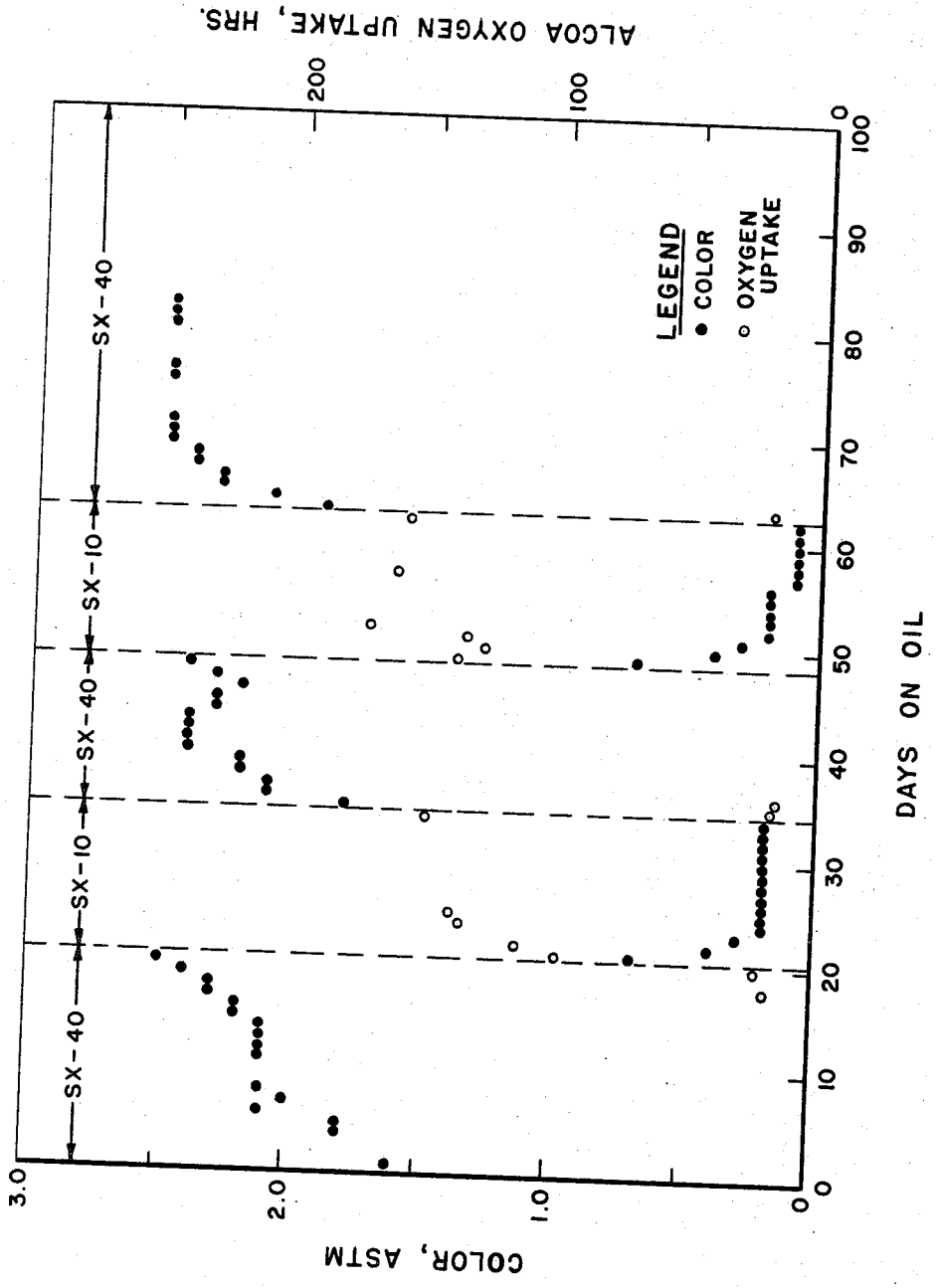
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REFINING OF LUBRICATING OIL AND REACTIVATION OF THE CATALYST

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REFINING OF LUBRICATING OIL AND REACTIVATION OF THE CATALYST

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This invention relates to the finishing of lubricating oils. It particularly relates to the mild hydrogenation of lubricating oil stocks in the presence of a suitable hydrogenation catalyst and hydrogen to obtain products of high quality. More particularly, it relates to the reactivation of the catalyst used in the mild hydrotreating of a lubricating oil.

Through the years numerous refining methods for lubricating oils have been used. Many of these include low-pressure fractionation, solvent extraction, solvent dewaxing, acid treating, and clay treating. Such lubricating-oil treatments are discussed in Kirk-Othmer "Encyclopedia of Chemical Technology," volume 10, The Interscience Encyclopedia, Inc., New York, pp. 147–153 (1953).

More recently, hydrotreating has been used as a means for improving the quality of raw lubricating-oil stocks. Such hydrogenation processes have been used generally to improve the color and stability of the oil and employ suitable hydrogenation catalysts. Typical catalysts for such hydrotreating are nickel-tungsten sulfide, cobalt molybdate, nickel molybdate, cobalt sulfide, molybdenum sulfide, cobalt oxide and molybdenum oxide. These catalytic materials are generally supported on a suitable carrier or support, such as alumina, magnesia, silica, or silica-alumina.

The present invention employs a suitable hydrogenation catalyst, for example, metals having hydrogenation activities and certain compounds of such metals. Typically, such metals may be selected from the Sixth and Eighth Groups of the Periodic Table and the oxides, sulfides or mixtures thereof. The preferred catalyst for the process is a conventional cobalt-molybdenum hydrogenation catalyst which comprises the oxides of cobalt and molybdenum on an alumina support. A typical example of such a catalyst would contain from about 2 to 4 percent by weight cobalt oxide and from 10 to 15 percent by weight of the oxides of molybdenum. Such catalysts and their preparation are well known in the art. Prior to its use in the hydrogenation of lubricating oils, the catalyst may be activated by subjecting it to a sulfiding treatment.

Hydrogenation may be used to treat both solvent-extracted lubricating-oil stocks and distillates. Such stocks may, or may not, have been previously dewaxed.

Commercially-acceptable refined lubricating oils may be obtained by the hydrotreating of a variety of raw feeds. Among the feed stocks which can be treated by our invention are those that will provide hydrogenated solvent-extracted base stocks which have Saybolt viscosities at 100° F. of about 100, 165, 330, 840 and 1400 and which are used to make finished S.A.E. 5W, 10W, 20, 40 and 50 grade motor oils, respectively.

Our invention comprises the hydrotreating of a lubricating oil which has a viscosity that does not exceed 45 SUS at 210° F. in the presence of a hydrogenation catalyst, that has been used prior to this to hydrotreat a

lubricating oil which has a viscosity of at least 70 SUS at 210° F., to partially restore the activity of the catalyst, which has declined as a result of the prior hydrotreating of the higher-viscosity oil. Apparently, this is due to deactivation of the catalyst.

It is known that as a high-viscosity, solvent-refined feed is being hydrofinished under mild hydrogenation conditions, the color of the resultant product darkens as time on oil proceeds. Surprisingly, we have found that processing a low-viscosity, solvent-extracted lubricating oil over the deactivated catalyst for a period of time is beneficial in restoring the ability of the catalyst to produce a product of good color when the catalyst is subsequently used to process the original high-viscosity, solvent-extracted lubricating oil.

In common commercial practice, the typical catalyst would be regenerated by conventional methods when product specifications cannot be met. In place of the conventional regeneration treatment, we have found a reactivation technique which permits more economical operation. For most efficient operation, the low-viscosity feed should be selected so that the product obtained from the catalyst-reactivation treatment can be used as feed for some other refining operation, for example, catalytic cracking. Through the use of our novel technique, the number of regenerations required for the particular hydrogenation catalyst can be reduced. This will culminate in a higher operating factor for the hydrogenation unit, a lower maintenance cost and longer ultimate catalyst life.

