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PRODUCING OXIDATION RESISTANT LUBRICANTS

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This invention relates to the production of oxidation resistant petroleum lubricating oils by processes involving catalytic hydrogenation.

It is known in the art that hydrogenation of petroleum lubricating oils is capable of improving the antioxidant additive response of the oils, as indicated by the oxidation resistant characteristics of the lubricating oils containing an antioxidant additive. The mechanism of such improvement has not however been fully understood. The present invention is based in part upon the recognition of an important factor involved in the hydrogenation of lubricating oils which factor has not previously been recognized. As a result of this lack of recognition, prior art hydrogenations have not been conducted under the necessary conditions for producing superior oxidation resistant lubricants without undesirable side effects.

When saturated, i.e. nonaromatic, hydrocarbon constituents of petroleum lubricating oil are subjected to hydrogenation conditions in the presence of aromatic hydrocarbons normally present in such oil, the use of conditions which most beneficially affect the additive response of the saturated constituents has undesirable effects on the aromatic constituents. The latter are converted to an excessive extent to undesirable products, e.g. solid carbonaceous deposits, rather than to products having a beneficial effect on the properties of the oil. The present invention provides a novel manner of hydrogenating petroleum lubricating oil components which produces maximum improvement of saturated hydrocarbons without accompanying undesirable effects.

The process according to the invention involves the separation of a saturated hydrocarbon fraction from a petroleum lubricating oil initially containing aromatic as well as saturated hydrocarbons. The saturated hydrocarbon fraction is then contacted with hydrogen in the presence of a hydrogenation catalyst at a temperature within the approximate range from 650 to 825° F. and at a pressure preferably within the approximate range from 100 to 2500 p.s.i.g., more preferably 500 to 1000 p.s.i.g. By hydrogenating in the absence of aromatic constituents originally present, undesirable effects that would otherwise be obtained under the conditions used are avoided, and it is made possible, in one embodiment, to hydrogenate the aromatic constituents separately under different conditions producing additional beneficial results.

Any known metallic hydrogenation catalyst can be employed in the hydrogenation of the saturated hydrocarbon fraction. Such catalysts include those comprising the metals, cobalt, molybdenum, platinum, nickel, iron, palladium, etc. or oxides or sulfides of such metals. Preferably the metallic catalyst is associated with a suitable known carrier such as bauxite, alumina, silica gel, silica-alumina composites, etc.

A preferred procedure involves the percolation of the lubricating oil in liquid phase through a bed of solid hydrogenation catalyst particles preferably having particle size within the approximate range from 4 to 30 mesh. The liquid hourly space velocity in such percolation is preferably within the approximate range from 0.25 to 5 volumes of charge per volume of catalyst bed per hour. The hydrogen consumption is preferably within the approximate range from 25 to 500 standard cubic feet of hydrogen per barrel of charge.

The saturated hydrocarbon fraction after subjection to the hydrogenation conditions set forth above, has improved additive response over that of the original lubricating oil and over that of the saturated hydrocarbon fraction prior to the hydrogenation. It is believed that this improvement is attributable at least in part to the use of conditions which bring about, in addition to other desirable effects, some opening of a naphthene ring in saturated hydrocarbons containing a plurality of naphthene rings.

It is desirable in some instances to subject the hydrogenated saturated fraction to a further refining step, e.g. a mild further hydrogenation or other suitable finishing treatment, in order to remove small amounts of undesirable cracked products formed during the previously described hydrogenation. Mild hydrogenation gives generally superior results to those obtained with other treatments, and is therefore preferred.

The hydrogenated saturated hydrocarbon fraction containing an alkylated phenol or other antioxidant additive can be employed alone as a lubricant in applications which require a high degree of oxidation resistance. Alternatively the saturated hydrocarbon fraction can be blended with a hydrogenated aromatic hydrocarbon fraction obtained as described subsequently. Blends obtained in this manner also have very good additive response resulting not only from the hydrogenation of the saturated hydrocarbon fraction, but also from the hydrogenation of the aromatic hydrocarbon fraction under different conditions.

