consist principally of refined oil and a certain quantity of the solvent. The solvent may be recovered from each of the separated phases by distillation or by washing with a suitable solvent, such as methyl or ethyl alcohol, or methyl ethyl ketone, etc., and may be re-used. We may treat the oil in several stages, using fresh solvent at each stage, or we may treat it in a countercurrent single or multi-stage treater, as is well known in the art. The operation may be carried out at ordinary temperatures, but it is often desirable to apply artificial cooling to increase the selectivity of the solvent by decreasing its solvent power for the paraffinic constituents of the oil. In other cases, it may be desirable to raise the temperature in order to increase the solubility of noxious components in the solvent. It is, however, necessary that the temperature be sufficiently high to prevent the solidification of the solvent.

The quantity of the solvent used may be varied within wide limits, and may be readily determined by one skilled in the art after determining the specific solvent which is to be employed, the temperature of the treatment, and the quality and/or yield of the oil desired. In general, the use of a greater quantity of solvent results in a greater degree of refinement but in a lower yield.

A number of specific embodiments of our invention are presented in the following examples, it being understood that the invention is not restricted to the particular materials nor the specific proportions mentioned therein.

Example I

A refined Pennsylvania oil was used for 1480 miles in a truck engine, drained from the crankcase, and tested. It then was agitated with 200% by volume of cresylic acid at 70° F. and allowed to stratify, whereafter the two strata were separated by decantation. The upper layer consisted principally of oil, but contained from 5 to 10% cresylic acid, which was removed by a three stage washing treatment, each stage consisting of washing with 100% by volume of 95% ethyl alcohol. The resulting oil, representing about 80% of the drained crankcase oil, was dried under reduced pressure at 200° F. to remove any alcohol remaining therein. The cresylic acid may be recovered from the heavy layer by a washing treatment or by distillation. The properties of the original oil, of the drained crankcase oil, and of the refined and dried oil are given in Table I.

Table I

Properties	Original oil before service	Used crankcase oil after 1,480 mi. service	Used crankcase oil after cresylic acid refining
Gravity, °A. P. I.	28.3	26.5	29.4
Viscosity at 100° F., S. S. U.	635	325	614
Viscosity at 210° F., S. S. U.	73.5	61.2	76.0
Viscosity index	105		114
Precipitation No.	0	0.50	0
Ash, percent	0	0.59	Trace
Organic acidity, mg. KOH/gm	0.028-0.308	3.50	0.03
Conradson carbon, percent by weight			
	0.9-1.20	3.09	0.58
A. S. T. M. dilution (D322-33)			
	0	10.4	0
Water by distillation, percent	0	0.05	0

These results show the properties of the regenerated crankcase oil to be superior to those of the

original oil, including the important characteristics of viscosity index, Conradson carbon and gravity.

Similar results were obtained with other solvents of our invention. These solvents are especially desirable because low boiling diluents frequently present in crankcase oil are so miscible in them that simultaneous and substantially complete removal takes place, thereby yielding purified oil that will be found to have little or no dilution by A. S. T. M. test D322-33. By low boiling diluents, we refer to hydrocarbons of the gasoline and kerosene or slightly higher boiling ranges, derived from motor fuel, together with pyrolytic decomposition products from the lubricating oil. Moreover, the solvents of our invention are particularly applicable because of their low solubility in the refined oil and the ease with which they may be removed by extraction with alcohols, etc.

Because of the great adaptability of these solvents for dissolving the noxious substances encountered in used oil, the use of absorption media, filters, centrifuges, and distillation are entirely obviated by our discovery, although it is understood that our invention is not limited to processes in which these auxiliary treatments are eliminated. Furthermore, the process of our invention may be so extended that the original solvent can be completely recovered either by suitable separation from the impurities by the use of solvents affecting the mutual miscibility, or by ordinary fractional distillation. Also, these two methods of recovering the solvent may be combined, as by applying one to the treatment of the solvent phase, and the other to the treatment of the oil phase.

