

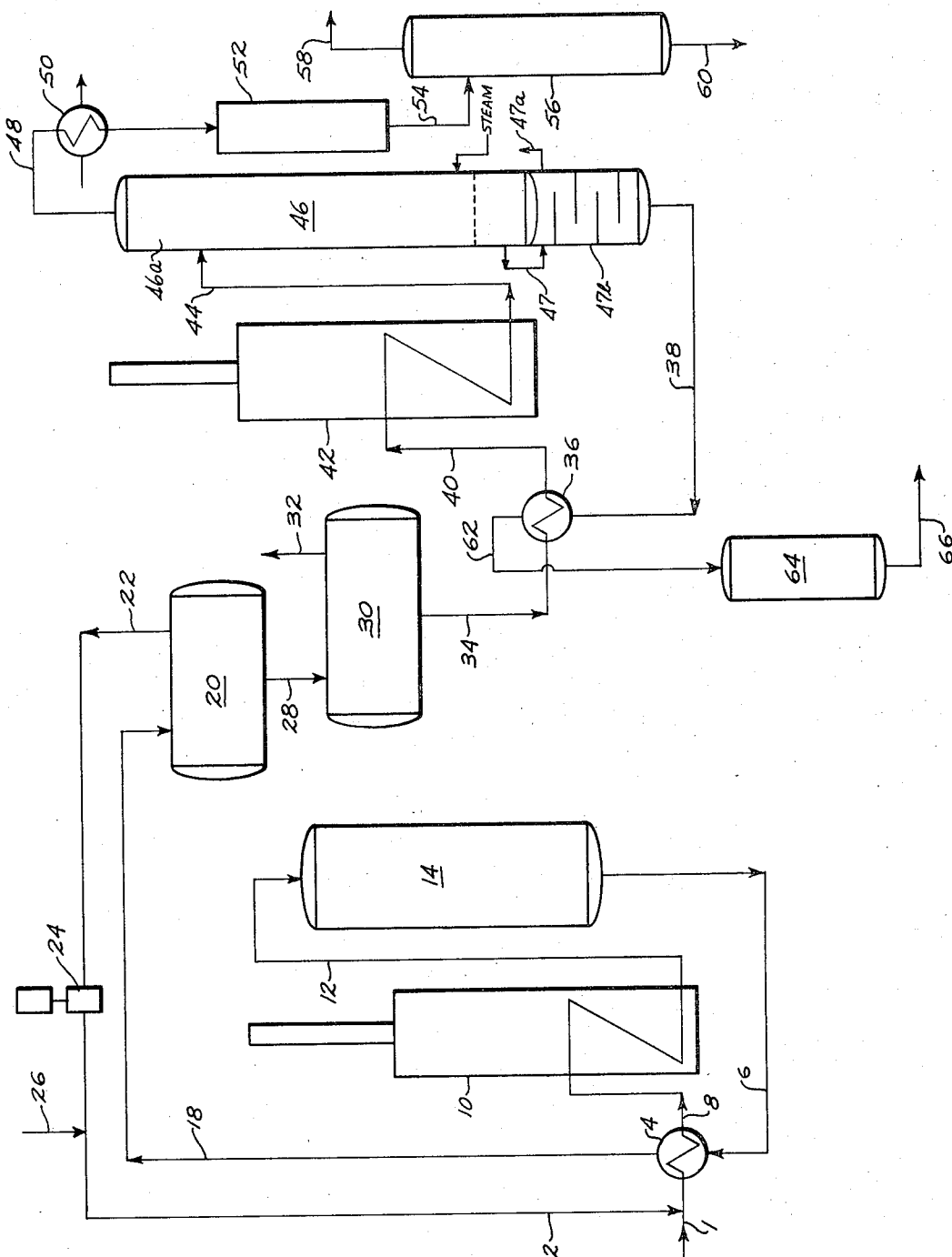
Feb. 20, 1968

R. E. DONALDSON ETAL

3,369,999

CLAY FINISHING OF CATALYTICALLY HYDROFINISHED LUBRICATING OILS

Filed Dec. 8, 1964



INVENTORS  
ROBERT E. DONALDSON,  
ALFRED C. GOERSS &  
JOHN R. STRAUSSER

*Dean Shurtle*

ATTORNEY

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3,369,999

## CLAY FINISHING OF CATALYTICALLY HYDROFINISHED LUBRICATING OILS

Robert E. Donaldson, Penn Hills Township, Allegheny County, and Alfred C. Goerss, O'Hara Township, Allegheny County, