

United States Patent

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[50] Field of Search..... 208/18, 23,
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[54] PROCESS FOR PRODUCING LUBRICATING OILS
WITH GOOD LOW TEMPERATURE HAZING
PROPERTIES
8 Claims, No Drawings
[52] U.S. Cl..... 208/33,
208/18, 208/87, 208/264
[51] Int. Cl..... C10g 23/02

ABSTRACT: A process for producing a finished lubricating oil with good low-temperature hazing properties from lubricating oil base stocks comprised substantially of components boiling above 800°F. and containing more than about 0.75 percent by weight sulfur by subjecting such base stock to hydrofinishing and then dewaxing the hydrofinished base stock.

PROCESS FOR PRODUCING LUBRICATING OILS WITH GOOD LOW TEMPERATURE HAZING PROPERTIES

This application is a continuation of application Ser. No. 754,475 filed Aug. 21, 1968 which is a continuation-in-part of our application Ser. No. 533,456, filed Mar. 11, 1966, both now abandoned.

Our invention relates to an improved process whereby lubricating oils with good low-temperature hazing properties are obtained from certain high sulfur content stocks.

It has previously been suggested in the art to prepare lubricating oils by subjecting crude lubricating oil stocks to a variety of treatments including deasphalting, solvent extraction, comparatively severe hydrogen treatment sometimes called hydrotreating, solvent dewaxing, acid treatment, clay contacting and more recently, mild hydrogen treatment sometimes called hydrofinishing. This last-mentioned mild hydrofinishing operation in many instances is employed in lieu of acid treatment and clay contacting and is employed mainly in the treatment of lubricating oil base stocks, as distinguished from crude lubricating oils, in order to remove odor and color forming materials which are considered to be objectionable in the final lubricating oil product. All of the above-mentioned operations contribute to the production of the final finished lubricating oil from the crude lubricating oil stock by removing undesirable constituents and/or hydrocarbon types from either the crude lubricating oil stock or the intermediate lubricating oil base stock. Generally, the prior art does not suggest any preferred order in which these various operations are to be conducted other than that dictated by economic or engineering expediences such as, for example, employing previously a treating technique which is effective to remove materials deleterious to subsequent treatment steps or which reduces the quantity of material to be treated in a subsequent step, the operation of which is more expensive.

One of the required characteristics or properties of a finished lubricating oil is that it be clear or bright and free from any cloud or haze even after storage at a low temperature for a period of time. In many instances this desirable characteristic or property of a lubricating oil can be obtained when employing any combination of one or more of the above-mentioned treating techniques. A typical example of the prior art operation includes solvent dewaxing an intermediate lubricating oil base stock followed by acid and clay contacting of the dewaxed base stock. In more modern refinery operations this scheme would require solvent dewaxing of a lubricating oil base stock followed by hydrofinishing of the dewaxed material to yield the finished lubricating oil. While this sequence of operations may in some instances be entirely satisfactory to yield a lubricating oil having good hazing properties, it has been found that in many instances it is quite unsatisfactory.

We have discovered that when treating certain types of lubricating oil base stocks the sequence of solvent dewaxing followed by hydrofinishing or hydrofinishing of a substantially wax-free lubricating oil base stock produces a finished lubricating oil having poor hazing properties and that when treating lubricating oil base stocks of this particular type, it is necessary to hydrofinish the base stock and then to subject the hydrofinished stock to a solvent dewaxing treatment.

The particular materials to which the process of our invention is applicable can be described as comparatively high boiling, high sulfur content lubricating oil base stocks. By the term lubricating oil base stock is meant a fraction or group of fractions usually produced at an intermediate point in the production of a lubricating oil which lacks but the final finishing operations, such as, for example, dewaxing, hydrofinishing, acid treatment or clay contacting, before being classed as a finished lubricating oil. Generally, such lubricating oil base stocks can be obtained from crude lubricating oil stocks, i.e., untreated materials boiling in the general range of lubricating oils, by atmospheric and vacuum distillation followed by deasphalting, such as propane deasphalting, solvent extraction, treatment in a Duo-Sol process, comparatively severe hydrogen treatment, i.e., hydrotreatment, etc., or any com-

bination of one or more of these treatments or none, depending upon the type of crude lubricating oil stock being considered and the type of finished lubricating oil desired as product.

