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PROCESS FOR PREPARING IMPROVED LUBRICATING OILS BY ACID TREATING THEN HYDROFINISHING THE LUBRICATING OILS

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1 Claim. (Cl. 208—264)

Our invention relates to a method for the manufacture of lubricating oil fractions of improved properties from naphthenic base crude oils.

Normal processing techniques employed in the production of lubricating oil fractions from naphthenic base crude oils involve vacuum distillation to produce a raw lube distillate fraction, acid treatment of that fraction to remove undesirable aromatic acid-type sludge-forming constituents and an earth treatment. By this means there have been produced lubricating oils which are useful in formulating cutting oils, in railroad diesel engine lubricants, and for other purposes.

It is desirable that high quality lubricating oils have good color and color stability and at the same time be highly stable towards oxidation. In accordance with our invention, we have devised a process whereby lubricating oil fractions of improved properties from the standpoints of odor, color stability and resistance to oxidation can be manufactured from naphthenic base crude oils. At the same time, the lubricating oils made when our process is carried out are not impaired from the standpoint of solubility characteristics, that is, the ability of the oils to dissolve additives and dissolve such sludge-forming materials as are produced when the oils are placed in service.

Our process is one which involves subjecting to a mild hydrogenation treatment a lubricating oil fraction which has been manufactured by distilling a naphthenic base crude oil to produce a distillate fraction, acid treating that distillate fraction in a particular way, neutralizing the acid treated fraction, washing it with water until free of sulfonates and then subjecting the oil to the mild hydrogenation treatment. Thus, the first step in our process involves subjecting naphthenic base crude oil, preferably a light reduced crude oil, to steam or vacuum distillation to remove low boiling components and asphalt bottoms and at the same time produce one or more raw lube distillate fractions having a SSU viscosity at 100° F. of from 50 to 6000 seconds. The lighter grades of distillate, after further refining as described below, are useful as base oils for cutting oils, rubber processing oils and other industry lubricants, and the heavier grades, after further refining as described below, are useful as base oils for railroad diesel engine lubricants.

The second step in our process involves treating the raw lube fraction with sulfuric acid which is of 93 to 98 percent by weight strength. Where the raw lube fraction has a SSU viscosity at 100° F. of 50 seconds, the amount of sulfuric acid employed is within the range from 5 to 10 pounds of acid per barrel of oil. On the

other hand, where the raw lube fraction has a SSU viscosity at 100° F. of 6000 seconds, the amount of sulfuric acid is within the range from 45 to 65 pounds of acid per barrel of raw lube distillate fraction. In acid treating fractions which have a SSU viscosity at 100° F. greater than 50 but less than 6000 seconds, the amounts of acid which can be used in the acid treating are intermediate to the amounts which can be used for treating the 50 SSU/100° F. oil and 6000 SSU/100° F. oil. After the acid treatment has been carried out, the sludge is removed from the oil and the oil is then neutralized with a conventional neutralizing agent, such as aqueous soda ash or aqueous caustic soda. After the aqueous solution of the neutralizing agent has been permitted to settle out, the oil is then washed with water until free of sulfonates (zero ash). The oil is then ready for the subsequent mild hydrogenation step. Acid treatment is essential to our process because other known processes for refining raw lubricant fractions, such as solvent extraction with furfural or phenol, lack the selectivity required for obtaining maximum oxidation stability together with high solubility characteristics.

The final step of our process consists of a mild hydrogenation employing a cobalt supported on alumina catalyst. Various methods for manufacturing such catalysts have been described in the art, such as in Byrns Patent 2,325,033, and the catalysts generally consist essentially of from about 2 to 5 percent by weight of cobalt oxide and from about 5 to 15 percent by weight of molybdic oxide, the balance being alumina. Suitable catalysts can also be prepared as described in Teter et al. application Serial No. 514,693, filed June 10, 1955. In the hydrogenation operation, a temperature of from 450 to 700° F., a pressure of from 400 to 700 p.s.i.g. and a weight hourly space velocity (weight units of oil per weight unit of catalyst per hour) of from 5 to 20 are used. The oil is hydrogenated while it is in admixture with from 500 to 2000 standard cubic feet of hydrogen per barrel of oil, and the operation is carried out in such manner that the hydrogen consumption amounts to from 5 to 30 standard cubic feet of hydrogen per barrel of oil feed. This mild hydrogenation has a decided economic advantage over the conventional earth finishing processes, and in addition it results in higher yields by eliminating earth adsorption loss and an improved odor, color, color stability, and oxidation stability of the finished oil.

A specific example which illustrates our process is as follows:

A Gulf Coast naphthenic light reduced crude obtained by atmospheric distillation of a whole naphthenic crude over caustic to neutralize organic acids inherent in the crude was charged to a vacuum distillation unit for further separation by distillation. The light reduced crude fraction was 42.6 percent by volume on the whole crude, and upon vacuum distillation several fractions were taken off near the tower top as light lube distillates, a fraction off near the tower middle as a medium lube distillate, a lower side-stream as a heavy lube distillate, with the tower bottoms being heavy reduced crude. The medium lube distillate which is a 17.5% heart cut fraction (on light reduced crude) was the specific starting material for this example. This material had the following physical tests: 19.3° API gravity, 440° F. flash point, 1972 SSU at 100° F. viscosity, 89.5 SSU at 210° F. viscosity, 11

viscosity index, 0° F. pour point, 138.5 specific dispersion, and 6— NPA color.

This medium lube distillate was then subjected to acid treatment to remove undesirable aromatic type sludge forming constituents, thereby effecting improvements in such properties as color and oxidation stability. This acid treatment was performed as a continuous process using 37 pounds of 98 percent sulfuric acid per barrel of charge stock and treatment at a temperature of 140° F. Acid sludge precipitation was aided by electrode sludge precipitators. After the sludge had been removed from the oil, the acid oil was then neutralized with a soda ash solution, heated to 180° F. to allow settling out of the spent soda solution and soaps, and given a hot water spray wash until the oil was free of sulfonates. The water solutions were then withdrawn and the oil given a simple air blowing until it was dry and bright. Overall yield of the acid treating and neutralizing processes was 79.7 volume percent. This treated oil, which was the charge to the finishing process, had the following properties:

Physical properties of charge stock to finishing process

Gravity, ° API	21.3
Flash, ° F.	440
Fire, ° F.	510
Viscosity, SUS at 100° F.	1310
Viscosity, SUS at 210° F.	76.7
Viscosity index	22.3
Pour, ° F.	—5
Color, NPA	3½
Color stability (NPA)[1]	3½ to 4½
Specific dispersion	133.9
Iodine No.	19.6
Sulfur, percent	0.18
Refractive index (N_D^{20})	1.5084

[1] 1 hour at 350° F. in rotating oven.

Normal finishing operations for treating such naphthenic oils consist of earth clay contact or percolation adsorptive techniques. The method of finishing employed in accordance with our invention differs from the normal finishing techniques in that in accordance with our invention a mild hydrogenation procedure is utilized. The improvement produced when our process is employed is shown by the information given below, in which a portion of the oil processed as described was finished by hydrogenation in accordance with our invention and a portion was finished by earth contacting. The hydrofinishing and earth contacting were performed in accordance with the following processing conditions:

	Hydrofinishing	Earth Percolation
Temperature, ° F	650	160.
Pressure, p.s.i.g.	500	
WHSV [1]	5	
Hydrogen to Oil Ratio, s.c.f./b.	1,500	
Catalyst Used	Cobalt Molybdate on Alumina.[2]	
Hydrogen Consumption, s.c.f./b.	12	
Product Yield, Volume Percent	100	99.1.
Earth Used		Floridin Neutral Clay.
Earth Dosage, Bbls./Ton		200.

[1] Weight Hourly Space Velocity (pounds of charge oil per pound of catalyst per hour).

[2] Analyzed approximately 3% cobalt oxide and 10 percent molybdic oxide by weight, the remainder being alumina.

A comparison of the products, after light steam stripping of the hydrofinished oil to remove dissolved light ends and hydrogen sulfide to yield 99.1 percent on charge, is as follows:

	Hydrofinished Product	Earth Finished Product
Gravity, ° API	21.5	21.3.
Flash, ° F	440	445.
Fire, ° F	510	510.
Viscosity, SUS at 210° F	75.7	76.6.
Viscosity, SUS at 100° F	1,260	1,300.
Viscosity Index	23.7	23.0.
Pour, ° F	—5	—5.
Color, NPA	3—	3½—.
Color Stability (NPA)	3— to 4—	3½— to 4½—.
Specific Dispersion	131.6	132.8.
Iodine No	18.3	19.5.
Sulfur, Percent	0.16	0.17.
Refractive Index (N_D^{20})	1.5080	1.5083.
Odor	Very Good	Fair.

The improved oxidation resistance of the hydrofinished oil is shown by the following test results:

Oil Oxidation Tests [1] (After 144 Test Hours):		
Viscosity Rise, SUS at 100° F	310	1,118
Naphtha Insolubles, Percent	1.12	3.10
Acid No	1.70	4.00
Catalyst Weight Loss, mg	0.0	9.6

[1] Oxidation tests carried out at 285° F. with oxygen bubbled through oil at a rate of 5 liters per hour, with a copper-lead catalyst. Initial oil sample is 300 cc. and an oil sample is taken every 48 hours, and 50 cc. of fresh oil added at that time to simulate oil makeup procedures.

We claim:

A method for the production of a lubricating oil fraction of enhanced color, color stability and oxidation stability which includes the steps of distilling a naphthenic base crude oil to produce a raw lube distillate fraction having a SSU viscosity at 100° F. of from 50 to 6000 seconds, acid treating the raw distillate fraction with sulfuric acid having a strength of from 93–98 percent by weight in amount varying from 5 to 10 pounds of acid per barrel of oil for a raw lube distillate fraction having a SSU viscosity at 100° F. of 50 seconds to from 45 to 65 pounds of acid per barrel for a raw lube distillate fraction having a SSU viscosity at 100° F. of 6000 seconds, neutralizing the acid oil and washing the oil with water until free of sulfonates, and then hydrogenating the acid-treated raw lube distillate by passing it into contact with cobalt molybdate supported on alumina catalyst at a temperature of from 450 to 700° F., a pressure of from 400 to 700 p.s.i.g., and a weight hourly space velocity of from 5 to 20 while the distillate is in admixture with from 500 to 2000 standard cubic feet of hydrogen per barrel of oil and is sufficient to improve the color, color stability and oxidation stability of the oil whereby from 5 to 30 standard cubic feet of hydrogen are reacted per barrel of oil.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,944,015 July 5, 1960

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 51 and 52, strike out "and is sufficient to improve the color, color stability and oxidation stability of the oil" insert the same after "oil" and before the period, in line 54, same column 4.

Signed and sealed this 4th day of April 1961.

(SEAL)
Attest: ERNEST W. SWIDER

[redacted]
Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents