Patented July 1, 1941 2,247,475

UNITED STATES PATENT OFFICE

2,247,475

MODIFIED LUBRICATING OIL

Ulric B. Bray, Palos Verdes Estates, and Donald E. Carr, Los Angeles, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

No Drawing. Application November 23, 1936, Serial No. 112,352

7 Claims. (Cl. 196—13)

This invention relates to lubricating oils and particularly to the improvement of very heavily treated or highly refined mineral lubricating oils to correct them for apparently undesirable effects such as corrosion of modern type bearings, ring-sticking and the like, due apparently to what may be termed "overtreatment" resulting in the removal of protective agents by deep-cutting modern solvent treating processes.

More recently the use of various selective solvents such as liquid sulfur dioxide-benzol mixture, phenol, dichlorethylether and the like have been employed for the extraction of both Eastern or paraffinic type, and Western or asphaltic and naphthenic type oils. These extractions resulted in the removal of large quantities of carbon-forming, naphthenic, unsaturated, and other types of materials not strictly paraffinic in nature which have been considered by many investigators to be less desirable in lubricating oils. However, it appears that not only have the undesirable materials been removed by such treating processes, but also protective agents of some type have been removed which prevent or counteract the formation of corrosive compounds, ring-sticking compounds and the like.

We have found that by segregating certain constituents from extracts which have been produced by these processes or from other similar extracts such as liquid sulfur dioxide extracts, such constituents can be added to or returned to the final lubricating product and thereby overcome the corrosive, ring-sticking and other characteristics above mentioned. The preferred fractions of these extracts are the intermediate or "heart cut" constituents; these may in general be considered as consisting largely of preferred stable aromatic materials associated with naphthenic constituents also removed by the action of the selective solvent. The heavier unstable aromatics, resinous and tarry materials and the like are objectionable and are removed as by some form of extraction or precipitation and discarded because they sludge too readily. The lighter materials preferably are also eliminated, as by means of some form of solvent extraction, because they tend to excessive ring sticking.

This invention therefore resides in the separation from the solvent extracts, obtained from extracting lubricating oil stocks as above described, of lighter gravity extract constituents consisting chiefly of stable aromatic fractions and naphthenes, and employing these in small percentages in the highly refined lubricating oils produced by said solvent treating processes, or similar very highly paraffinic oils exhibiting similar characteristics. More particularly the invention includes the use of intermediate or "heart cut" fractions of said solvent extracts from petroleum lubricating stocks, as represented by materials having a gravity in the order of 13° to 18° A. P. I. The invention further includes the modified mineral oil products or blends so obtained.

As illustrative of this invention, oils such as a deasphalted and dewaxed S. A. E. 50 lubricating distillate are extracted with liquid sulfur dioxide, and the extract (after driving off the sulfur dioxide) mixed with propane at atmospheric pressure, under which conditions a considerable proportion of the extract goes into solution with the propane. Again, the same type of dewaxed S. A. E. 50 lubricating distillate may be extracted with phenol according to known procedures to yield an extract having a gravity of about 12° A. P. I. at 60° F., the raffinate being highly paraffinic. For purposes of this extraction about 250 volume-percent of phenol are used at 125° F. and the extract is in turn extracted with 8 volumes of propane at 90° to 100° F. After driving off the propane, this yields a propane-soluble phase amounting to about 60% of the phenol extract. In this fashion the heavy materials including petroleum resins and tarry bodies in general and unstable and highly aromatic materials are rejected and lighter portions of the extracts are obtained which have good lubricating properties in themselves. By acid-treating the propane-soluble fraction while still dissolved in the propane and employing about 25 lbs. of 98% sulfuric acid per barrel of oil at 80° F., the propane being present to the extent of about 5 to 8 volumes, and then following with a treatment of 5% clay at somewhat elevated temperature, namely about 350° F., remaining unstable aromatic and kindred materials are removed whereby a valuable naphthenic and aromatic oil stable in character and of unusually high viscosity and flash point is obtained. Such oil has a viscosity gravity constant of .888 and an A. P. I. gravity of 16.2, as against the V. G. C. of .903 and an A. P. I. gravity of 13.7 for the propane-soluble portion without acid treatment, and as against a V. G. C. of .918 and a gravity of 11.5 for the phenol extract itself before propane treatment. The temperatures given are merely indicative. For instance, the propane extraction of the phenol extract may be run at temperatures anywhere from around 70 to 90° F. up to 170° F., this treatment causing the propane to reject the heavy insoluble tar phase while taking a heavy lubricating material into