The lubricating oil base stocks treated in accordance with our invention must also have a sulfur content of at least about 0.75 percent by weight. Usually these materials will be found to have a sulfur content of at least about 1.0 percent by weight.

Generally, the lubricating oil base stocks treated in accordance with our invention are comprised substantially of components boiling above about 800° F. and contain at least about 0.75 percent by weight sulfur. Lubricating oil base stocks having a 10 percent point of about 750° to about 775° F. or above are quite suitable. Lubricating oil base stocks having a 10 percent point of at least about 800° F. can be treated in accordance with the process of our invention with particularly advantageous results. These comparatively high-boiling lubricating oil base stocks will generally be found to have an average molecular weight above about 375 and usually above about 400.

The process of our invention is suitable for treatment as an entity of the entire spectrum of lubricating oil base stocks meeting the above description as well as treatment of individual lubricating oil base stock fractions. These individual fractions generally have a range of from about 90° to about 120° F. between their 10 percent and 90 percent points and are usually considered as having a nominal spread of about 100° F. between their 10 percent and 90 percent points. The process of our invention can also treat the lubricating oil base stocks described above either alone or in admixture with other lubricating oil base stocks.

It is believed that the higher boiling lubricating oil base stocks which also have a comparatively high sulfur content initially, i.e., before hydrofinishing, comprise certain larger sulfur containing molecules which upon hydrofinishing and the removal of sulfur therefrom become insoluble in or at least have a lower solubility in the remaining hydrofinished components, thereby creating the problem of hazing, particularly at low temperatures. This theory appears to be borne out by the fact that high sulfur content lube oil base stocks having a comparatively low-boiling range do not develop hazing tendencies upon hydrofinishing nor do comparatively high-boiling lube oil base stocks having a sufficiently low sulfur content.

Of the three major types of hydrogen-treating operations generally associated with the lubricating oil field, i.e., hydrocracking, hydrotreating and hydrofinishing, the hydrogen-treating operation employed in our invention is termed hydrofinishing. Generally, hydrocracking is an extremely severe operation wherein comparatively high-boiling hydrocarbons, for example, stocks containing components boiling above the general lubricating oil range or above 1,000° F., are treated so as to effect somewhat random severing of carbon-to-carbon bonds, thereby resulting in a substantial overall reduction in molecular weight and boiling point of the treated material while concomitantly effecting a substantial increase in API gravity in order to produce large quantities of materials boiling below about 600° F. and a somewhat lesser quantity of materials boiling in the lubricating oil range from about 600° to about 1,000° or 1,100° F. In hydrocracking, at times, the production of lubricating oils can be merely incidental to the production of gasoline and furnace oil.

The next most severe hydrogen-treating operation is termed hydrotreating and is generally considered to be intermediate hydrocracking and hydrofinishing in its severity. Thus, hydrotreating effects a significant amount of molecular rearrangement, while not effecting the excessive and random breakdown of molecules effected in hydrocracking. Generally, hydrotreating is primarily employed for the saturation of aromatics but is still sufficiently severe so as to effect, at times, a significant reduction in boiling range of the treated material.

Finally, the least severe hydrogen-treating operation, termed hydrofinishing, operates primarily for the removal of minor quantities of contaminants and color-forming bodies found in lubricating oils or lubricating oil base stocks. Thus, hydrofinishing is effective, for example, to reduce the sulfur content of the materials treated along with other contaminants and color forming bodies but does not result in any significant increase in API gravity or any significant reduction in the boiling range of the treated material. Usually any increase in API gravity effected by hydrofinishing will be less than about 5° API. Furthermore, at times it would even appear that the boiling range of the treated material has even been increased somewhat as indicated by a slight increase in the ASTM 10 percent and even 30 percent points.