A typical hydrogenation process would be the one described in U.S. Patent application S.N. 435,941, which was filed on Mar. 1, 1965 and has a common assignee with this application. In such a hydrogenation process, the following conditions are used: a temperature within the range from about 500° F. to about 695° F., preferably, from 550° F. to 650° F.; a liquid hourly space velocity within the range from about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, preferably, from 0.5 to 1.0 volume of hydrocarbon per hour per volume of catalyst; a hydrogen partial pressure within the range from about 500 to about 1200 p.s.i.a., preferably from 700 to 900 p.s.i.a.; a hydrogen consumption within the range from about 10 standard cubic feet of hydrogen per barrel of hydrocarbon to about 300 standard cubic feet of hydrogen per barrel of hydrocarbon, preferably, from 20 to 250 standard cubic feet of hydrogen per barrel of hydrocarbon; and a hydrogen flow to the reactor within the range from about 50 to about 1000 standard cubic feet of hydrogen per barrel of hydrocarbon, preferably, from 200 to 800 standard cubic feet of hydrogen per barrel of hydrocarbon.

Example

The following test produced results which demonstrate the applicability of our invention.

A catalyst bed, which consisted of 100 cubic centimeters of a typical 1/16-inch extruded cobalt molybdenum catalyst, was used in the hydrogenation of the lubricating oils involved herein. The catalyst bed was one foot in length. Hydrocarbons and hydrogen were passed down through the catalyst bed in the hydrogenation zone and were then sent to a gas-liquid separator. Unstripped hydrogenated product was obtained from the separator.

Hydrogenation conditions included a hydrogen partial pressure of 800 p.s.i.a., a temperature of 600° F., a liquid hourly space velocity of 1.0 volume of hydrocarbon per hour per volume of catalyst, and a hydrogen addition rate of 400 standard cubic feet of hydrogen per barrel of hydrocarbon. Several hydrocarbon feed stocks were employed. These included one solvent-extracted 10-grade oil and four solvent-extracted 40-grade oils. The results obtained from inspections made on these feed stocks are listed in Table I.

TABLE I

Feed	A	B	C	D	E
Feed grade	SX-40	SX-40	SX-40	SX-10	SX-40
Color, ASTM		8+	8+	1.4	8+
Gravity, degrees API	27.2	26.1	26.7	30.1	26.3
Viscosity at 100° F., SUS	400.9	1069	999.9	172.3	1036
Viscosity at 210° F., SUS	58.53	86.60	84.54	44.17	86.28
Viscosity index		86	88	89	88
Sulfur, weight percent		0.42	0.39	0.27	0.42
Flash point (COC), ° F		565	540		
Refractive index at 20° C			1.4932		1.4954
Total nitrogen, p.p.m			242		276
Basic nitrogen, p.p.m			102		108
Hydrogen, weight percent			13.35		

Feed A was used for the first four days of the test. Feed B was employed for a period from the 5th day through the 15th day. Feed C was used from the 16th day through the 20th day. Feed D was used from the 21st day through the 34th day. Feed E was used from the 35th day through the 48th day. Feed D was used from the 49th day through the 62nd day. Feed E was used from the 63rd day through the 82nd day.

Prior to the test, the catalyst was sulfided by treatment with a gas mixture consisting of approximately 8% hydrogen sulfide in hydrogen. The catalyst was treated with this gas overnight at atmospheric pressure and a temperature between 700 and 725° F. The gas flow rate was 1.0 cubic feet per hour.

The color and oxidation stability of samples of the product were obtained. These values are presented in the accompanying figure. In this figure, both ASTM color and the value for ALCOA oxygen uptake are plotted against days on oil. The ALCOA oxygen uptake method is an oxygen absorption method of the general type which have been used for some time in laboratories of some of the oil companies, other manufacturers and electric utilities, where appraisal of the oxidation stability of oils is important. This method, which has recognized limitations, has been suggested for use as a process-control test and is intended as a secondary test for oxidation stability.

This method of test consists of subjecting an oil sample, in the presence of an oxygen atmosphere and solid copper catalysts, to a moderately elevated temperature. After the oxygen atmosphere has been sealed off in the test flask, continuous pressure observations are made. The pressure ultimately drops with oxygen absorption by the oil. The end-point is a fixed pressure drop. The value of the oxidation stability of the tested oil is the number of hours between the start of the test and the time when the pressure has dropped 60 mm. from the maximum developed pressure.

A detailed description of the apparatus employed and the test method has been published in "ASTM Standards on Electrical Insulating Liquids and Gasses", 1st edition, American Society for Testing Materials, Philadelphia, Pa., December 1959, Appendix II, pp. 314–317.

The application of this method may be made to include oils, either inhibited or non-inhibited. Each oil tested contained two oxidation inhibitors, 0.25% hindered phenol and 0.05% aromatic amine, and 0.1% rust inhibitor, an alkylated dicarboxylic acid.

For the first 20 days on oil, a solvent-extracted 40-grade oil was hydrogenated over the catalyst. From the 20th day through the 34th day, a solvent-extracted 10-grade oil was hydrotreated over the catalyst. This was followed by the hydrotreating of a solvent-extracted 40-grade oil through the 48th day on oil. Then until the end of the 62nd day, a solvent extracted 10-grade oil was passed over the catalyst. From the 63rd day through the 82nd day on oil, a solvent-extracted 40-grade oil was hydrotreated over the same catalyst. Hence, the solvent-extracted 40-grade oil and the solvent-extracted 10-grade oil were alternated.

The results show that each time the lower viscosity oil was used, the oxidation stability of the hydrofinished oil increased as the number of days on oil increased. Moreover, when the solvent-extracted 40-grade oil was returned to the process, the oxidation stability of the product returned to a low-value and initially the ASTM color showed an improved value for that grade of oil. As the test proceeded with the grade-40 oil, the ASTM color value began to increase, indicating that the color was becoming poorer.

From the foregoing description it can be seen that the catalyst used to hydrotreat petroleum lubricating oils of relatively high viscosity can be reactivated for use over a period of time by using the deactivated catalyst to hydrotreat a lubricating oil having a relatively low viscosity.

The foregoing example and specification clearly demonstrate a method for partially restoring the activity of a hydrogenation catalyst used in the hydrotreating of lubricating oils. The example is presented for illustration only and is not intended to limit our invention.

We claim:

1. In a process for the hydrotreating of a high-viscosity petroleum lubricating oil wherein said lubricating oil is hydrotreated under hydrogenation conditions in the presence of a hydrogenation catalyst until the activity of said catalyst declines to an undesirable level, said catalyst consisting essentially of hydrogenation components selected from the group consisting of cobalt, molybdenum, the oxides, sulfides and mixtures thereof, on an alumina base, the improvement which comprises subsequently employing said catalyst to hydrotreat a low-viscosity petroleum lubricating oil for a time sufficient to at least partially restore the hydrogenating activity of said catalyst and, after the hydrotreating of said low-viscosity petroleum lubricating oil, employing said catalyst to hydrotreat said high-viscosity petroleum lubricating oil.

2. In a process for the hydrotreating of a first petroleum lubricating oil, which has a viscosity of at least 70 SUS at 210° F., wherein said first lubricating oil is hydrogenated under hydrogenation conditions in the presence of a hydrogenation catalyst consisting essentially of hydrogenation components selected from the group consisting of cobalt, molybdenum, the oxides, sulfides, and mixtures thereof, on an alumina base, the improvement which comprises subsequently using said catalyst to hydrotreat a second petroleum lubricating oil, which has a viscosity that does not exceed 45 SUS at 210° F., for a time sufficient to partially restore the hydrogenating activity of said catalyst and, after the hydrotreating of said second petroleum lubricating oil, using said catalyst to hydrotreat said first petroleum lubricating oil.