solution. The temperature for the acid treatment may vary somewhat but should not be excessive and preferably should not extend above about 100° F. The clay treatment may be carried on according to any known or preferred procedure.

Similar treatments of liquid sulfur dioxide extract or of extract obtained with mixtures of liquid sulfur dioxide and benzene may be made. These extracts of course vary to some extent, but in each instance the heavy portions will be removed as by precipitation with propane or by acid treatment or both, and the lighter materials may also be removed when objectionable. It is always desirable to reject the heaviest portions of the extracts in some manner, of which the propane solution method is a convenient procedure; this readily eliminates the unstable aromatics. Where the light constituents are objectionable because of being present in amount to produce excessive ring sticking or for other reason, they may be eliminated as by another selective solvent extraction which recovers desirable constituents. Again, series treatments of lubricating stocks with the solvents mentioned may be relied upon to obtain the desired intermediate or "heart cut" extract. Here the first step will be comparatively light and will remove the heavy tarry and unstable highly aromatic materials. The next cut will be deeper and may recover the desirable intermediate fractions of the present invention. The next cut may then be still deeper so as to remove objectionable lighter materials such as naphthenes. Of course, it is to be understood that in practice each of these three stages of extractions may consist of a plurality of steps.

All of these "heart cut" fractions which have been freed from both the heavier and lighter constituents are in themselves good lubricating materials as above indicated, and when blended with heavily refined or very highly paraffinic lubricating oils, as heretofore mentioned, impart to said oils the desirable characteristics sought by the present invention, that is, to overcome corrosiveness, ring sticking and the like. They also impart oiliness and improved film strength.

The intermediate extracts and in some instances mixed intermediate and light extracts, such as those having an A. P. I. gravity of about 13° to 18° and being free from tarry and resinous materials and unstable highly aromatic materials, are then added to the above mentioned highly refined lubricating raffinates in comparatively small quantities, in the order of 5% to 10% of the lubricating oil. This includes the portions of phenol extracts and liquid sulfur dioxide extracts soluble in propane at temperatures around normal, for example from about 60° or 70° F. to 100 or 110° F., and also includes the lightly acid treated propane-soluble portions of said extracts as above described. The acid treatment is used to eliminate heavier constituents which may not be desired but which, however, were taken into solution in the propane. Not only the extracts obtained from lubricating fractions may be employed but extracts obtained from transformer oils and spray oils by liquid sulfur dioxide treatment, as effected by the well known Edeleanu process, may be employed in like manner. Where series treatments are employed, the intermediate extracts will, in general, be preferred, although the final extracts also sometimes have value when not too rich in ring-sticking constituents. Such extracts may be used without propane treatment or acid treatment. Other solvents than the phenol, liquid sulfur dioxide and benzol-sulfur dioxide above mentioned, may be employed such as dichlorethyl ether, furfural and others known for selective extraction, including nitrobenzene and chloraniline.

Any form of extract of the character described is within the scope of this invention regardless of the method of obtaining it. For example, the lubricating stock may be exhaustively vacuum distilled to leave a heavy resinous fraction. This heavy residue may then be solvent extracted to obtain a cut having the desirable stable aromatic materials within the range above described. The heavy portions will be discarded and the lightest portions may be either retained or discarded according to their ring-sticking and other characteristics, as above described.

