

1

2,948,669

PRODUCTION OF SUPERIOR NEUTRAL OILS

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The present invention relates to the production of neutral oils possessing superior qualities. More particularly, our invention relates to the production of neutral oils from heavier lubricating oil fractions and to the in situ production of epoxides and epoxide derivatives therein.

It has been found that requirements of motors, whether automotive, such as trucks, automobiles and the like, or of the fixed-machine type, such as factory machinery, etc., are such that unfortified lubricating oil fractions are generally unsatisfactory for use. It is known that certain desirable properties, such as anti-oxidation, anti-corrosion, anti-wear and detergency characteristics may be imparted to lubricating oil fractions by the addition thereto of selected additives. Thus, for example, sulfonates or naphthenates may be added for detergency, and sulfurized, phosphorized or sulfurized-phosphorized fatty oils may be added for increased wear and load-bearing characteristics. In many cases, the additives are quite different in chemical structure from the component molecules making up the body of the lubricating oils. Such differences in chemical properties as well as physical properties between the additive and the lubricating oil fraction may create difficulties such as poor compatibility of the additive with the oil, or a shorter period of usefulness of the blend in the motor than would be expected. The additive also may act to depress or decrease a desired characteristic present in the oil before addition of the additive. Such a circumstance may require a second additive to restore the lost or diminished desirable property. Moreover, additive components of dissimilar structure from the lubricating oil frequently may be easily removed from solution, that is, they may precipitate and form sludge at high temperatures or on long continued use at normal temperatures. Moreover, such additives not infrequently have been found to undergo decomposition more rapidly than the natural components of the lubricating oil and to break down into engine-fouling, degradation products. These degradation products may seriously interfere with the oiliness or anti-wear characteristics of the lubricating oil, and also may promote or catalyze deterioration, break-down and polymerization of other components of the formulation. If the functional group responsible for the special properties were part of a naturally occurring lubricating oil molecule, breakdown of the agent would be decreased. Moreover, many more functional groups would be available for use than are presently available in additives due to difficulties with instability and/or insolubility in lubricating oil fractions. Thus, enhanced compatibility and longer service life would result if the functional groups were attached to lubricating oil molecules rather than to a separately prepared agent.

Neutral oils have recently become more extensively utilized in motor oil formulations, with consequently decreased application of bright stock fractions. Therefore, an oversupply of bright stock fractions is to be

2

expected in the future unless other uses for such fractions can be found.

We have unexpectedly discovered a process for the utilization of heavier lubricating oil fractions, especially bright stocks or other heavy residua, such as the vacuum residuum obtained in the manufacture of lubricating oil fractions, for the production of neutral oils possessing in-situ-formed additives which enhance the anti-oxidation, anti-corrosion, anti-wear, lubricity, or detergency characteristics of the neutral oil fractions.

Accordingly, it is an object of our invention to provide a process for the preparation of superior neutral oil fractions.

It is another object of our invention to provide a process for the preparation in situ of lubricating oil additives of increased compatibility with lubricating oil fractions.

It is another object of this invention to provide superior neutral oils fortified with in-situ-prepared lubricating oil additives in a simple, inexpensive process.

It is still another object of our invention to provide for the conversion of heavy lubricating oil fractions into neutral oils of superior properties without removal of olefins so produced.

It is still another object of our invention to provide for the preparation of superior neutral oils having epoxides and/or epoxide reaction products formed in situ in an inexpensive, simple manner from lubricating oil component molecules.

In general, therefore, our invention lies in the conversion of a heavy lubricating oil fraction into a neutral oil and the concomitant production of compatible epoxides and/or epoxide reaction products in the neutral oil to fortify its natural properties.