In the hydrofinishing operation of our process the operating conditions employed can include a temperature from about 400° to about 850° F. and preferably from about 600° to about 750° F., a pressure in the range from about 800 to about 3,000 p.s.i.g. and preferably from about 1,000 to about 2,000 p.s.i.g., a liquid hourly space velocity in the range from about 0.1 to about 10.0 and preferably from about 1.0 to about 4.0 volumes of lubricating oil base stock per volume of catalyst per hour and a hydrogen circulation rate in the range from about 1,000 to about 20,000 s.c.f./bbl. and preferably from about 2,000 to about 7,000 s.c.f./bbl. The catalyst employed in the hydrofinishing operation in accordance with our invention can be any of the hydrogenating catalysts well-known in the art such as, for example, group VI and group VIII metals, their oxides and sulfides, or mixtures thereof, either alone or supported on a suitable carrier. These suitable carriers generally include materials which have extremely low-cracking activity, if any, and can be described as having a cracking activity significantly below 35 on the Kellogg cracking activity scale. Usually such materials will have a Kellogg cracking activity of less than about 25 and preferably less than about 20. Examples of catalysts which we have found to be advantageous for use in our invention are combinations of nickel, cobalt and molybdenum on an alumina support such as, for example, a catalyst of the type described in U.S. Pat. No. 2,880,171, and a combination of nickel and tungsten on alumina. Catalysts such as these can also contain a small quantity of silica such as, for example, less than about 5 percent by weight or even lower.

In the solvent-dewaxing treatment of our invention we have found that any of the well-known solvents usually employed by the art to effect dewaxing are quite satisfactory. Generally, we prefer to employ a blend of methylethylketone and toluene in about a 50—50 mixture as the solvent. The particular temperature employed in any solvent dewaxing treatment in accordance with our invention is that which would normally be required to provide a product having a desired pour point, usually about +10° F. or lower.

In order to illustrate our invention in greater detail, reference is made to the following examples.

EXAMPLE I

In this example a 52 percent Kuwait reduced crude having the inspections shown in table I below was subjected to vacuum distillation to provide two comparable medium distil-

late fractions, the inspections for which are also shown in table I.

TABLE I

	Reduced Crude	Medium Distillate Fraction A/Fraction B	
Gravity, °API	16.0	20.4	21.1
Viscosity, SUS at			
100° F.	—	530	489
210° F.	160	60.8	58.5
Pour Point, °F.	—	+95	+100
Sulfur, % by Wt.	811	2.9	2.7
Carbon Residue, % by Wt.	8.0	1.3	0.2
Distillation, Vacuum, °F.			
5%	—	801	793
10	708	811	809
30	805	848	835
50	924	865	862
70	—	897	882
90	—	934	924
95	—	967	940

Each of the Fractions A and B were then subjected to furfural extraction at substantially the same conditions including a solvent to oil volume ratio in the range from about 1.5 to about 2.0 and a temperature at the tower tops of 220° F. Inspection data for the raffinates from the solvent extraction of the two fractions are shown in table II below.

TABLE II

	Fraction A Raffinate	Fraction B Raffinate
Gravity, °API	29.0	28.8
Viscosity, SUS at		
100° F.	260	278
210° F.	51.6	52.3
Sulfur, % by Wt.	1.39	1.2

The solvent extracted fraction A was then subjected to a solvent dewaxing treatment employing a 50—50 mixture of methylethylketone and toluene. The primary and secondary solvent dilution ratios employed were 1.15 and 1.85, respectively, and the filtration temperature employed was -14° F. The yield of dewaxed oil was 80.9 percent by volume. This dewaxed oil was then subjected to hydrofinishing at a temperature, measured at bed outlet, of 685° F., a pressure of 1,755 p.s.i.g. and a liquid hourly space velocity of 2.5.

