

1

2,846,356

## HYDROREFINING FOLLOWED BY HEAT STABILIZING

Ivor W. Mills, Glenolden, Pa., and William E. Bonnet, New Castle, Del., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

No Drawing. Application October 11, 1955  
Serial No. 539,924

6 Claims. (Cl. 196—24)

This invention relates to the refining of petroleum by means of hydrogenation, and more particularly to the preparation by such means of refined waxes or of specialty oils, for example transformer oil, cable oils, refrigerator oils, etc.

It is known in the art to produce specialty oils and other petroleum products of various kinds by means of refining processes including hydrogenation, but the prior processes have not been entirely satisfactory from the standpoint of the oxidation stability and other properties of the petroleum products obtained thereby. Furthermore, the prior processes have in general not been able to produce even a reasonably satisfactory product by hydrogenation without using such hydrogenation in combination with other refining operations, such as solvent refining, clay treating, etc.

The requirements for specialty oils produced from petroleum are quite rigid in many instances, and difficult to obtain by ordinary refining processes. Thus for example transformer oils produced from petroleum must, in order to be satisfactory for use in the electrical industry, pass certain severe tests with regard to oxidation stability, non-corrosiveness to copper, etc. Other specialty oils such as cable oils and refrigerator oils must also meet rigid requirements with regard to oxidation stability and other properties.

The present invention provides a novel manner of producing specialty oils and other products by means of hydrogenation, whereby products having remarkably good oxidation stability and other properties can be obtained. The properties obtainable in the process according to the invention are generally markedly superior to the properties obtained in the conventional prior art processes for producing specialty oils.

The process according to the invention involves treatment of a petroleum charge stock by catalytic hydrogenation under particular conditions as subsequently more fully described, and then subjection of the hydrogenated oil to a different set of conditions as subsequently more fully described. Both of these operations in the treatment according to the invention are essential to the obtaining of specialty oils having the desired improved properties. Thus the two operations cooperate to produce the distinctly superior properties of the products obtained in accordance with the invention.

Although the process of the invention involves more than one operation, it represents a substantial advance with regard to convenience and ease of carrying out the process over prior art processes which have required, in addition to a hydrogenation stage, conventional prior art refining operations such as solvent refining, acid treating, clay treating, etc. In the process according to applicants' invention, the procedure subsequent to the hydrogenation, though essential to the obtaining of satisfactory results, is simple and convenient as compared with such prior art refining operations. It is to be understood that prior art refining operation such as solvent refining, acid treating, clay treating, etc. can be employed

2

according to the invention in conjunction with the operations which are essential to applicants' process, but the use of such prior art refining operations is not an essential feature of the invention, and very satisfactory results can be obtained in their absence.

The hydrogenation conditions which are employed in the first step of the process according to the invention include hydrogenation temperatures within the approximate range from 650° F. to 750° F. and hydrogen pressures within the approximate range from 1000 to 2000 p. s. i. g. Liquid hourly space velocities within the approximate range from 0.25 to 2 volumes of charge per volume of catalyst bed per hour can advantageously be used in fixed bed operation, and residence times corresponding to such space rates are generally satisfactory. The hydrogen consumption obtained under such conditions is generally within the approximate range from 250 to 500 standard cubic feet per barrel of charge.

Any suitable hydrogenation catalyst can be used according to the invention, e. g. various metals or oxides or sulfides thereof. Metals which can be used in one or more of these forms include cobalt, nickel, iron, manganese, chromium, molybdenum, magnesium, platinum, copper, zinc, vanadium, etc. Mixtures or combinations of such oxides or sulfides, e. g. cobalt molybdate, etc., can be employed. Other known hydrogenation catalysts can be employed. Any suitable catalyst base or support can be employed, e. g. bauxite, alumina, silica gel, clay, silica-alumina compositions, kieselguhr, pumice, charcoal, activated carbon, various aluminum silicates, etc. Other known bases can be employed. The catalyst may be prepared by any of the known methods for preparation of hydrogenation catalysts.

It is preferred according to the invention that the catalyst base or support which is employed have a pH of at least about 9, since it has been found that a catalyst base or support which has too low pH will result in the obtaining of excessive cracking of hydrocarbons during the hydrogenation under the conditions set forth above.

A preferred manner of carrying out the hydrogenation according to the invention involves passing the petroleum charge through a stationary bed of solid hydrogenation catalyst in the presence of hydrogen. However, any other suitable contacting method, such as a slurry type of operation with filtration of the catalyst from the hydrogenated product, can be employed if desired. The hydrogenation can be performed in the presence of a suitable diluent for the charge stock, e. g. petroleum naphtha or other low viscosity hydrocarbon diluent, etc., but generally the use of such diluent is not necessary.

The charge stock employed according to the invention is a straight run petroleum fraction which has A. P. I. gravity not substantially greater than 40, and preferably from 20 to 30. Generally the charge stock will be a gas oil or lubricating oil fraction. However the invention is also applicable to other petroleum fractions such as waxes, etc.

