

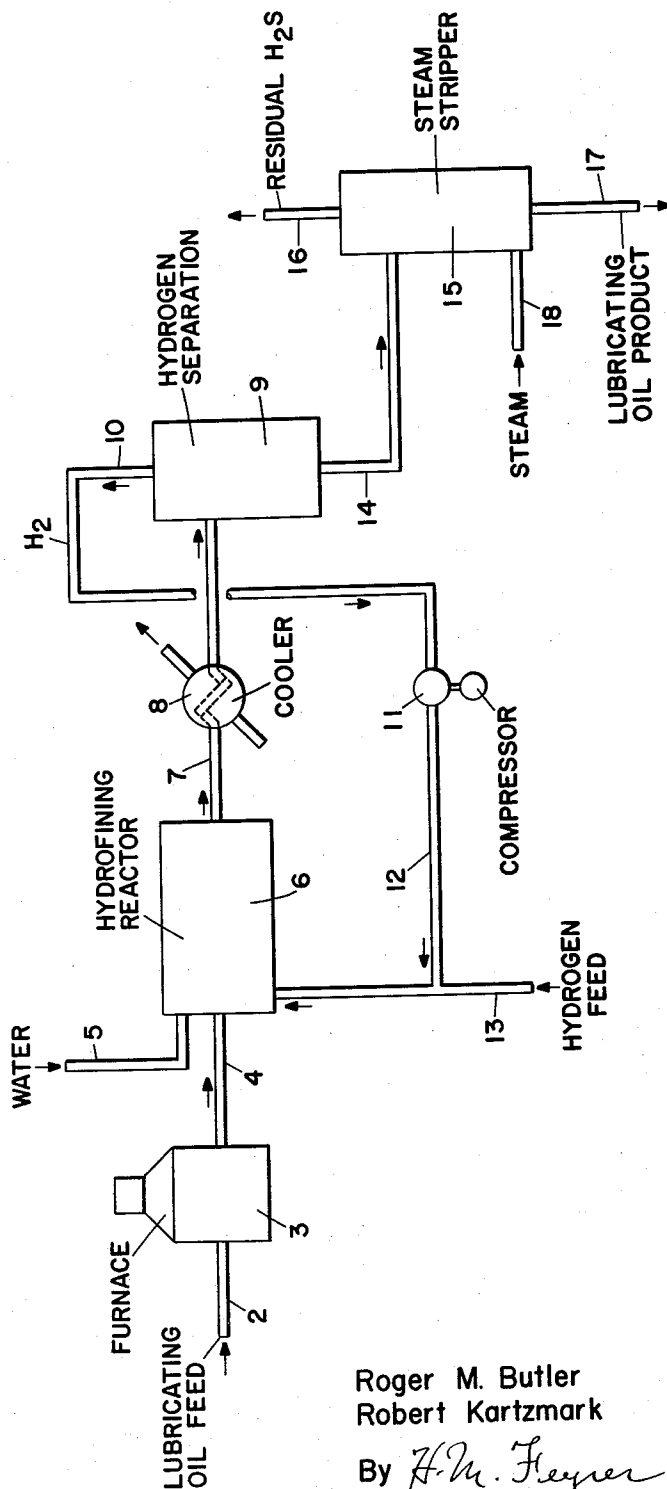
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R. M. BUTLER ET AL

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HYDROFINING LUBRICATING OIL

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Roger M. Butler
Robert Kartzmark

Inventors

By *H. M. Freyer*

Attorney

1

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HYDROFINING LUBRICATING OIL

Roger M. Butler and Robert Kartzmark, Sarnia, Ontario, Canada, assignors to Esso Research and Engineering Company, a corporation of Delaware

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The present invention is concerned with a process for the hydrofining of hydrocarbons boiling in the lubricating oil boiling range. The invention is more particularly concerned with an improved hydrofining process for upgrading and improving the color of petroleum lubricating oils.