The conditions employed in the hydrogenation of the aromatic hydrocarbon fraction include temperatures within the approximate range from 450 to 750° F. and preferably at least 550° F. The pressure is preferably within the approximate range from 150 to 3000 p.s.i.g. Any suitable metallic hydrogenation catalyst such as those described previously can be employed. The catalyst may be the same as, or different from, that employed in the hydrogenation of the saturated hydrocarbons. Catalysts comprising cobalt molybdate are preferred. Preferred contacting technique involves percolation, as described previously with respect to hydrogenation of the saturated fraction. The liquid hourly space velocity is preferably within the approximate range from 0.5 to 10 and the hydrogen consumption within the approximate range from 25 to 1000 standard cubic feet per barrel.

The hydrogenation of the aromatic fraction is performed, in this embodiment, under conditions which inhibit excessive formation of solid carbonaceous deposits. Factors contributing to this inhibition include low temperature, high hydrogen pressure and high space rate. The saturated fraction, on the other hand, is hydrogenated under conditions of greater severity, in the sense of conditions which would tend to result in excessive formation of solid carbonaceous deposits if performed in the presence of the aromatic hydrocarbons. The saturated fraction is not necessarily hydrogenated at a higher temperature, lower hydrogen pressure, and higher space rate than the aromatic fraction; however, the conditions in the saturated hydrocarbon hydrogenation which would tend to increase carbonaceous products in the presence of aromatic hydrocarbons, are more predominant, as compared with those conditions which would tend to decrease such products, than in the aromatic hydrocarbon

hydrogenation. In the light of the present specification, a person skilled in the art can determine such combinations of conditions. Preferably, the temperature in the hydrogenation of the saturated fraction is higher than in the hydrogenation of the aromatic fraction, e.g. at least 25° F. higher.

The hydrogenated aromatic hydrocarbon fraction has improved oxidation resistance as compared with the aromatic fraction prior to the hydrogenation. The product also has improved viscosity index and color.

The hydrogenated aromatic fraction can be blended with the hydrogenated saturated fraction in the same proportions as in the original lubricating oil. Alternatively the fractions can be blended in different proportions. Usually, where blends are employed, each component comprises at least 10 volume percent of the blend.

The original separation of a saturated hydrocarbon fraction from the oil can be carried out in any suitable manner. Preferably the separation involves the use of a selective adsorbent such as silica gel, activated alumina, activated carbon, etc. Preferably the adsorbent is employed in the form of particles having size within the approximate range from 10 to 300 mesh, more preferably 25 to 200 mesh. The temperature employed in such separation is preferably within the approximate range from 50 to 300° F. The separation is preferably performed in the presence of a suitable diluent such as petroleum naphtha. The contacting of the lubricating oil with the selective adsorbent is preferably followed by contacting the adsorbent, containing adsorbed constituents of the oil, with a suitable liquid desorbent such as benzene, xylene, acetone, etc. Various desorbents for use in processes for separating petroleum fractions according to hydrocarbon type on a selective adsorbent are well known in the art, and any of the known desorbents can be employed for the purpose of the present invention, the separation according to hydrocarbon type being in itself a conventional operation.

The saturated hydrocarbon fraction obtained in the separation preferably contains less than 5% aromatic hydrocarbons. Similarly the aromatic fraction preferably contains less than 5% of saturated hydrocarbons. Aromatic hydrocarbons, for purposes of the present disclosure, are hydrocarbons which contain one or more aromatic rings in the molecule.

If desired, the separation by means of selective adsorbent can be conducted in such manner that a small fraction, e.g. about 5%, of the oil is retained on the adsorbent after the removal of the aromatic fraction. This 5% represents an undesirable material which is preferably excluded from the aromatic fraction.

If desired, the separation of the original lubricating oil can be performed by a solvent extraction process employing well known solvents for aromatic hydrocarbons, e.g. furfural, phenol, etc. However the use of an adsorption-desorption operation is preferred in that it provides a sharper separation between aromatic and saturated (i.e. non-aromatic) constituents.

It is within the scope of the invention to separate the original oil into a plurality of saturated hydrocarbon fractions having different composition, and hydrogenate one or more of such saturate fractions separately from the other components of the oil. It is also within the scope of the invention to separate the original oil into a plurality of aromatic fractions having different composition and hydrogenate one or more of such fractions separately from other constituents of the oil.

In one embodiment, a raffinate produced in solvent extraction, and still containing a substantial quantity, e.g. about 15 weight percent, of aromatics, is separated by adsorbent-desorption technique into a substantially aromatic-free saturated hydrocarbon fraction and a substantially saturate-free aromatic hydrocarbon fraction. The respective fractions are then hydrogenated under conditions previously indicated as suitable for each. The extract produced in the solvent extraction is preferably not used in the final lubricating oil, though it is within the scope of the invention to include it, preferably after being hydrogenated under the conditions previously set forth for hydrogenation of aromatic fractions.

The charge oil according to the invention is a petroleum lubricating oil having Saybolt Universal viscosity at 100° F. of at least 50 seconds, and more preferably at least 100 seconds. Usually the lubricating oil will not have a viscosity of more than about 300 Saybolt Universal seconds at 210° F. Preferably not more than 5 volume percent of the charge oil has boiling point below 600° F.

The following example illustrates the invention:

Naphthenic crude oil having viscosity-gravity constant of about 0.89 is distilled to produce an acid-free distillate having Saybolt Universal viscosity at 100° F. of 100 seconds. 200 parts by weight of this distillate are percolated through 1200 parts by weight of 28 to 200 mesh silica gel in an elongated column. Following the introduction of the lubricating oil distillate together with n-pentane diluent into the gel column, additional n-pentane is introduced into the column in order to desorb saturated components of the original oil. The effluent pentane containing saturated hydrocarbons is distilled in order to remove pentane and obtain a saturated hydrocarbon fraction constituting about 55% of the original oil. This fraction contains less than 1% aromatic hydrocarbons. Following the pentane, a mixture of 75% benzene and 25% pentane is introduced into the gel column to desorb aromatic hydrocarbons. The effluent solvent containing aromatics is distilled to remove solvent and obtain as residue an aromatic fraction comprising about 40% of the original oil.

The saturated hydrocarbon fraction is contacted with a solid hydrogenation catalyst comprising about 12.5% cobalt molybdate on an alumina carrier. The saturated fraction is percolated through a bed of the catalyst at a temperature of 675° F. and pressure of 800 p.s.i.g. and liquid hourly space velocity of one. The hydrogenated product has increased oxidation resistance (inhibited) over that of the saturates prior to hydrogenation, as determined by a standard test involving determination of the length of time elapsed before the oil, containing 0.4% of added 2,6-ditertiary butyl p-cresol as inhibitor, absorbs or reacts with a predetermined amount of oxygen. The product is further increased in oxidation resistance, as determined by this test, by subjection to further hydrogenation at 600° F. and 500 p.s.i.g. and liquid hourly space velocity of one, employing the same catalyst as in the preceding hydrogenation.

The aromatic hydrocarbon fraction is percolated at 600° F. and 500 p.s.i.g. through a bed of solid hydrogenation catalyst comprising 20% molybdenum disulfide on a bauxite carrier. The liquid hourly space velocity is one. The hydrogenated aromatic fraction has increased oxidation resistance, as determined by the standard test referred to above, over the aromatic fraction prior to hydrogenation.

The saturated hydrocarbon fraction with inhibitor can be employed alone as a lubricating oil or in a blend with the hydrogenated aromatic fraction, the blend for example containing about 40 parts of hydrogenated aromatic fraction and 55 parts of hydrogenated saturate fraction. The hydrogenated saturate fraction, and also the blend thus obtained have superior oxidation resistance to an oil obtained by hydrogenating the original lubricating oil distillate under typical conditions such as those used in hydrogenating the aromatic fraction.

Hydrogenation of the aromatic and saturated fractions separately avoids subjection of the separated aromatic hydrocarbons to the high temperature conditions required in the hydrogenation of the saturated fraction. The aromatic hydrocarbons tend to undergo undesirable reactions, such as coke-forming reactions, at the higher temperatures.