The second step of the process according to the invention involves the heating of the hydrogenated oil to a temperature within the approximate range from 450° F. to 650° F. for a period of at least 5 minutes, in the absence of a hydrogenation catalyst. The purpose of the second stage is to eliminate the corrosive nature which the hydrogenated oil, without further treatment, exhibits. It is believed that this corrosive nature is attributable to the presence of elemental sulfur in the hydrogenated oil, and that the elimination of corrosiveness by means of the heating step involves the reaction of elemental sulfur with hydrocarbons in the oil to produce hydrogen sulfide, which can then be readily removed from the oil, e. g. by steam stripping.

It is not fully understood why the subsequent heating is

required following the hydrogenation in order to eliminate elemental sulfur. It might be thought that the conditions for conversion of elemental sulfur to hydrogen sulfide would be present to at least the same extent during the hydrogenation as during the subsequent heating step. Nevertheless, it has been found that the heating step is essential to obtain a non-corrosive oil.

As stated previously, the heating step is performed in the absence of a hydrogenating catalyst. Preferred operation involves the passage of the hydrogenated oil from the hydrogenation zone directly into a heating zone which contains no hydrogenating catalyst. The hydrogenated oil generally contains some dissolved hydrogen, but in the absence of a hydrogenation catalyst, the subjection of the hydrogenated oil to temperatures of 450° F. to 650° F. does not produce any substantial further hydrogenation of the oil.

The heating step should be carried out under a pressure sufficient to prevent any flashing or bubbling of the liquid oil, since flashing or bubbling tends to result in the production of an oil which is not completely free from corrosiveness to copper. Generally a pressure of at least 100 p. s. i. g. will be required, though in some instances lower pressures can be employed. Generally it is not necessary to employ a pressure in the heating stage greater than 500 p. s. i. g., though higher pressures can be employed if desired.

The heating should continue for at least about 5 minutes, in order to provide sufficient time for the reaction of elemental sulfur with hydrocarbons contained in the oil. In cases where the oil is passed continuously through a heating zone, for example a heated coil, the space rate should therefore be chosen in such a way as to provide a residence time of at least 5 minutes in the heating zone. Generally it will not be necessary to continue the heating for more than 150 minutes, though longer heating times can be employed if desired. Where temperatures of 550° F. or higher are employed, heating times of 30 minutes or less will usually be sufficient.

Hydrogen sulfide can be stripped from the products of the second step according to the invention by any conventional means for such stripping. In some cases at least, it will also be desirable to strip a small amount of the hydrocarbon products from the oil obtained from the second stage, since a small amount of cracking generally occurs during the process according to the invention, producing light hydrocarbons which should be removed from the products in order to obtain satisfactory specialty oils. Generally it will not be necessary to remove more than about 5 percent of the hydrocarbons in such a stripping operation.

It is to be understood that the operations in the process according to the invention can be carried out either in batch or continuous operation; however, continuous operation is generally preferred.

Oxidation inhibitors can be added to the products obtained according to the invention, and in some but not all instances the addition of an oxidation inhibitor is essential to the obtaining of a product having optimum properties. Thus for example, to produce a transformer oil having satisfactory properties in the most demanding applications, it is generally necessary to employ an oxidation inhibitor. Where such an inhibitor is employed, the amount is preferably within the approximate range from 0.01 to 10 weight percent.

Any suitable oxidation inhibitor of the prior art can be employed, a considerable variety of such inhibitors being known, all of which are generally suitable for employment in the products obtained according to the present invention. Preferred oxidation inhibitors are the alkylated phenol oxidation inhibitors, which are well known as a class in the prior art. Preferred alkylated phenol oxidation inhibitors for use according to the invention are the polyalkyl aryl hydroxy compounds such as 2,6-ditertiary butyl-4-methyl phenol, 2,4-dimethyl-6-tertiary octyl phe-

mol, 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, 2,6-ditertiary amyl phenol-4-tertiary butyl phenol, 2,4,6-triisopropyl phenol, etc.

Other 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 products obtained according to the invention can be further refined, prior to or subsequent to the addition of an oxidation inhibitor if any, according to the conventional practices of the prior art. Thus for example the products can be treated with an absorbent material such as clay, etc. However a particular advantage of the invention resides in the fact that highly satisfactory products can be obtained without employing such conventional prior art refining operations, and in preferred operation according to the invention such refining operations are not employed.

The following example illustrates the invention:

Naphthenic lubricating oil having A. P. I. gravity of about 24.5 was hydrogenated at a temperature of about 675° F. and a pressure of 1500 p. s. i. g. and the hydrogenation products were subsequently heated at a temperature of about 475° F. for 2 hours in the absence of hydrogenation catalyst in order to remove elemental sulfur from the hydrogenated oil.

The charge stock was obtained by vacuum distillation of naphthenic base crude to obtain, among other distillates, a distillate having A. P. I. gravity of about 24.5. This distillate was then hydrogenated under the conditions mentioned previously by passage downwardly through a stationary bed of solid hydrogenation catalyst comprising about 20 percent molybdenum sulfide on an alumina base. The liquid hourly space velocity was 0.5 volume of oil per volume of catalyst bed per hour. The decrease in refractive index obtained as a result of the hydrogenation was 0.0132; the A. P. I. gravity of the product was about 28.5. The oil obtained as a product of the hydrogenation was then subjected to heating by batch operation under the conditions mentioned previously, hydrogen sulfide and light ends being stripped from the product by means of nitrogen to obtain a product having A. P. I. gravity of about 26.5.