3. Process of claim 2 wherein said catalyst consists essentially of about 2 to about 4 weight percent cobalt oxide and about 10 to about 15 weight percent molybdenum oxides on an alumina base.

4. In a process for the hydrotreating of a high-viscosity petroleum lubricating oil, wherein said high-viscosity lubricating oil is hydrogenated in a hydrogenation zone at a temperature within the range from about 500° F. to about 695° F. and a hydrogen partial pressure within the range from about 500 to 1200 p.s.i.a., said high-viscosity lubricating oil being passed through said hydrogenation zone at a liquid hourly space velocity within the range from about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, in the presence of a hydrogenation catalyst consisting essentially of hydrogenation components selected from the group consisting of cobalt, molybdenum, the oxides, sulfides, and mixtures thereof, on an alumina base, the improvement which comprises subsequently using said catalyst to hydrotreat a low-viscosity petroleum lubricating oil to at least partially restore the hydrogenating activity of said catalyst and, after the hydrotreating of said low-viscosity petroleum lubricating oil, using said catalyst to hydrotreat said high-viscosity petroleum lubricating oil.

5. Process of claim 4 wherein the hydrogenation conditions for the hydrotreating of said low-viscosity lubricating oil include a temperature within the range from about 500° F. to about 695° F., a hydrogen partial pressure within the range from about 500 to 1200 p.s.i.a., a liquid hourly space velocity within the range from about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen consumption rate of about 10 to about 300 standard cubic feet of hydrogen per barrel of hydrocarbon.

6. Process of claim 4 wherein said catalyst consists essentially of about 2 to about 4 weight percent cobalt oxide and about 10 to about 15 weight percent molybdenum oxide on an alumina base.

7. Process for the partial restoration of the ability of a partially spent hydrogenation catalyst to produce good color and stability when being used to hydrotreat a high-viscosity petroleum lubricating oil, said catalyst consisting essentially of hydrogenation components selected from the group consisting of cobalt, molybdenum, the oxides, sulfides, and mixture thereof, on an alumina base, which process comprises subsequently using said catalyst to hydrotreat a low-viscosity petroleum lubricating oil under

hydrogenation conditions and, after the hydrotreating of said low-viscosity petroleum lubricating oil using said catalyst to hydrotreat said high-viscosity petroleum lubricating oil.

8. Process for the partial restoration of the ability of a partially spent hydrogenation catalyst to produce good color and stability when being used to hydrotreat a first petroleum lubricating oil, which has a viscosity of at least 70 SUS at 210° F., said catalyst consisting essentially of hydrogenation components selected from the group consisting of cobalt, molybdenum, the oxides, sulfides, and mixtures thereof, on an alumina base, which process comprises subsequently using said catalyst to hydrotreat a second petroleum lubricating oil, which has a viscosity which does not exceed 45 SUS at 210° F., under mild hydrogenation conditions and, after the hydrotreating of said second petroleum lubricating oil, using said catalyst to hydrotreat said first petroleum lubricating oil.

9. Process of claim 8 wherein said mild hydrogenation conditions include a temperature within the range from about 500° F. to about 695° F., a hydrogen partial pressure within the range from about 500 to about 1200 p.s.i.a,. a liquid hourly space velocity within the range from about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen consumption rate between about 10 standard cubic feet of hydrogen per barrel of hydrocarbon and 300 standard cubic feet of hydrogen per barrel of hydrocarbon.

10. Process of claim 8 wherein said catalyst consists essentially of about 2 to about 4 weight percent cobalt oxide and about 10 to about 15 weight percent molybdenum oxides on an alumina base.

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