Hydrofining is a catalytic hydrogen-treating process to improve the quality of a wide range of petroleum stock. The process is primarily used to improve odor, appearance, color, stability, combustion characteristics and other quality factors unique to a given product. Hydrofining is especially important since it minimizes fluctuation in product quality due to changes in crude source and achieves this with 100% yield of liquid product.

An unique use of hydrofining is its application to lubricating oils. This process has been successfully applied to most all types of lubricating oil and has been found to possess many advantages over previous lube oil treating techniques. Not only is it possible to control lube quality from varying crude sources but equipment is relatively simple, operation is continuous, and there is no major waste disposal problem.

Prior to the present invention, it was generally believed that it was impossible to obtain an improvement in lubricating oil color without hydrofining at the relatively high temperature of about 600° F. By hydrofining at this relatively high temperature, it is impossible to decolorize the lubricating oil without removing an appreciable quantity of sulfur.

Although the removal or reduction of sulfur content from some lubricating oils is required or advantageous, it is equally true that sulfur acts as a natural inhibitor and is therefore beneficial in lubricating oils used under conditions which favor oxidative reactions. Under these conditions, various oxygenated materials are formed which may be acidic in nature and act as further oxidation catalysts or attack alloy bearings, form polymeric materials which plate out on hot engine parts, or act as a binder in holding together sludge which impairs piston ring performance and plugs oil lines and filters.

To improve resistance against oxidative degradation, it is common to add certain inhibitors such as sulfur, phosphorus or zinc compounds to the lubricating oil. These compounds are used in amounts of from 0.1% or less up to 4 wt. percent. A process which would improve color and protect the natural inhibitors would reduce or eliminate the need for these added inhibitors and therefore be a marked improvement in the art.

The object of this invention is to provide the art with an improved hydrofining process for the improvement of color of lubricating oil. It is also the object of this invention to provide a method of improving the color of lubricating oil without the removal of sulfur.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that petroleum lubricating oils can be upgraded, particularly with reference to color improvement, without removing an appreciable quantity of sulfur by hydrofining at low temperatures in the presence of water or steam. The results obtained from this improved hydrofining process are equivalent to those resulting from hydrofining methods using higher temperatures.

The process of the present invention may be more fully understood by referring to the accompanying draw-

2

ing illustrating diagrammatically a flow plan of one embodiment of the same. Referring specifically to the drawing, a dewaxed feed oil consisting of hydrocarbon fractions boiling in the lubricating oil boiling range (about 700° F. to 1100° F., at 760 mm. pressure) is introduced into furnace zone 3 by means of feed line 2. The lubricating oil is heated to a temperature of from 450-550° F. In accordance with the present invention, this heated lubricating oil fraction is withdrawn from zone 3 into feed line 4 and introduced into hydrofining reactor zone 6. Simultaneously with the introduction of lubricating oil feed into zone 6, hydrogen is introduced into zone 6 by means of line 12 and water is introduced into zone 6 by means of line 5. The temperature, pressure, and other operating conditions in zone 6, which will be hereinafter described, are adjusted to secure a hydrofining operation.

The hydrofined product is withdrawn from zone 6 by means of line 7, passed through a cooling zone 8 and then introduced into a hydrogen separation zone 9. Hydrogen is removed overhead from separation zone 9 by means of line 10, recompressed in compressor zone 11 and then preferably recycled to zone 6 via line 12. Fresh hydrogen is added to recycle hydrogen line 12 by means of line 13 and introduced into reactor 6 with the recycle hydrogen.

The hydrofined product, free of hydrogen, is removed from the bottom of zone 9 by means of line 14 and introduced into steam stripper 15. Steam is introduced into stripper 15 by means of line 18 and temperature and pressure are adapted to effect the removal of hydrogen sulfide and any light or low boiling hydrocarbons by means of line 16. A hydrofined lubricating oil product having a satisfactory color is withdrawn from zone 15 by means of line 17.

The conditions in the hydrofining reactor are set forth in tabular form below.