The products obtained from the heating operation were tested for oxidation stability by means of a modification of ASTM test D943-54. According to this modification, 300 ml. of oil and 6 ml. of distilled water were placed in a tube, and an oxidation catalyst consisting of coupled iron and copper wire was immersed in the oil. The oxidation test was carried out at 95° C. with 3 liters of oxygen per hour being introduced into the tube. Periodically samples were removed from the oil being tested, and the interfacial tension of the sample was determined by means of ASTM test D971-48T, the sample then being returned to the testing zone. The life of the oil tested was determined as the number of hours which elapsed under the conditions of the test before the interfacial tension of the oil decreased to below 20 dynes per centimeter.

For purposes of comparison, an oil was tested which was obtained from a similar naphthenic distillate by means of furfural refining to obtain a raffinate constituting about 85 percent of the initial charge, this raffinate subsequently being treated with 10 pounds of concentrated sulfuric acid per barrel and 10 pounds of Attapulugus clay per barrel. In both cases, the oxidation stability test was performed with the oil containing 0.08 weight percent of 2,6-ditertiary butyl-4-methyl phenol as oxidation inhibitor.

The following table shows the results obtained:

|                                                      | Oil life—hours |
|------------------------------------------------------|----------------|
| Charge oil refined with furfural, acid and clay----- | 300            |
| Charge oil refined by hydrogenation and heating----  | 640            |

This table shows that the hydrogenation and subsequent heating according to the invention are capable of producing an oil which is greatly superior in oxidation stability to an oil obtained by conventional prior art refining methods.

The heating stage was determined to be essential to the obtaining of a satisfactory product, since the hydrogenated oil prior to heating failed the copper strip test, whereas the hydrogenated oil after the heating passed the same test. The copper strip test involves the immersion of a copper strip, polished according to ASTM standards, in the oil to be tested, and the maintenance of the oil at 212° F. for 3 hours. The copper strip is then observed to determine whether it has undergone substantial staining during the test, and the oil is considered to fail the test if substantial staining has occurred.

The invention claimed is:

1. Process for refining petroleum which comprises: contacting a petroleum distillate fraction having boiling range at least as high as that of gas oil and having A. P. I. gravity not substantially greater than 40 with hydrogen at a temperature within the approximate range from 650° F. to 750° F. and a pressure of 1000 to 2000 p. s. i. g. in the presence of a hydrogenation catalyst, said contacting being performed under conditions providing a product having improved oxidation stability in the presence of an antioxidant additive and also having corrosive properties with respect to copper; separating the contacted fraction from catalyst; subsequently subjecting said fraction to a temperature within the approximate range from 450° F. to 650° F. for at least five minutes in the absence of a hydrogenation catalyst, thereby to obtain a suitably non-corrosive product; and removing hydrogen sulfide from the product.

2. Process for preparing a transformer oil which comprises: contacting a straight run naphthenic petroleum distillate fraction having boiling range at least as high as that of gas oil and having A. P. I. gravity within the approximate range from 20 to 30 with hydrogen at a temperature within the approximate range from 650°

F. to 750° F. and a pressure of 1000 to 2000 p. s. i. g. in the presence of a molybdenum-containing hydrogenation catalyst, said contacting being performed under conditions providing a product having improved oxidation stability in the presence of an antioxidant additive and also having corrosive properties with respect to copper; separating the contacted fraction from catalyst; subsequently subjecting said fraction to a temperature within the approximate range from 450° F. to 650° F. for at least five minutes in the absence of a hydrogenation catalyst, thereby to obtain a suitably non-corrosive product; removing hydrogen sulfide from the product; and adding an oxidation inhibitor to the product.

3. Process according to claim 1 wherein said hydrogenation catalyst comprises molybdenum sulfide.

4. Process according to claim 1 wherein the first-named temperature is about 675° F.

5. Process for refining petroleum which comprises: contacting a petroleum distillate fraction having boiling range at least as high as that of gas oil and having A. P. I. gravity not substantially greater than 40 with hydrogen at a temperature within the approximate range from 650° F. to 750° F. and a pressure of 1000 to 2000 p. s. i. g. in the presence of a hydrogenation catalyst, said contacting being performed under conditions providing a product having improved oxidation stability in the presence of an antioxidant additive and also having corrosive properties with respect to copper; separating the contacted fraction from catalyst; subsequently subjecting said fraction to a temperature within the approximate range from 550° F. to 650° F. for 5 to 30 minutes in the absence of a hydrogenation catalyst, thereby to obtain a suitably non-corrosive product; and removing hydrogen sulfide from the product.

6. Process according to claim 5 wherein said subjecting is performed at a pressure within the approximate range from 100 to 500 p. s. i. g.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

2,717,855 Nicholson ----- Sept. 13, 1955

##### FOREIGN PATENTS

418,926 Great Britain ----- Nov. 2, 1934