More particularly, our process comprises a sequential procedure involving the mild cracking of a heavier lubricating oil fraction, and the production of olefins thereby, and the epoxidation of the olefins in situ in the oil. Further, our process may extend to the reaction of the epoxides so formed with a substance containing a chemically active hydrogen atom, such as a mercaptan, a primary or secondary amine, an alkanol amine, an organic acid (or acid anhydride) such as a thio-acid, a dithio-acid, a sulfonic or polysulfonic acid, or a mono-, di- or polyhydric phenol, thiophenol, or enol, among other reactive compounds.

A particular point of novelty in our invention lies in the unique utilization of olefins formed during the cracking step of our process as basic material for the preparation of desirable lubricating oil agents, thus eliminating the tedious and expensive procedure of separating the olefins from the solution before utilizing the oil produced during the cracking operation. The olefins themselves are generally recognized as deleterious to the performance of lubricating oil fractions, since they tend to promote corrosion and sludge formation, and therefore should be removed from neutrals prepared by cracking heavier oil fractions. Since neutrals prepared from residua are more expensive than those initially obtained by vacuum distillation due to the olefin separation step, this method of preparing neutrals is not commercially utilized.

Neutral oil is ordinarily obtained from crude oil by subjecting topped crude to the steps of vacuum distillation, followed by solvent refining, solvent dewaxing and clay contacting. The vacuum distillation divides the oil into a number of fractions including a neutral oil lubricating oil fraction and a cylinder stock, or residuum. The residuum is then usually subjected, in the process of preparing finished bright stock, to deasphalting by propane or other suitable solvent, and to solvent refining with phenol, followed by solvent dewaxing and a subse-

quent clay contacting operation. Residuum before the solvent refining step may be utilized as the feed oil in our process. Alternatively, finished bright stock used for blending various oil fractions and consisting of a heavy viscous residual oil with a reddish color, or unfinished bright stock not subjected to solvent dewaxing to remove microcrystalline wax fractions, and/or clay treating, may be utilized as the feed in our process. The solvent dewaxing step may employ any one or more of a number of suitable solvents, or solvent mixtures, or solvent and anti-solvent mixtures, e.g., a mixture of methyl ethyl ketone and toluene in a ratio of solvent mixture to oil of 1:1 to 4:1, depending on the nature and viscosity of the charge material. The bright stock obtained varies in viscosity and other properties according to the type of crude oil and the number, type and sequence of refining steps to which it has been subjected. Preferably, the oil fraction utilized as the starting material in the process of our invention is residuum or cylinder stock such as vacuum residuum from the initial treating step of the crude oil, since it has a lower initial cost than finished bright stock. Any crude oil may be utilized as the starting material for the vacuum distillation, or any other type of distillation which separates the neutral oil fractions and other fractions from the heavier, less volatile, residual lubricating oil fraction. The crude oil, for example, may be Mid-Continent, Pacific Coast, Gulf Coast, Pennsylvania or other type of crude oil which has been subjected to the necessary separation of neutral oils from residuum by appropriate distillation or other methods.

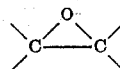
As the first step in the process of our invention, the bright stock or heavy lubricating oil fraction, such as vacuum residuum, is subjected to a mild cracking operation and simultaneous distillation under moderately elevated temperature and decreased pressure. A cracked product is obtained comprising a neutral oil having as much as 50% olefins. Neutral oils may be defined as distillate lubricating oils with viscosities usually not above 200 sec. at 100° F. The degree of unsaturation in the neutral oil produced in our process depends upon the specific conditions of cracking and the characteristics of the feed oil. The cracking is carried out at a relatively low temperature to reduce the severity of degradation of the oil components. Thus, conditions are milder than utilized for the preparation of, for example, gasoline from heavy residuum. The temperature is correlated with the reduced pressure of the system. Thus, temperatures of approximately 300° to 600° F. may be utilized with pressures of 2 mm. Hg to 25 mm. Hg where bright stocks of average viscosity of 150-160 are utilized as the feed oils. Thus, as a non-limiting example of this step of our invention, a bright stock obtained from the processing of a Van Zandt crude oil and having a viscosity of 150 SUS at 210° F. was slowly distilled at 1-4 mm. of mercury pressure and 350° F. to give a 50% yield of an unsaturated neutral oil having a bromine number of 25, an average molecular wt. of 390 and a viscosity of 45.2 SUS at 210° F. Sometimes it may be desirable to dewax the product.

