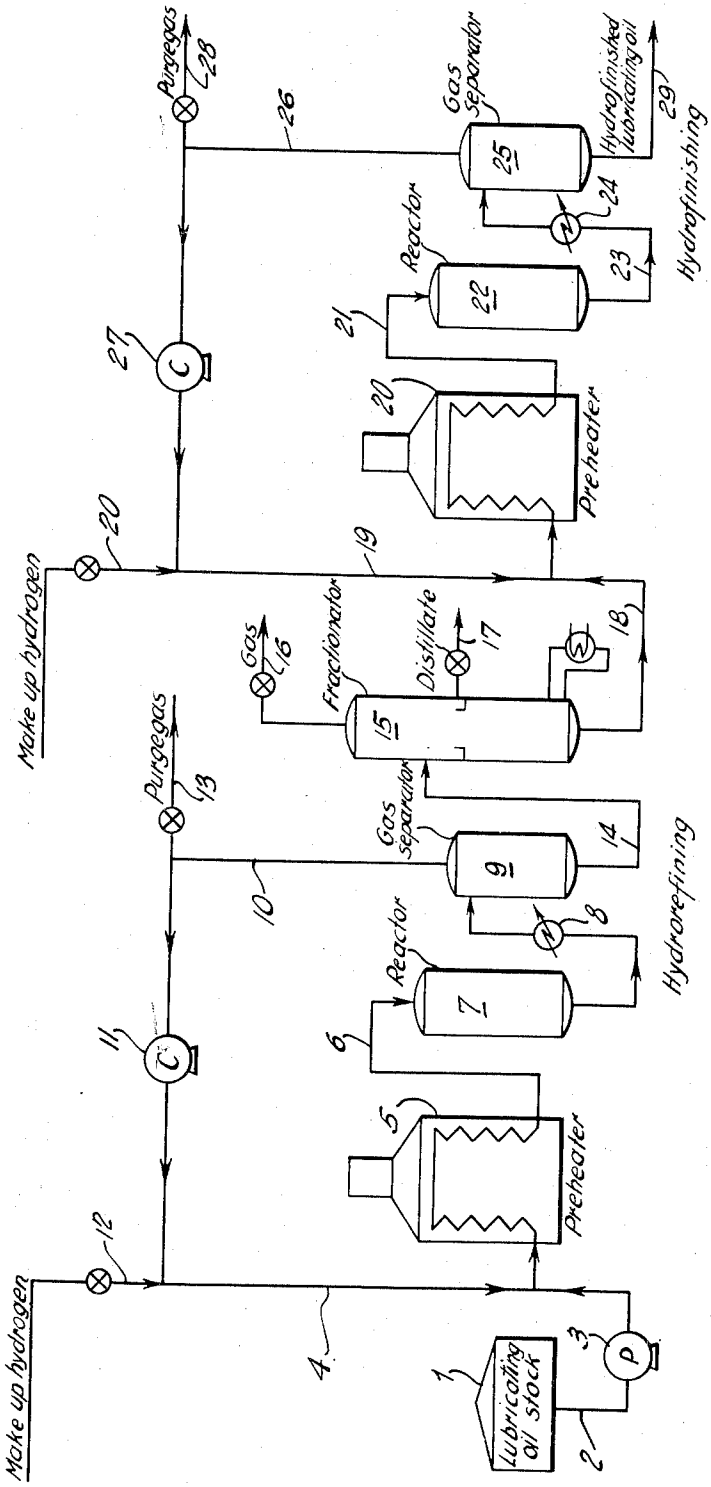
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PROCESS FOR IMPROVING LUBRICATING OILS BY HYDRO-REFINING IN A FIRST STAGE AND THEN HYDROFINISHING UNDER MILDER CONDITIONS

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PROCESS FOR IMPROVING LUBRICATING OILS BY HYDRO-REFINING IN A FIRST STAGE AND THEN HYDROFINISHING UNDER MILDER CONDITIONS

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This invention relates to improvements in the manufacture of lubricating oils. More particularly, it relates to a two-step process in which a lubricating oil stock is treated with hydrogen to produce an intermediate product of improved viscosity index and this intermediate product is further treated with hydrogen to produce a lubricating oil of improved stability and resistance to oxidation. In the process of this invention, a hydrocarbon lubricating oil stock is hydrogenated at temperatures in the range of 600 to 800° F. in the presence of a hydrogenation catalyst to convert the said lubricating oil stock to an intermediate product of improved viscosity index and this intermediate product is subjected to further catalytic treatment with hydrogen at temperatures in the range of about 400 to 650° F. to produce a lubricating oil product of improved oxidation stability.

Lubricating oils are conventionally refined by methods including the steps of distillation, solvent refining, acid treating, clay contacting and solvent dewaxing. When residual type lubricating oils are processed, an additional step of deasphalting is usually required. In the processing steps listed above, distillation is employed as a means of separating the crude oil into fractions of suitable viscosity. Solvent refining, with, for example, furfural, sulfur dioxide or phenol, is ordinarily used as a means of removing cyclic compounds and thereby improving viscosity index of the treated oil. Viscosity index is an important characteristic of a lubricating oil indicative of the resistance of the oil to change in viscosity with change in temperature. Acid treating is employed to improve the color, stability and resistance to oxidation of lubricating oils. Clay contacting is used to further improve the color and to neutralize the oil after acid treating. Solvent dewaxing is used to lower the pour point of the oil, and deasphalting is employed to remove asphaltic bodies.

All of the characteristics noted above, that is, viscosity range, viscosity index, color, stability, resistance to oxidation, pour point and freedom from asphaltic bodies are important. The requirements of various lubricating applications differ greatly so that different oil characteristics may be limiting when manufacturing lubricating oils for different applications. Therefore to obtain a satisfactory lubricating oil, a balance of various characteristics is necessary depending upon the requirements of the intended application.

Mild hydrogenation of lubricating oil stocks is known in the prior art as a means of refining an oil for the improvement of viscosity index. This method of refining lubricating oils has an advantage over solvent refining in that the yields of treated oil are much higher for the mild hydrogenation process. The present process is an improvement over prior processes for refining lubricating oil by mild hydrogenation. We have found that lubricating oil stocks refined by mild hydrogenation for the improvement of viscosity index may be further treated with hydrogen under conditions less severe than ordinarily used for mild hydrogenation to produce a lubricating oil

of unexpectedly good stability and resistance to oxidation.

The first step of the process of this invention, mild hydrogenation, is employed to produce significant improvement in oil quality as measured by mass units, for example, viscosity index and carbon residue. This treatment is accompanied by some splitting which produces light ends, a reduction in viscosity and consumption of varying amounts of hydrogen. For simplicity this step will be referred to hereafter as hydrorefining.

The second stage hydrogen treatment in contrast results in little or no change in viscosity, negligible consumption of hydrogen and little reduction in the flash point. This step will be referred to hereafter as hydrofinishing.

The hydrorefining step may be carried out employing a wide range of operating conditions and catalysts. For example, temperatures of about 600 to 800° F., pressures of about 500 to 10,000 p. s. i. g. and space velocities from about 0.1 to 5.0 may be used. In a preferred embodiment of this invention, however, operating conditions comprising temperatures of 625 to 725° F., pressures of about 3,000 p. s. i. g. and space velocities of about 1.0 to 2.0 volumes of oil per hour per volume of catalyst are employed. Hydrogenation catalysts comprising metals of the 6th and 8th groups of the periodic table, their oxides, sulfides, or mixtures thereof may be employed in the hydrorefining step of this invention. We have found that a nickel sulfide-tungsten sulfide catalyst having a composition represented by the empirical formula

$$1NiS \cdot 0.75WS_2$$

and cobalt molybdate are particularly suitable for the process of this invention.

The hydrofinishing step of this process is conducted under much milder conditions than employed in the hydrorefining step. Temperature and pressure are relatively low for example, about 400 to 650° F. and 750 to 5,000 p. s. i. g., respectively. Hydrogenation catalysts suitable for use in the hydrorefining step are also satisfactory for the hydrofinishing process. However, we prefer Raney nickel, platinized charcoal, cobalt molybdate and composite catalysts comprising alumina, platinum and combined halogen for the hydrofinishing step of our process.

Other lubricating oil refining processes may be employed with the two stage process of this invention either before the hydrorefining step, between the two steps, or after the hydrofinishing step. However, in any series of processing steps, we prefer the hydrorefining step to precede the hydrofinishing step. It is also desirable in some cases to fractionate the hydrorefined intermediate product and to hydrofinish only selected fractions thereof.