To indicate the efficacy of the different solvents in improving the color of used oils, the following example is presented:

Example II

The original Pennsylvania lubricating oil used in Example I had an A. S. T. M. color of 8- and a refractive index (n_D^{20}) of 1.4943. After 1480 miles of service in a truck engine its color was opaque. Several samples were separately refined with equal volumes of the solvents tabulated below, after the method outlined in Example I. The colors and refractive indexes of the raffinates were as follows:

Table II

Solvent	Raffinates	
	Color, A. S. T. M.	Refractive index, n_D^{20}
Benzaldehyde	7-	1.4866
Quinoline	7	1.4864
Nitrobenzene	7+	1.4849
o-Toluidine	8-	1.4931
Cresylic acid	8	1.4916
Phenol	8+	1.4857

These results show that the several solvents improved the color of the used oil to about that of the original oil. In every case, the refractive index was improved over the original value.

Similar improvements were also obtained from the treatment of oils other than those of Pennsylvania origin, and under widely varying methods of treatment. To illustrate the application of our process in the treating of a used Western oil, the following examples are presented:

Example III

A Coalinga oil was refined by extraction with liquid sulfur dioxide and kerosene extract and subjected to 1650 miles service in a 4 cylinder passenger car and drained from the crankcase. It then was given a two stage extraction treatment, each stage consisting of mixing the oil with 100% of quinoline at 40° F., and the resulting phases were separated. The quinoline was recovered from the oil phase leaving the second stage by washing with methyl alcohol. The properties of the original oil, the drained crankcase oil, and the refined oil are given in Table III.

Table III

	Original oil before service	Used crankcase oil after 1,650 mi. service	Used crankcase oil after quinoline refining
Gravity, °A. P. I.	24.5		25.4
Viscosity at 100° F., S. S. U.	517	538	544
Viscosity at 210° F., S. S. U.	56.0	58.9	59.4
Viscosity index	42	59	62
Refractive index, n_D^{20}	1.4996		1.4940
Conradson carbon, percent by weight	0.01	0.69	0.04
Sligh No.	18		25
Organic acidity, mg. KOH/gm.	0.025	0.75	0.025
Color, A. S. T. M.	2½	Opaque	4

These results indicate that the refined crankcase oil is superior to the original oil in refractive index, gravity and viscosity index and only slightly inferior in other respects.

Example IV

The same used oil as described in Example III was extracted once with 25% by volume of p-chlorophenol at 70° F. The raffinate oil was superior in most observed properties to the original unused oil, as shown in the table below:

Table IV

	Original oil before service	Used crankcase oil after 1,650 mi. service	Used crankcase oil after p-chlorophenol refining
Viscosity at 100° F., S. S. U.	517	536	670
Viscosity at 210° F., S. S. U.	56.0	58.9	62.1
Viscosity index	42	59	49
Refractive index, n_D^{20}	1.4996		1.4979
Color, A. S. T. M.	2½		5+

Similar improvements in the properties of oils may be realized by deliberately oxidizing new oils instead of subjecting them to service. These oils may or may not have been subjected to a preliminary refining treatment, such as acid treatment, clay treatment, extraction with selective solvent, etc., and may or may not have been dewaxed. According to one mode of operation, we oxidize the oil by blowing air through it while it is heated to a temperature between 120° F. and 500° F., either in the presence or in the absence of water or steam, or by a combination of steps comprising an oxidation in the absence of water and an oxidation in the presence of water. Thus, good results have been obtained by blowing air through oil for 100 hours in the absence of water, and then for 45 hours in the presence of steam. The temperature was maintained between 200° and 400° F., which is our preferred temperature range. The oxidized oils then are extracted with solvents in the manner described above to produce oils of improved properties. In order to reduce the time of the desired oxidizing treatment, hydrocarbon

oils may be contacted with air under a substantial superatmospheric pressure of the order between about 50-200 lbs./sq. in. Further, our oxidizing process may be carried out in the presence of catalysts which either accelerate or decelerate the artificial aging of the oil.