This step may also be carried out by careful steam distillation in the manner set forth in Wagner et al. Patent No. 2,155,745. The neutral type of oil prepared by this step exhibits a viscosity of about 65 to 350 SUS at 100° F.

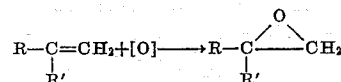
After the neutral oil has been prepared in accordance with the procedure above, and olefins are present in substantial amount in the oil fraction, the unsaturated hydrocarbons in the neutral oil are converted to epoxides in the second step of our process. The unsaturated hydrocarbons may be low or high molecular weight olefins, diolefins or other compounds of petroleum origin containing one or more unsaturated bonds. These are compatible with the neutral oil so produced, since they are de-

rived from the components initially present in the feed oil.

The epoxide structure



is introduced into the oil according to the following generic equation:



wherein R and R' denote the hydrocarbon radicals normally found in the oil.

The epoxidation procedure may be carried out by any known method. Thus, epoxidation may be carried out with peroxyacids such as peracetic or perbenzoic acids, with inorganic peroxides such as hydrogen peroxides or barium peroxide, by air oxidation with or without a suitable catalyst, or by hypohalogenation followed by dehydrohalogenation. With peracids such as peracetic or perbenzoic acids, the epoxidation reaction may be carried out batchwise in the presence of a suitable buffering agent at temperatures ranging from room temperature to 40° C., according to the method disclosed in U.S. Patent 2,411,762, November 26, 1946. The extent of reaction is determined either by titration of aliquots of the solution for epoxy oxygen according to the method of Swern et al. (Anal. Chem. 19, 414 (1947)), or from analyses for residual peroxyacid (D'Ans and Frey, Ber. 45, 1845 (1912); Z. anorg. Chem. 84, 145 (1913)).

Alternately, the epoxidation may be carried out either batchwise or as a continuous process by first generating the peroxyacid in situ from a mixture of hydrogen peroxide and acetic acid in the presence of an acid ion-exchange resin, then proceeding as above.

Thus, a mixture of the unsaturated neutral oil obtained from the cracking operation, hydrogen peroxide in concentrations ranging from 50% to 90%, and glacial acetic acid is passed through an ion-exchange resin of the sulfonated type, and recirculated until the desired epoxide content (as determined by titration) is obtained.

The amount of peracetic acid or other peracid or peroxide utilized may vary widely, depending upon the extent of epoxidation desired and upon the quantity of unsaturated hydrocarbons present per unit volume of the neutral oil. The epoxidation ordinarily may be accomplished without resort to greatly increased temperature and/or pressure. A typical epoxidation reaction involves the epoxidation of the unsaturated neutral with a mixture of sodium acetate and peracetic acid at room temperature and ordinary pressure. The oil layer, after the reaction, contains a considerable proportion of epoxides. Optionally, it may be subjected to washing with water and dilution with hexane, washing with sodium bicarbonate solution to a neutral reaction with litmus paper, followed by washing with sodium chloride solution, drying, and removal of the hexane by distillation. The epoxide may be concentrated by extraction. Yields of 40% epoxides or more, based on the amount of unsaturated compounds present in the cracked neutral oil charged to this epoxidation step, can be obtained.

An alternate but equally suitable method for the production of the epoxides in situ in the cracked neutral lubricating oil fraction obtained by step one comprises hypochlorination of the unsaturates in the oil followed by dehydrochlorination. Thus, for example, the unsaturated neutral oil may be stirred with an aqueous solution of hypochlorous acid and the product then treated with strong aqueous caustic alkali solution or other strong base. The quantities of reactants may vary widely.