It is to be understood that in some instances after the heavier portions of the extract have been eliminated, the lighter materials may be retained so long as they do not produce ring sticking or other objectionable results in the use to which the product is to be put. For example, some oils would be highly desirable for ordinary gasoline internal combustion engines but will produce excessive ring sticking in Diesel engines. For a general purpose oil, only the heart cut or intermediate fraction of the extracts will be returned to the heavily refined lubricating oils mentioned. By reason of having eliminated the heavy materials including the unstable highly aromatics, and by reason of having eliminated the lighter extract materials which tend to ring-sticking or other difficulties, the resultant blend of the highly refined or highly paraffinic oil and intermediate extract constituents will produce non-corrosive, non-sticking, non-sludging paraffinic-type lubricating oil of great desirability for all practical engine lubricating purposes, and for other purposes as well.

Suitable extract fractions sometimes may be obtained by making a single selective-solvent extraction, and then treating the extract with sulfuric acid somewhat as above outlined to remove the heavy, tarry, highly aromatic and reactive constituents and similar materials and yield a stable aromatic-type extract of the present invention.

The highly paraffinic oils with which these extracts are blended are in general those having very low viscosity-gravity constants (V. G. C.) such as those from .800 V. G. C. to about .808 V. G. C. These oils have a viscosity index (V. I.) higher than about 85. Thus a heavily solvent refined dewaxed lubricating oil produced by countercurrent or series solvent extraction (as with a benzene-liquid sulfur dioxide mixture) may have a viscosity-gravity constant of .805 to .808 and a viscosity index of about 90. Again, a very high gravity high grade Eastern crude such as Cabin Creek (Penn.) crude will yield a lubricating "Bright stock" of about .801 V. G. C. and about 105 V. I. with 27.5 A. P. I. gravity and about 145 seconds Saybolt viscosity at 210° F. These oils are not thoroughly satisfactory for such uses as airplane and Diesel engine lubricants, because they tend to corrosion of bearings and ring-sticking. It is to such oils as these that the herein described extracts are adapted in varying amounts such as 5% to 10% or more to overcome such objectionable characteristics. Such blends will have V. G. C.'s of about .811 to .815 according to the amount of extract added to produce the desired modification.

The term "viscosity index" (V. I.) is defined by Dean and Davis in Chemical and Metallurgical Engineering, vol. 36, 1929, page 618. The viscosity index of a lubricating oil is an indication of its composition or type, i. e., whether it is a paraffin or naphthene base oil. Paraffin base oils are arbitrarily assigned a viscosity index of 100, and certain naphthene base oils from the Gulf Coast are assigned a viscosity index of 0 and mixed base oils lie between these extremes. The term "viscosity-gravity constant" (V. G. C.) is defined by Hill and Coats in the Journal of Industrial and Engineering Chemistry, vol. 20, page 641 (1928). This constant represents the paraffinicity or naphthenicity of a given oil. A high value indicates a high degree of naphthenicity while low values indicate relatively greater paraffinicity. Lubricating oils from natural crudes range from .903 (for an extreme Gulf Coast type) to .807 for an extreme Pennsylvania type, or even beyond.

Somewhat similar ends may be obtained by regulating the solvent extraction in the production of a lubricating oil with solvents. The common method of treatment is by countercurrent flow of dewaxed, deasphalted lubricating stock and selective solvent. By withdrawing a portion only of an extract from an intermediate stage of the solvent treatment or from a final stage of the solvent treatment, and reintroducing that portion near that end of the system where the solvent is introduced and the refined oil removed, a portion of that extract will remain in the final oil but the heavy constituents thereof will have been largely removed by the incoming fresh solvent. In this manner a portion of the desired extract is returned to the oil, an opportunity however being afforded for removal of the heavy unstable constituents.

As a further modification, one of the above described extracts from which the heavy constituents have not yet been removed, may be added to the highly refined lubricating oil which it is desired to modify, and the mixture thereof may be treated for the purpose of removing said heavier constituents of the extract. This may be by means of a clay treatment according to any well known procedure such as that employing 5 percent of a filtering or bleaching clay at temperature in the neighborhood of 350° F.

Again, a product may be obtained by adding a quantity of the original dewaxed stock to the highly refined lubricating oil product and clay treating to remove the heavy constituents and other constituents removable by clay. The quantity of stock added will be that sufficient to introduce the necessary proportions of said desired modifying constituents. This procedure may be followed where the remaining lighter constituents, which would normally occur in an extract and are not removable by the clay, do not possess objectionable ring-sticking or other characteristics. While these clay treating methods may sometimes be employed, they are not preferred. The preference rests with the use of extracts from which the heavy extractibles have been eliminated, and particularly the above mentioned "heart cut" or intermediate extract fractions from which the lighter extractibles also have been removed.

Where lubricating type oils have been subjected to clay treatment to remove various constituents, a fraction akin to the "heart cut" can be obtained from the clay by extraction with suitable solvents to remove the adsorbed constituents, the heaviest thereof being rejected if necessary as by propane treatment. The remaining constituents are those to be employed for addition to said highly refined or "over-refined" lubricating oil to overcome the objectionable stated characteristics of corrosiveness and the like.

In using these various fractions they are blended with said "over-refined" or highly refined lubricating oil in varying quantities as from a few percent up to 15 or 20%, according to the potency of the extract. In many instances, around 7 or 8% have been found highly efficient. These added materials are in themselves good lubricants, impart good film strength and oiliness characteristics, are resistant to carbon and varnish formation and have a stabilizing effect in general upon the oils, especially upon those low viscosity-gravity constant raffinates above referred to as highly refined or over-treated. The purpose is to introduce only that portion of the described portions which will impart the desired characteristics. This statement applies also to those variations of the process where fractions containing objectionable heavy and other constituents are added and the blend clay treated to remove heavy, readily reactive and other undesired materials.

These blends have had their corrosive and varnish-forming or ring-sticking characteristics reduced to negligible amounts. Thus, said highly treated or highly paraffinic oils have been modified by return of natural constituents in order to restore the non-corrosive and non-ring-sticking characteristics which they would have borne had the above mentioned protective constituents not been removed by heavy refining. This renders such highly paraffinic oils thoroughly serviceable under practical lubricating conditions. Where extracts are themselves solvent extracted for separation of intermediate from lighter constituents, such as ring-sticking materials, the same type of selective solvent elsewhere mentioned may be used.

The extract fractions above mentioned as having lubricating characteristics in themselves when employed for the present purposes, contain large quantities of complex organic materials including sulfur compounds, nitrogen compounds, aromatics, unsaturates, and the like. Presumably some or all of these constituents have the desired effects. The heavy tarry and resinous constituents and unstable aromatic and unsaturated constituents as well as asphaltenes have been largely removed, thereby leaving only relatively stable materials together with naphthenic constituents carried along in the treatment. The materials desired have an A. P. I. gravity range between about 13° and 18°. They appear to be solvents or plasticizers for gums and varnishes which tend to form in engine operation and cause ring sticking, and to overcome or inhibit formation of corrosive constituents. This theory is presumed to represent their function but applicants do not wish to be bound thereto.

The addition of the fractions herein described to over-refined or heavily refined lubricating oils which tend to possess corrosive or ring-sticking characteristics, produces a stabilizing effect upon such highly treated oils of low V. G. C. and prevents or greatly reduces such corrosiveness and ring sticking. Also there is a tendency to resist formation of carbon and variation at high operating temperatures thereby especially adapting these oils to extreme service coonditions as in the case of airplane engines and Diesel engines.