In another embodiment of the invention, the separation by means of silica gel and desorbents is performed in such manner that the effluent desorbent containing aromatic constituents is divided into two fractions. The earlier aromatic effluent desorbent fractions are recovered separately from the later effluent desorbent fractions. Upon removal of desorbent from the earlier desorbent fractions, a hydrocarbon fraction is obtained constituting a mononuclear aromatic hydrocarbon concentrate. From the later desorbent fractions, polynuclear aromatic hydrocarbons are obtained. The mononuclear aromatic concentrate, which constitutes about 20% of the original oil, is hydrogenated at the conditions set forth above for the hydrogenation of the aromatic fraction. The hydrogenated material can be used alone as a lubricant or blended with hydrogenated saturates or with the remainder of the aromatics (hydrogenated or unhydrogenated) or in any other desired combination.

Generally similar results to those obtained above are obtained in a similar treatment of lubricating oils derived from paraffinic or paraffinic-naphthenic base crudes. The latter types of crude generally contain lesser amounts of aromatic hydrocarbons than in the case of naphthenic crudes, but the results obtained are qualitatively the same. Generally similar results are also obtained employing other hydrogenation catalysts such as those referred to previously.

The process according to the invention provides a product which is particularly susceptible to improvement by known antioxidant additives generally. Examples of suitable additives which are advantageously added to the product are the alkylated phenol oxidation inhibitors, which are well known as a class in the prior art, e.g. the polyalkyl aryl hydroxy compounds such as 2,6-ditertiary butyl-4-methyl phenol, 2,4-dimethyl-6-tertiary octyl phenol, pentamethyl phenol, pentaethyl phenol, tritertiary butyl phenol, 2-isopropyl-4,6-dimethyl phenol, 2-tertiary butyl-4,6-dimethyl phenol, 2-tertiary amyl-4,6-dimethyl phenol, 4-methyl-2,6-diisopropyl phenol, 2,6-ditertiary amyl phenol-4-tertiary butyl phenol, 2,4,6-triisopropyl phenol, etc. Other known types of oxidation inhibitors can also be employed, for example various compounds of sulfur, phosphorus or sulfur and phosphorus, various amines, etc. Examples of such oxidation inhibitors are sulfurized lauryl oleate, sulfurized terpenes, alkyl sulfides, tributyl phosphite, lecithin, diphenyl amine, etc.

The invention claimed is:

1. Process for producing oxidation resistant lubricants which comprises separating petroleum lubricating oil into a saturated fraction and an aromatic fraction, contacting the saturated fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature of 650 to 825° F., contacting the aromatic fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature of 450 to 750° F., the severity of the latter contacting being less than that of the first-named contacting, and blending the hydrogenated aromatic fraction with the hydrogenated saturated fraction.

2. Process for producing oxidation resistant lubricants which comprises separating distillate petroleum lubricating oil into a saturated fraction and an aromatic fraction, contacting the saturated fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature in the range from 650 to 825° F., a pressure in the range from 100 to 2500 p.s.i.g. and a liquid hourly space velocity in the range from 0.25 to 5, and contacting the aromatic fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature in the range from 450 to 750° F., a pressure in the range from 150 to 3000 p.s.i.g., and a liquid hourly space velocity in the range from 0.5 to 10, and blending the hydrogenated saturated fraction with the hydrogenated aromatic fraction.

3. Process for producing oxidation resistant lubricants which comprises separating petroleum lubricating oil into a saturated fraction and a concentrate of mononuclear aromatic hydrocarbons, contacting the saturated fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature of 650 to 825° F., contacting said concentrate with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature of 450 to 750° F., the severity of the latter contacting being less than that of the contacting of the saturated fraction with hydrogen, and blending the hydrogenated concentrate with the hydrogenated saturated fraction.

4. Process for producing oxidation resistant lubricants which comprises separating petroleum lubricating oil by selective adsorption treatment with a granular solid adsorbent capable of producing a saturated product containing less than 5 percent of aromatic hydrocarbons, thereby to obtain a saturated fraction containing less than 5 percent of aromatic hydrocarbons and an aromatic fraction, and contacting the saturated fraction with hydrogen in the presence of a metallic hydrogenation catalyst at a temperature of 650 to 825° F.

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