A further method of treatment to produce epoxides is the reaction of the neutral oil containing the unsaturated with a stream of air or oxygen under atmospheric

or superatmospheric pressures, while keeping the reaction mixture in a neutral or slightly alkaline condition. Thus, a nonlimiting example of this method comprises reacting the neutral oil at 10–20 atm., 100°–150° C., and a pH of 8.0 with air. Magnesium oxide or sodium carbonate, etc. may be present as base catalyst. Other methods of preparing epoxides from olefins as are known in the prior art and which will operate successfully in a neutral oil medium without deleteriously affecting the medium may be utilized in the second step of this process of our invention. The particular operating conditions of each epoxidation procedure vary with the characteristics of the charge material, the reactants and other factors, including the yield of epoxides desired.

The epoxidized neutral oil components so prepared from the compatible olefins present in the neutral oil have desirable oiliness and acidity reduction characteristics which enhance the quality of the neutral oil. Thus, even if the third step of the process, namely conversion of the epoxides to selected highly effective derivatives is not practiced, neutral oil of substantially improved lubricating and acid-reduction properties may be produced by the combined procedure of steps 1 and 2 of our process. The epoxidized neutral oils are of particular importance in crankcase formulations for modern vehicles, due to the ability of the epoxide materials to react with acidic bodies formed by oxidation of the neutral oil during normal and severe use and to neutralize them. Thus, epoxide groups in the epoxidized oils are not only more compatible than externally produced epoxides and less likely to precipitate from the neutral base oil, while producing no untoward reactions in the oil nor masking valuable characteristics of the base oil, but said epoxides also are in themselves oiliness agents and antacids, tending to keep the oil non-corrosive and thereby prolonging the service life of the oil and the engines. Engines in contact with the epoxidized neutrals are kept free from rust over longer periods of time.

As a third step in our invention, the neutral oil containing the epoxidized unsaturated lubricating oil components may be subjected to further treatment designed to react the epoxides in a manner well-known in the prior art, that is, by conventional reaction of an epoxide with one or more selected substances containing chemically active hydrogen atoms, such as a mercaptan, a primary or secondary amine, an alkylamine, an organic acid or anhydride, particularly a dithiophosphoric acid such as dioctylthiophosphoric acid, a mono-, di- or polyhydric phenol or thiophenol or enol. Ordinarily, greatly increased temperatures and/or pressures are unnecessary in order to bring about the desired in situ preparation of the epoxide derivatives. Thus, for example, the neutral oil containing the epoxides may be reacted with a sufficient amount of mercaptan to convert all or some of the epoxides present into mercaptan-epoxide derivatives, such as substituted hydroxy sulfides.

Mercaptans are organic compounds containing the radical SH. Suitable non-limiting examples of mercaptans effective in our process are alkanethiols such as ethane-, methane-, or decanethiol and benzyl mercaptan, dithiols such as 1,2-ethanedithiol, hydroxy thiols such as 2-mercapto-ethanol, and various other substituted thiols such as 2-dibutylamino ethanethiol. The reaction between the epoxides and the mercaptans results in the formation of oxidation-resistant materials, which in turn impart this desirable characteristic to the neutral oil in which they are dissolved. As a non-limiting example of the third step of our process, a 150 vis., SUS at 100° F., neutral oil containing 5% by wt. of epoxides may be treated with a theoretical excess of benzyl mercaptan in the presence of alkali, such as an aqueous sodium hydroxide solution to yield an anti-oxidant type of neutral oil. The reaction takes place at low temperature with the alkali serving as a promoter or catalyst. Thus, the temperature may be, for example 125–200° C. or

lower. Other catalyst and promoter compounds are also available, and the reaction may be carried out at normal pressure, preferably, however, at increased pressure and temperatures higher than 200° C. if no catalyst is present. The speed of reaction and the proportion of components necessarily depend upon the mercaptans used and the amount and type of epoxides to be reacted.

Reaction of amines with the epoxidized neutral under known reaction conditions as a third step in our process produces neutral oil which possesses detergency, anti-rust properties and reserve alkalinity to combat acidic bodies formed during the use of the oil in internal combustion engines under normal and severe operating conditions. Corrosion and wear are thereby materially decreased. Thus, for example, aromatic diamines and epoxy compounds may be reacted to produce anti-oxidants in a manner set forth in U.S. 2,576,448 (E. F. Hill and H. Baldwin, November 27, 1951). Another method for the preparation of amines is set forth in U.S. 2,325,533 (J. B. Montgomery et al., July 27, 1943), in which aryl alkyl amino compounds containing an hydroxyl radical are formed from epoxides and amines. Aliphatic amines, such as "fatty" amines, for example, octadecylamine, octadecenylamine and hexadecylamine; lower molecular weight amines, such as propylamine, butylamine, etc.; aromatic amines, such as benzylamine; and indeed, any amine soluble in neutral oils may be utilized in our process. Other suitable examples are diamines, such as p-phenylene diamine, and ethylenediamine; and hydroxyamines, such as ethanol- and di-ethanolamine.

Hydrogen cyanide or alkali cyanides, such as sodium cyanide, potassium cyanide or lithium cyanide, may also be reacted with our epoxides of neutral oils to produce agents having increased lubricity. A suitable non-limiting example is as follows. Gaseous hydrogen cyanide is bubbled through 10 liters of an epoxidized neutral oil of 150 vis., SUS at 100° F., containing 6% epoxides, at room temperature (65° F.) and for a period sufficient to convert all epoxide groups.

Mono-, di- or polyhydric phenols, such as phenol, catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, quercitol and inositol among others, may be used as the reagent to produce epoxide derivatives exhibiting detergency. Thiophenols may also be used in place of the phenols in the reaction with the epoxides of the neutral oil. A suitable non-limiting example is the reaction of thiophenol in the presence of sodium or potassium hydroxide at temperatures from 150° C. to 250° C. for 4–15 hours, with epoxides to produce a sulfur-containing derivative in the neutral oil.

On completion of the above step of conversion of epoxides to derivatives, a neutral oil formulation has been obtained which is ready for use without further necessity of refinement. The fortified neutral oil may be used as a lubricant alone or be added to other mineral oil fractions; alternatively, it may have one or more property-modifying agents added to it. The neutral oil obtained by step two of the above process may likewise be utilized directly as a lubricating oil, or with added ingredients, or be added to other mineral oil fractions or formulations. The following examples further illustrate our invention:

Example I

A bright stock obtained from the processing of Van Zandt crude oil by the steps of vacuum distillation, propane deasphalting, solvent extraction with phenol, and dewaxing with methyl ethyl ketone, is utilized as the feed. The bright stock has a viscosity of 150 SUS at 210° F. and is utilized in 240 gram amount. When the bright stock is slowly distilled at 1–4 mm. Hg pressure in a vacuum distillation unit operating at a pot temperature of 317–404° F., a product is obtained having a bromine number of 25, an average molecular weight of 390 and a viscosity of 35.2 SUS at 210° F. A yield of

50% of the initial charge of material is obtained in the form of highly unsaturated neutral oil. A 20 gram sample of the oil is reserved for testing as indicated below.

The remainder, approximately 100 grams, of the unsaturated neutral oil is then subjected to admixture in an open kettle with 1.5 grams of commercial grade of sodium acetate and 38 grams of 40% peracetic acid in water. The mixture is stirred mechanically for a period of 7.6 hrs. at 87° F., external cooling being applied in order to keep the reaction at the indicated temperature. The oil layer is then washed several times with an excess of water, diluted with an equal amount of hexane, washed with an excess of sodium bicarbonate solution until neutral to litmus paper, washed with saturated sodium chloride solution, and dried. The hexane is removed by distillation and the yield of epoxides in the neutral oil, based on the oxirane number and the bromine number of the unsaturated neutral, is 40%.