HYDROFINING CONDITIONS

	Preferred	Range
Temperature, ° F.	500	450-550.
Pressure, p.s.i.g.	400	250-1500.
Feed rate, v./hr./v.	1.0	0.2-4.0.
H ₂ feed, s.c.f./b.	500	10-1000.
H ₂ consumption, s.c.f./b.		less than 100.
Water, lbs./b.	2	.25-20.

In the present invention the introduction of either water or steam to the hydrofining reactor is contemplated. This introduction may be accomplished in several different manners. Either water or steam may be added separately as shown in the drawing or either may be added to the lubricating oil before the oil enters the reactor zone. If steam is used it may be added to the hydrogen before the hydrogen enters the reactor zone. When using water in the present invention, it is preferred to use distilled water, although ordinary undistilled water can be employed. If steam is used, it need only be at sufficient pressure to enter the system.

The quantity of water used in the present invention may vary from .25 to 20 pounds of water per barrel of oil, although the preferred amount is about 2 pounds of water per barrel of lubricating oil feed. The exact explanation of why the addition of the water improves the lubricating oil color is not known. It appears that the water has the effect of making the catalyst more active. Accordingly, a very small quantity of water is operable and the addition of large quantities of water do not seem to interfere with the improvement in color.

Stated another way, the quantity of water added may be based on the volume percent of water vapor in the hydrogen atmosphere during hydrofining. The quantity

of water vapor in the hydrogen atmosphere is in the range of about 5 to 50 volume percent. The preferred amount is about 40 volume percent. When utilizing a continuous hydrofining system with a hydrogen gas rate of 100 to 1000 standard cubic feet per barrel of oil, 40 volume percent of water in the hydrogen atmosphere would correspond to a water content of approximately 2 to 20 pounds of water per barrel of lubricating oil feed. The amount of water shown in the examples which follow is approximately 40 volume percent or 2.2 pounds of water per barrel of lubricating oil feed.

The catalyst utilized in the present process may comprise known hydrofining catalysts. While the preferred catalyst of the present invention comprises cobalt molybdate on alumina, or molybdenum sulfide on alumina, the use of a specific hydrofining catalyst is not required or considered essential to the invention. In the preferred cobalt molybdate catalyst, the amount of cobalt oxide is about 1% to 4% and of molybdenum oxide about 12% to 16% based on the weight of the catalyst. The molybdenum sulfide on alumina catalyst may consist of about 15% to 20% molybdenum sulfide based on the weight of the catalyst. The catalyst may be prepared by any known methods.

Regeneration of the catalyst may be required periodically depending largely upon the nature of the feed stock. This regeneration is conveniently carried out at a temperature of about 900° F. with an oxygen containing gas.

The process of the present invention may be more fully understood by the following examples illustrating the same.

Example I

A dewaxed, non-extracted light lubricating oil distillate from Leduc type crude having the following inspections:

Inspection:	Feed
Gravity, ° API	25.2
Viscosity @ 100° F., SUS	122
Tag Robinson Color	1½
Aniline point, ° F	170
Sulfur, wt. percent	0.63

was hydrofined in a 2-liter laboratory autoclave using 163 grams of a catalyst consisting of 18 wt. percent molybdenum sulfide and 82 wt. percent gamma alumina. The pressure utilized was 400 p.s.i.g. and the temperature was 500° F. Each run was for a duration of five hours and 800 cc. of lubricating oil were charged in each run. The results of these runs are as follows:

Run No.	cc. Water added to each charge	Tag Robin-son Color
756	5	10¼
757	5	10½
758	5	10½
759	5	10½
760	0	9¾
761	0	8¾
762	0	9
763	0	5½
764	5	9
765	5	9¼

From the above example, it is apparent that when hydrofining a lubricating oil in accord with the present invention, the color of the lube oil product is materially improved by the addition of water when hydrofining at a temperature of 500° F.

Example II

In this example, the same type feed and hydrofining conditions as were used in Example I were employed. The catalyst used was 131 grams of a catalyst consisting of 14 wt. percent molybdenum oxide, 2.5 wt. percent cobalt oxide and 83.5 wt. percent gamma alumina. 800 cc.

of lubricating oil were again charged in each run. Care was taken to dry the catalyst and oil before Run No. 810.

Run No.	cc. Water added to each charge	Tag Robin-son Color	Wt. percent Sulfur
810	0	9	0.59
811	0	9¼	0.68
812	0	6½	0.62
813	0	4¾	0.68
814	0	6	0.64
815	5	9	0.65
816	5	9	0.62
817	5	10¼	0.58
818	5	10	0.61
819	5	9½	0.62

The data of Example II clearly show that a marked improvement in lubricating oil color is obtained by the use of water in accord with this invention. Also, the data show that even though a color improvement is obtained at a temperature of 500° F. when using water, it is accomplished with little or no removal of sulfur.

Example III

The lubricating oil feed, catalyst, and hydrofining conditions employed in runs 713 and 714 are the same as those used in Example II, with the exception of the hydrofining temperature, which is noted below. Runs 813 to 816 are repeated from Example II.

Run No.	Water, cc.	Hydrofining Temperature °F.	Tag Robin-son Color	Wt. percent Sulfur
713	0	600	11¼	0.36
714	0	600	12¼	0.43
813	0	500	4¾	0.68
814	0	500	6	0.64
815	5	500	9	0.65
816	5	500	9	0.62

The information obtained from runs No. 713 and No. 714 shows that although improvement in color can be obtained by hydrofining at a temperature of 600° F., the use of this relatively high temperature necessarily results in sulfur removal. The information obtained from runs No. 813 and No. 814 shows that hydrofining at 500° F. does not remove sulfur, but little color improvement is obtained. Runs No. 815 and No. 816 were made by hydrofining at a temperature of 500° F. using water in accord with the present invention and color improvement was obtained without sulfur removal.

The advantage of this invention will be apparent to those skilled in the art. Improved products of superior color characteristics can be obtained in a simple, economical process. The process provides a method of improving color without the removal of sulfur from the feed and thereby protects the natural oxidation inhibitors which are removed in normal hydrofining operation. This improvement is of such a simple nature, it can be added to existing hydrofining equipment with practically no cost.

It is understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for upgrading and improving the color of a petroleum lubricating oil which comprises hydrofining a lubricating oil feed boiling in the range of about 700° F. to 1100° F. at 760 mm. pressure at a temperature of about 450° to 550° F. and pressure of from about 250 to 1500 p.s.i.g., in contact with a hydrofining catalyst and in the presence of a hydrogen atmosphere containing from about 5 to 50 volume percent of water vapor thereby improving the color of the oil without removing an appreciable quantity of sulfur.
2. The process defined in claim 1 in which the hy-

5

drogen feed rate is in the range of 10 to 1000 standard cubic feet per barrel of lubricating oil feed.

3. A process for upgrading and improving the color of petroleum lubricating oil which comprises hydrofining a lubricating oil feed boiling in the range of about 700° F. to 1100° F. at 760 mm. pressure at a temperature of about 450° to 550° F. and pressure of from about 250 to 1500 p.s.i.g., in contact with a hydrofining catalyst and in the presence of added water in quantities ranging from about 0.25 to 20 pounds of water per barrel of lubricating oil feed thereby improving the color of the oil without removing an appreciable quantity of sulfur.

4. The process defined in claim 3 in which the hydrogen feed rate is in the range of 10 to 1000 standard cubic feet per barrel of oil lubricating feed.

6

5. The process defined in claim 4 where the water is added to the lubricating oil feed before hydrofining.

6. The process defined in claim 4 in which the water is added to the hydrofining process in the form of steam.

7. The process defined in claim 6 in which the steam is added to the lubricating oil feed before hydrofining.

8. The process defined in claim 6 in which the steam is added to the hydrogen feed before hydrofining.

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