As opposed to the sequence of treatment described immediately above the solvent extracted fraction B was first subjected to hydrofinishing at a temperature, measured at bed outlet, of 698° F., a pressure of 1,755 p.s.i.g. and a liquid hourly space velocity of 2.5. This hydrofinished oil was then subjected to solvent dewaxing employing a 50—50 blend of methylethylketone and toluene. The operating conditions of the dewaxing treatment included primary and secondary solvent dilution ratios of 1.18 and 1.58, respectively, and a filtration temperature of -10° F. The inspection data of certain of the intermediate materials and the finished products obtained from fraction A and fraction B are shown in table III below.

TABLE III

	Fraction A		Fraction B	
	Dewaxed raffinate	Dewaxed and hydro- finished raffinate	Hydro- finished raffinate	Hydro- finished and dewaxed raffinate
Gravity, °API	28.5	29.3	31.8	30.2
Viscosity, SUS at ° F.:				
100	368	320	226	317
210	55.3	53.3	49.5	53.7
Viscosity Index	91	95	113	100
Pour point, ° F.	-5	+5	+100	+5
Sulfur, percent by weight	1.25	0.14	0.05	0.05
Carbon residue, percent by weight	0.12	0.06	0.06	0.06
Distillation, vacuum, ° F., percent:				
10	813	831	815	836
30	839	855	840	864
50	873	870	860	884
70	904	901	882	906
90	954	952	919	942

Haze test appearance:		
40° F. for 24 hours	Heavy floc	Bright.
40° F. for 48 hours		Do.
10° F. for 24 hours		Do.
10° F. for 48 hours		Do.

From the inspections shown in table I it will be noted that the distillate fractions A and B are substantially identical and that both fractions have a high sulfur content (2.9 percent and 2.7 percent) as well as being comparatively high boiling stocks, i.e., having a 10 percent point greater than 800° F. (811° and 809° F.). Both of these substantially identical fractions were then subjected to the same type solvent extraction treatment under almost identical conditions but the raffinate from the solvent extraction of fraction A was subjected to dewaxing prior to hydrofinishing, while the raffinate from the

the extraction was then subjected to solvent dewaxing employing a 50—50 blend of methylethylketone and toluene to provide a charge stock to the hydrofinishing unit having inspections also shown in table IV. After hydrofinishing, the product was tested for hazing tendencies and the inspection data for the product together with results of the haze test are also shown in table IV. For purposes of comparison, certain of the inspections of the intermediate material as well as the final product obtained in the treatment of fraction A as described in example I are also shown in table IV.

TABLE IV

	Charge	Raffinate	Dewaxed raffinate	Dewaxed and hydrofinished raffinate	Dewaxed raffinate, Fraction A, Example I	Dewaxed and hydrofinished raffinate, Fraction A, Example I
Gravity, °API	26.3	31.4	30.0	30.2	26.5	29.3
Viscosity, SUS at, °F.:						
100	292		238	237	368	320
150	95.0	78.5				
210	50.8	47.6	49.0	48.9	55.3	53.3
Viscosity index	87	112	101	100	91	95
Pour point, °F.	+85	+95	+5	+10	-5	+5
Color, D 1500	(1)	L 2.0	L 1.5	L 0.5	L 7.0	L 1.0
Sulfur, percent by weight	0.26	0.07		0.03	1.25	0.14
Distillation, vacuum, °F., percent:						
10	795	769	771	810	813	831
30	810	800	800	828	839	855
50	828	818	816	845	873	870
90	886	868	877	884	954	952
Haze test—appearance:				Bright		(2)
40° F. for 24 hours				Do.		(2)
40° F. for 48 hours						

¹ L 5.0 dil.

² Heavy floc.

solvent extraction of fraction B was subjected to hydrofinishing and the hydrofinished material was then dewaxed. A comparison of the product inspections shown in table III clearly demonstrates that, although the products obtained from fractions A and B would appear to be almost identical on the basis of inspections such as gravity, viscosity, pour point, carbon residue and distillation, quite unexpectedly the product obtained from fraction B in accordance with the process of our invention satisfactorily passed the haze tests at both 40° and 10° F. while the product obtained from fraction A was found to have formed a heavy floc after only 24 hours at 40° F. In light of the results obtained with the product from fraction A in the 40° F. haze test, this fraction was not subjected to the 10° F. haze test.