An advantage of this process is that it produces lubricating oils of high viscosity index and unexpectedly good stability and resistance to oxidation.

Another advantage of this process is that it accomplishes product quality improvement comparable with that obtained with the three steps of solvent refining, acid treating, and clay contacting employed in conventional refining of lubricating oil stocks.

Another advantage of the process of this invention is that it produces high yields of lubricating oils and avoids the yield losses inherent in solvent refining and acid treating.

The accompanying drawing diagrammatically illustrates the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or material described.

A lubricating oil stock from external storage 1 is charged through line 2 by pump 3. Hydrogen-rich gas from line 4 is combined with the lubricating oil stock and

the combined feed is heated in preheater **5**. The preheater effluent is passed through line **6** to reactor **7**. Reactor **7** is operated under hydrorefining conditions and contains a hydrogenation catalyst, for example, nickel sulfide-tungsten sulfide. Effluent from reactor **7** is cooled in heat exchanger **8** and discharged into gas separator **9**. Hydrogen-rich gas from separator **9** is withdrawn through line **10** and is recycled by compressor **11** through hydrogen recycle line **4**. Make-up hydrogen from an external source, not shown, is supplied to the unit through line **12** which discharges into recycle line **4**. A stream of recycle gas may be withdrawn through purge gas line **13** in order to maintain the hydrogen concentration of the recycle gas.

Liquid from gas separator **9** is withdrawn through line **14** and directed to fractionator **15**. Fractionator **15** is employed to separate the small amount of gas and distillate which are produced as a result of splitting reactions encountered in hydrorefining. Gas is withdrawn through line **16** and distillate through line **17** for utilization of these streams in other facilities, not shown. The bottoms product from fractionator **15** is a hydrorefined lubricating oil stock of improved viscosity index. This intermediate product is withdrawn through line **18** and is combined with recycle hydrogen from line **19** and passed to preheater **20**. Effluent from preheater **20** is transferred through line **21** to reactor **22**. Reactor **22** is operated under hydrofinishing conditions and contains a hydrogenation catalyst, for example, cobalt molybdate. Product from reactor **22** is withdrawn through line **23**, cooler **24** and is discharged into gas separator **25**. Hydrogen-rich gas from gas separator **25** is withdrawn through line **26** and is recycled by means of compressor **27** and hydrogen recycle line **19**. Make-up hydrogen from an external source, not shown may be added to recycle line **19** through line **20**. The purity of the hydrogen recycle stream may be controlled by withdrawing purge gas through line **28** as required. The liquid in gas separator **25** is hydrofinished lubricating oil. This oil is withdrawn through line **29** and is discharged to other facilities, not shown, for blending and compounding to produce desired lubricating oil products.

The invention is further illustrated in the following examples:

EXAMPLE I

Tests on an 18.8° API gravity lubricating oil stock are shown in Table I, column A and show poor color, viscosity index and unsatisfactory stability. This oil is conventionally refined for viscosity index and color improvement by solvent refining, acid treating and clay percolation to produce a lubricating oil stock with the results shown in column B. The solvent refined, acid treated and clay percolated lubricating oil of column B is then further refined under hydrofinishing conditions by contacting with hydrogen at 500° F., 3,000 p. s. i. g. pressure in the presence of a catalyst comprising 0.5 weight percent platinum, 0.8 weight percent aluminum fluoride, and 98.7 weight percent alumina. Tests on the hydrofinished product are shown in column C of Table I.

The ASTM oxidation test D943–53T and the heat test in this and all other examples are run on inhibited samples containing 0.300 weight percent of methyl ditertiarybutyl phenol, .015 weight percent alkenyl succinic acid, .0025 weight percent mono- and di-lauryl acid ortho phosphate and 0.0005 weight percent phenol. The heat test reported is a stability test in which an oil sample, copper wire and iron wire, are placed in a beaker and heated in an oven at 225° F. for 100 hours. The appearance of the oil at the end of this test is reported as the heat test.

Column B of Table I shows the yield losses encountered in the conventional refining of lubricating oil stocks by solvent refining and acid treating. Column C shows that the hydrofinishing step is accomplished without further yield loss. Comparing columns B and C, the increase from 1320 to 1900 hours in the ASTM oxidation test shows that the hydrofinishing step results in an improvement in the stability of the treated oil.