These disclosures are to be taken as illustrative and not limiting of the generic invention, it being evident that other variations within the scope of the claims may be developed by those skilled in the art. Thus, fractions kindred to the described "heart cut," and having similar characteristics and performing like functions, may be used even though their gravity be different, for example somewhat lighter in specific gravity.

We claim:

1. Highly refined paraffinic type lubricating oil of low viscosity gravity constant and otherwise having tendencies to develop corrosive and ring sticking characteristics, containing added minor proportions of non-paraffinic selective-solvent-extract fractions from petroleum lubricating stocks which fractions are substantially entirely stable aromatic and naphthenic materials and are free from tarry, unstable, highly reactive and highly aromatic fractions obtainable from said stocks by solvent extraction.

2. A lubricant comprising a highly refined paraffinic type lubricating oil otherwise substantially entirely free from all non-paraffinic materials and otherwise possessing ring sticking characteristics, containing added minor proportions of stable, non-paraffinic, intermediate fractions of extract derived from solvent extracts from petroleum lubricating stocks, said intermediate fractions having lubricating properties and being free from the lightest extract constituents and from the heaviest extract constituents including the more unstable and reactive constituents.

3. Mineral lubricating oil comprising heavily solvent-treated paraffinic lubricating oil, and added minor proportions of solvent extract fractions of lubricating oil stock added as such, which fractions are soluble in selective solvents for non-paraffinic fractions of the type represented by liquid sulphur dioxide, liquid sulphur dioxide-benzol mixtures, phenol and dichlorethyl ether, said fractions being free from the lightest constituents and also from the heavy and more unstable and more reactive constituents of the lubricating oil stock relatively more soluble in said selective solvents.

4. An over-refined low V. G. C. highly paraffinic lubricating oil containing an added petroleum extract fraction added as such and obtained from a petroleum lubricating oil stock, said extract fraction being soluble in selective solvents for non-paraffinic materials of the petroleum lubricating oil stock and being of relatively high molecular weight and of aromatic character relatively less soluble in said selective solvents and free from heavy, tarry and highly aromatic and reactive constituents relatively more soluble in said selective solvents, said extract fraction having a gravity in the order 13° to 18° A. P. I. and being present in quantity sufficient to impart to the blend freedom from the characteristic of developing substantial corrosive and ring-sticking tendencies.

5. A method for producing lubricating oils comprising treating a petroleum lubricating stock for the removal of paraffin and asphalt therefrom, treating the dewaxed, deasphalted stock with a selective solvent and recovering from the stock a solvent extract containing heavy, aromatic, resinous, tarry, unsaturated and naphthenic constituents, separating said extract, removing the selective solvent from the extract, treating the extract with a precipitant to eliminate heavy, highly aromatic and reactive constituents and tarry and resinous materials and to yield a relatively stable aromatic and naphthenic fraction, treating said fraction with a selective solvent for the separation of lighter naphthenic constituents and yielding a relatively stable naphthenic and aromatic type fraction, and blending with a dewaxed, deasphalted, highly refined paraffinic type lubricating oil a quantity in the order of several percent of said relatively stable aromatic-type extract fraction sufficient to impart non-corrosive and non-ring-sticking characteristics to said raffinate.

6. A method according to claim 5 wherein the highly paraffinic raffinate is treated with said selective solvent to possess a viscosity-gravity-constant below about 0.810, and the stable aromatic fraction to be added to said raffinate is treated to possess a viscosity-gravity constant of about 0.880–0.910 and a gravity above about 13° A. P. I.

7. A mineral lubricating oil containing as major constituents highly refined solvent-treated paraffinic type mineral lubricating oil fractions and added stable non-paraffinic lubricating fractions added as such including non-reactive aromatic and naphthenic materials soluble in selective solvents for said non-paraffinic materials, the lubricating oil being free from reactive and unstable fractions which would be relatively more soluble in said selective solvents and being substantially free from the characteristic of developing corrosion and ring sticking tendencies.

ULRIC B. BRAY.
DONALD E. CARR.