It will also be noticed from a comparison of the inspection data of the materials charged to the hydrofinishing step with the inspection data of the hydrofinished materials that no substantial production of lower boiling materials is effected in a hydrofinishing operation. Thus, in table III it is shown that the API gravity of the hydrofinished material from fraction A had an API gravity only 2.8° greater than the material charged to the hydrofinishing step. Additionally, it will be noticed that the ASTM 10 percent and 30 percent points of the hydrofinished material from fraction A are somewhat higher than the corresponding distillation points of the charge to the hydrofinishing step. Similarly it will be noticed that the API gravity of the raffinate from fraction B, shown in table II and the charge to the hydrofinishing step, is only 3° less than the API gravity of the hydrofinished raffinate shown in table III.

EXAMPLE II

In this example a blend of medium neutral distillates obtained from an Ordovician crude and a Delta lube mixture, which blend had the inspection data shown in table IV below, was subjected to a furfural extraction and the raffinate from

From the inspection data shown in table IV above for both the charge stock and the solvent extracted raffinate it will be seen that the intermediate lubricating oil base stock obtained from the blended crude lubricating oil stock, although having a 10 percent boiling point of about 770° F., has a sulfur content substantially below 0.75 percent. From an examination of the data shown for the hydrofinished product obtained from this material, it will be seen that no hazing problem exists. From a comparison of the results obtained in this example with the resultant product obtained from fraction A of example I and shown in the last two columns of table IV, it will be noted that when treating a feed stock having a very similar boiling range but having a high sulfur content, i.e., above about 1 percent, a serious hazing problem does exist.

EXAMPLE III

In this example a comparison is made between the finished lubricating oils obtained from a paraffinic-type oil versus the finished lubricating oils obtained from a naphthenic type oil. The paraffinic-type crude employed in this example was obtained from a reduced Kuwait crude of substantially the type described in example I. The Kuwait crude lubricating oil stock was separated into various fractions and such fractions were subjected to solvent extraction, solvent dewaxing and then hydrofinishing in substantially the same manner as described in example I. The material employed to illustrate naphthenic-type oils were crude lubricating oil fractions obtained from Tia Juana crude oil. Inasmuch as the Tia Juana lubricating oil base fractions had such an extremely low pour point and a low wax content they were not subjected to solvent dewaxing but rather were hydrofinished directly. The following table V shows the sulfur content of the various lubricating oil base stock fractions as well as the inspections of various hydrofinished lubricating oils obtained from the fractions of the two crudes mentioned above.

TABLE V

Fraction.....	Lube source					
	Kuwait			Tia Juana		
	Sulfur content of base fraction, percent by weight					
	1.22	1.25	1.25	1.1	1.4	1.5
	Light Neutral	Medium neutral sidestream	Medium neutral	Light Distillate	Medium Distillate	Heavy Distillate
Inspections:						
Gravity, °API.....	32.9	32.6	29.3	27.1	26.3	25.1
Viscosity, survey: section:						
100° F.....	102	108.1	320	101	204	546
210° F.....	39.5	40.0	53.3	38.3	44.3	58.3
Viscosity index.....	97	96	95	36	51	53
Sulfur, percent by weight.....	0.04	0.05	0.14	0.09	0.11	0.09
Pour point, ° F.....	0	+20	+5	-60	-45	-15
Carbon-type composition ASTM D 2140 percent by weight carbon atoms in:						
Aromatic rings.....	3	8	6	13	12	11
Naphthenic rings.....	32	24	29	32	30	29
Paraffinic chains.....	65	68	65	55	58	60
Distillation, vacuum, ° F. corresponding to 760 mm. Hg, percent:						
10.....	721	742	831	686	756	818
30.....						
50.....	749	763	870	693	762	83
70.....						
90.....	823	792	952	708	800	885
Haze test appearance:						
40° F. for 24 hours.....	Bright	Bright	(1)	Bright	Bright	(1)
40° F. for 48 hours.....	do	do	(1)	do	do	(1)
Average molecular weight.....	355	360	460	320	360	445

¹ Heavy floe.