Table I

	A Lubricating Oil Charge Stock	B Conventionally Refined Lubricating Oil Stock	C Hydrofinished, Conventionally Refined Lubricating Oil Stock	D Hydrorefined Lubricating Oil Stock	E Conventionally Finished Hydrorefined Lubricating Oil Stock	F Hydrofinished Hydrorefined Lubricating Oil Stock
Yield, Volume Percent Charge.		80	80	93.2	91.0	93.2.
Color, ASTM	4 minus	1		1 minus	1 minus	"Water White."
Viscosity Index	minus 3	25.5	22.5	32.5	28	35.5.
ASTM Oxidation Test, D943-53T, Hours to 2 Neut. No.[1]	Unsatisfactory	1,320	1,900	650	825	2,875.
Heat Test [1]	do	Darker				Unchanged.

[1] Inhibited oil.

The lubricating oil stock shown in column A of Table I is also refined by treating under hydrorefining conditions to produce a lubricating oil stock with the results shown in column D of Table I. In this example, the hydrorefining conditions employed comprise contacting the oil with hydrogen at a temperature of 690° F., a pressure of 3,000 p. s. i. g., a volumetric space velocity of 1.97 volumes of oil per hour per volume of catalyst, in the presence of a nickel sulfide-tungsten sulfide catalyst having a composition represented by the empirical formula $1NiS \cdot 0.75WS_2$. The hydrorefined lubricating oil stock shown in column D is finished by the conventional refining steps of acid treating, water washing, neutralizing, steaming, brightening by air blowing, and finally clay percolation to produce the finished lubricating oil with the results shown in column E of Table I.

Comparison of column B with column D shows that an oil of higher viscosity index is obtained by hydrorefining than by conventional refining for the improvement of this characteristic. However, it will be noted that poorer resistance to oxidation is exhibited by conventionally finished hydrorefined oil, column E, as compared with the processing sequence of conventional refining followed by hydrofinishing, column C.

In a test employing the process of this invention, that is, hydrorefining followed by hydrofinishing, the hydrorefined lubricating oil stock shown in column D is hydrofinished by contacting with hydrogen at 500° F., 3,000 p. s. i. g. pressure in the presence of a catalyst comprising 0.5 weight percent platinum, 98.7 weight percent alumina and 0.8 weight percent aluminum fluoride. Tests on the hydrofinished, hydrorefined lubricating oil are shown in column F. Column F shows that an oil of unexpectedly good stability and resistance to oxidation is produced by hydrorefining following by hydrofinishing, and that the oil produced is superior to the conventionally refined and

hydrofinished oil shown in column C or the hydrorefined and conventionally finished oil shown in column E. It will also be noted that a higher yield of finished oil is obtained by hydrorefining followed by hydrofinishing.

EXAMPLE II

The lubricating oil charge stock employed in Example I is hydrorefined using a nickel sulfide-tungsten sulfide catalyst and hydrofinished using a catalyst comprising platinum, aluminum fluoride, and alumina under the conditions and with the results shown in Table II.

Table II

Hydrorefining:			
Reactor Temp., ° F.	699	621	650.
Recycle Hydrogen Ratio, cu. ft./bbl.	10,000	10,000	10,000.
Pressure, p. s. i. g.	3,000	3,000	3,000.
Liquid, v./v./hr.	1.6	1.0	1.0.
Yield, Vol. Percent, Charge	90.0	91.8	86.7.
Hydrorefined Product:			
Viscosity Index	42.0	17.5	36.5.
ASTM Oxidation Test, D943-53T, Hours to 2 Neut. No.[1]	1,535		
Heat Test [1]	Darker		
Hydrofinishing Conditions:			
Reactor Temp., ° F.	500	500	500.
Pressure, p. s. i. g.	3,000	3,000	3,000.
Yield, Vol. Percent, Charge	90.0	91.8	86.7.
Color, ASTM	Water White.	Water White.	Water White.
Viscosity Index	43.0	24.0	38.
ASTM Oxidation Test, D943-53T, Hours to 2 Neut. No.[1]	>3,000	>2,000	>2,850.
Heat Test [1]	Unchanged.	Unchanged.	Unchanged.

[1] Inhibited oil.

Table II shows that an oil of exceptional oxidation resistance and heat stability is produced by the process of this invention, that is, hydrorefining followed by hydrofinishing.