The epoxidized oil is aged at 250° F. for 60 hours in the presence of air. The free organic acid developed during the aging test is negligible compared to that of a sample of ordinary neutral tested under the same conditions but containing no epoxides.

Example II

A Van Zandt 200 viscosity, SUS at 100° F., neutral oil obtained as a lubricating oil fraction by vacuum distillation of a Van Zandt crude is substituted for the neutral oil obtained by the first step of Example I. The subsequent step of epoxidation is carried out according to the process as defined in the second step of Example I. It is found that the neutral oil contains no epoxide. This result is obtained since no appreciable amount of unsaturates, principally olefins, are present in the feed neutral oil. Therefore, the treatment according to the second step does not yield epoxides unless the first step has been carried out.

It is seen from the above that the process of our invention results in the preparation of a superior neutral oil of any desired viscosity from heavier lubricating oil fractions, including residuum or cylinder stock or bright stock. The finished oil may be used alone as a lubricating oil or may have various additives added thereto, or may in turn be added to lubricating oil formulations. The neutral oil exhibits no incompatibility with the epoxides and/or epoxide derivatives formed in situ and may possess increased detergency, oxidation stability, anti-corrosion, anti-wear, lubricity, and other properties or combinations of properties, depending upon the particular epoxy compounds or derivatives thereof formed and upon the number and particular conditions involved in the steps of the process. As seen from the example above, when neutral oil which has not been derived from step 1 of our process is treated, that is, when neutral oil not containing substantial amounts of unsaturated constituents is used, as in Example II, the desired results are not obtained. Our process is not only adaptable to the preparation of a wide range of fortified neutral oils of various enhanced properties, but also has the advantages of simplicity and the utilization of a plentiful feed, that is, heavy lubricating fractions, for new formulations incorporating additives of increased compatibility with mineral oils.

Such modifications of our process, manipulative procedures and equipment as are within the skill of those

versed in the art are contemplated as within the purview of our invention.

We claim and particularly point out as our invention:

1. The process of preparing neutral lubricating oil comprising lightly cracking residual petroleum oil having a viscosity higher than that of neutral oil under conditions to convert it to distillate oil having a viscosity corresponding to that of neutral oil containing a substantial amount of unsaturated hydrocarbons, and epoxidizing said converted oil under conditions to form a substantial amount of epoxides in situ.
2. Process in accordance with claim 1 in which said unsaturated hydrocarbons are epoxidized by means of a peroxy acid in the presence of a buffering agent at a temperature between room temperature and 40° C.
3. Process in accordance with claim 2 in which the peroxy acid is peracetic acid and the buffering agent is sodium acetate.
4. Process in accordance with claim 1 in which the resulting product is reacted with a mercaptan.
5. The process of claim 1 in which said residual petroleum oil is selected from the group consisting of bright stock, cylinder stock and residua remaining on separation of neutral lubricating oil fractions and lighter hydrocarbon fractions from crude oil.
6. The process of claim 1 in which the epoxy groups of said epoxidized neutral oil are further reacted with a compound containing a chemically active hydrogen atom to form a product which further enhances the lubricating qualities of said epoxidized oil.
7. The process of claim 6 in which said compound is a mercaptan.
8. The process of claim 7 in which said mercaptan is benzyl mercaptan.
9. The process of claim 7 in which said mercaptan is methanethiol.
10. The process of claim 9 in which said mercaptan is 1,2-ethane dithiol.
11. The process of claim 6 in which said compound is selected from the group consisting of primary amines, secondary amines and alkylolamines.
12. The process of a claim 11 in which said compound is stearylamine.
13. The process of claim 11 in which said compound is benzylamine.
14. Process in accordance with claim 6 in which said compound is from the group consisting of mercaptans, alkyl-, aryl- and alkanolamines, phenols, hydrogen cyanide, alkali metal cyanides, thiophenols and organic di-thiophosphoric acids.
15. The process of claim 14 in which said compound is phenol.
16. The process of claim 14 in which said compound is dioctyldithiophosphoric acid.

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