We claim as our invention:

1. A method of refining hydrocarbon lubricating oil stock containing constituents of relatively high viscosity index and constituents of relatively low viscosity index, which comprises contacting said stock with a gas containing free oxygen at a temperature from about 120° F. to about 500° F. for a time sufficient to convert a substantial portion of said constituents of relatively low viscosity index into oxidation products preferentially soluble in a liquid solvent from the group consisting of hydroxy-aromatic compounds, nitrocyclic compounds, aromatic aldehydes, amino-aromatic compounds, and nitro-aromatic compounds, and insufficient substantially to convert said constituents of relatively high viscosity index into oxidation products, whereby the materials resulting from the said oxidation step which are least soluble in said solvent have a higher viscosity index than the viscosity index of the stock, contacting the material from the aforementioned oxidation step with a sufficient quantity of the said solvent to form two liquid phases, separating the resulting phases, and removing the solvent from the oil phase.

2. The method according to claim 1 in which the solvent is cresylic acid.

3. The method according to claim 1 in which the solvent is quinoline.

4. The method according to claim 1 in which the solvent is para-chlorophenol.

5. A method of refining hydrocarbon lubricating oil stock containing constituents of relatively high viscosity index and constituents of relatively low viscosity index, which comprises contacting said stock with a gas containing free oxygen at a temperature from about 200° F. to about 400° F. for a time sufficient to convert a substantial portion of said constituents of relatively low viscosity index into oxidation products preferentially soluble in a liquid solvent from the group consisting of hydroxy-aromatic compounds, nitrocyclic compounds, aromatic aldehydes, amino-aromatic compounds, and nitro-aromatic compounds, and insufficient substantially to convert said constituents of relatively high viscosity index into oxidation products, where by the materials resulting from the said oxidation step which are least soluble in said solvent have a higher viscosity index than the viscosity index of the stock, contacting the material from the aforementioned oxidation step with a sufficient quantity of the said solvent to form two liquid phases, separating the resulting phases, and removing the solvent from the oil phase.

6. A method of refining hydrocarbon lubricating oil stock containing constituents of relatively high viscosity index and constituents of relatively low viscosity index, which comprises contacting said stock with a gas containing free oxygen at a temperature from about 120° F. to about 500° F. in the presence of hydrogen oxide for a time sufficient to convert a substantial portion of said constituents of relatively low viscosity index into oxidation products preferentially soluble in a liquid solvent from the group consisting of hydroxy-aromatic compounds, nitrocyclic compounds, aromatic aldehydes,

amino-aromatic compounds, and nitro-aromatic compounds, and insufficient substantially to convert said constituents of relatively high viscosity index into oxidation products, whereby
5 the materials resulting from the said oxidation step which are least soluble in said solvent have a higher viscosity index than the viscosity index of the stock, contacting the material from the
10 aforementioned oxidation step with a sufficient quantity of the said solvent to form two liquid phases, separating the resulting phases, and removing the solvent from the oil phase.

7. A method of refining hydrocarbon lubricating oil stock containing constituents of relatively high viscosity index and constituents of
15 relatively low viscosity index, which comprises contacting said stock with a gas containing free oxygen under conditions obtaining in the crankcase of an internal combustion engine for a time
20 sufficient to convert a substantial portion of said

constituents of relatively low viscosity index into oxidation products preferentially soluble in a liquid solvent from the group consisting of hydroxy-aromatic compounds, nitrocyclic compounds, aromatic aldehydes, amino-aromatic
5 compounds, and nitro-aromatic compounds, and insufficient substantially to convert said constituents of relatively high viscosity index into oxidation products, whereby the materials
10 resulting from the said oxidation step which are least soluble in said solvent have a higher viscosity index than the viscosity index of the stock, contacting the material from the
15 aforementioned oxidation step with a sufficient quantity of the said solvent to form two liquid phases, separating the resulting phases, and removing the solvent from the oil phase.

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