EXAMPLE III

In another test, a lubricating oil stock is hydrorefined using a nickel sulfide-tungsten-sulfide catalyst at a temperature of about 650° F. and at a pressure of 3000 p. s. i. g. A sample of the hydrorefined oil is applied to an aluminum disc which is then heated at a temperature of 644 to 680° F. for thirty minutes. At the end of this heating period the aluminum disc is found to be stained. The hydrorefined lubricating oil is hydrofinished at a temperature of 500° F., a pressure of 3000 p. s. i. g. employing a Raney nickel catalyst. A sample of the hydrorefined and hydrofinished lubricating oil is applied to an aluminum disc and heated at 644 to 680° F. for thirty minutes. The aluminum disc is found to be free of stain. This test indicates that the hydrofinishing step has improved the stability of the oil so that aluminum is not stained in contact with the oil at high temperature.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method of processing a hydrocarbon lubricating oil stock to enhance the quality thereof which comprises subjecting said lubricating oil stock in admixture with hydrogen and in the presence of a hydrogenation catalyst to conditions of mild hydrogenation such that said lubricating oil stock is converted to an intermediate product of improved viscosity index, and subjecting said intermediate product in admixture with hydrogen and in the presence of a hydrogenation catalyst to a temperature of about 400 to 650° F., a pressure of about 750 to 5000 p. s. i. g. and for a time such that said intermediate product is converted to a lubricating oil of improved oxidation stability.

2. The method of claim 1 in which the catalyst employed in processing the intermediate product is selected from the group consisting of nickel and platinum.

3. A method of processing a hydrocarbon lubricating oil stock to enhance the quality thereof which comprises subjecting said lubricating oil stock in admixture with hydrogen and in the presence of a catalyst comprising nickel sulfide and tungsten sulfide to a temperature of 625 to 725° F., a pressure of about 3,000 p. s. i. g. and a space velocity of about 1.0 to 2.0 volumes of oil per hour per volume of catalyst to convert said lubricating oil stock to an intermediate product of improved viscosity index, and subjecting said intermediate product in admixture with hydrogen and in the presence of a catalyst comprising platinum, alumina, and a combined halogen to a temperature of about 400 to 650° F., and a pressure of about 1000 to 5000 p. s. i. g. to convert said intermediate product to a lubricating oil of improved oxidation stability.

4. The method of processing a hydrocarbon lubricating oil stock to enhance the quality thereof which comprises subjecting said lubricating oil stock in admixture with hydrogen and in the presence of a hydrogenation catalyst comprising cobalt molybdate to conditions of mild hydrogenation, such that said lubricating oil stock is converted to an intermediate product of improved viscosity index and subjecting at least a portion of said intermediate product in admixture with hydrogen and in the presence of a hydrogenation catalyst to a temperature of between 400 and 650° F., a pressure of between 750 and 5,000 p. s. i. g. and for a time such that said intermediate product is converted to a lubricating oil of improved oxidation stability.

5. The method of processing a hydrocarbon lubricating oil stock to enhance the quality thereof which comprises subjecting said lubricating oil stock in admixture with hydrogen and in the presence of a hydrogenation catalyst comprising nickel sulfide and tungsten sulfide to conditions of mild hydrogenation, such that said lubricating oil stock is converted to an intermediate product of improved viscosity index and subjecting at least a portion of said intermediate product in admixture with hydrogen and in the presence of a hydrogenation catalyst to a temperature of 400 to 650° F., a pressure of between 750 and 5,000 p. s. i. g. and for a time such that said intermediate product is converted to a lubricating oil of improved oxidation stability.

6. A method of processing a hydrocarbon lubricating oil stock to enhance the quality thereof which comprises subjecting said lubricating oil stock in admixture with hydrogen and in the presence of a catalyst comprising cobalt molybdate to conditions of mild hydrogenation, such that said lubricating oil stock is converted to an intermediate product of improved viscosity index and subjecting at least a portion of said intermediate product in admixture with hydrogen and in the presence of a catalyst comprising platinum, alumina and a combined halogen to a temperature of 400 to 650° F., and a pressure of about 1,000 to 5,000 p. s. i. g. to convert said intermediate product to a lubricating oil of improved oxidation stability.

7. The method of claim 6 in which the combined halogen is aluminum fluoride.

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