It will be first noticed that the pour points of the Tia Juana lube oil fractions are substantially lower than those of the corresponding Kuwait lube oil fractions. It will also be noticed that a hazing problem exists with the medium neutral Kuwait lube oil fraction while the medium distillate lubricating oil fraction from the Tia Juana crude has no such problem. It will also be noticed that the problem of hazing does not appear to be dependent upon the portion of the crude lubricating oil, that is, light, medium or heavy, from which the fraction was obtained but rather appears to be dependent upon the average molecular weight of the material in the fraction as indicated by the boiling range of the material. Thus, it will be noticed that while the medium neutral Kuwait has a hazing problem, the medium distillate Tia Juana does not, yet the fractions, either from the Kuwait or the Tia Juana crudes, which have an average molecular weight above about 375 to 400 or which have a 10 percent point above about 800° F. do have a severe hazing tendency after hydrofinishing.

To illustrate further that subjecting a lubricating oil fraction obtained from a comparatively high boiling, high sulfur content material which demonstrates hazing tendencies after hydrofinishing to a subsequent solvent dewaxing treatment in accordance with our invention eliminates the hazing problems, the Tia Juana heavy distillate lubricating oil fraction was subjected to dewaxing employing a 50—50 blend of methylethylketone and toluene at a temperature of -5° F. After such solvent dewaxing treatment the Tia Juana heavy distillate lubricating oil showed no hazing at 40° F. after 48 hours.

We claim:

1. A process for producing a finished lubricating oil with good low-temperature hazing properties from a lubricating oil base stock which has been subjected to solvent extraction for the removal of aromatics therefrom and which is comprised

substantially of components boiling above about 800° F., having a 10 percent boiling point of at least 750° F. and containing more than about 0.75 percent by weight sulfur which comprises subjecting such lubricating oil base stock to hydrofinishing by contacting it with hydrogen in the presence of a catalyst comprising a hydrogenating component selected from the group consisting of (a) nickel, cobalt and molybdenum and (b) nickel and tungsten supported on a carrier having a cracking activity on the Kellogg scale of less than about 35 under hydrofinishing conditions of space velocity, a pressure from about 1,000 to about 2,000 p.s.i.g. and a temperature from about 600° to about 750° F. thereby effecting removal of color-forming bodies from the base stock without any significant increase in API gravity or significant reduction in the boiling range and then subjecting the hydrofinished base stock to a solvent dewaxing treatment

2. The process of claim 1 wherein the lubricating oil base stock has a 10 percent boiling point of at least 800° F.

3. The process of claim 1 wherein the lubricating oil base stock is a fraction having a range from about 90° to about 120° F. between its 10 percent boiling point and its 90 percent boiling point.

4. The process of claim 2 wherein the lubricating oil base stock is a fraction having a range from about 90° to about 120° F. between its 10 percent boiling point and its 90 percent boiling point.

5. The process of claim 1 wherein the lubricating oil base stock contains more than about 1.0 percent by weight sulfur.

6. The process of claim 1 wherein the lubricating oil base stock is obtained from a paraffinic-type crude oil.

7. The process of claim 1 wherein the lubricating oil base stock is obtained from a naphthenic type crude oil.

8. The process of claim 1 wherein the catalyst carrier has a cracking activity on the Kellogg scale of less than about 25.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,617,475 Dated November 2, 1971

Inventor(s) R. G. Goldthwait, J. R. Murphy, W. C. Offutt and
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It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Column 4, Table I, Line 14, before the first column,
"811" should be deleted.

Column 8, Table V, under 760 mm.Hg, percent, across from 50,
"83" should be --835--.

Signed and sealed this 18th day of April 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents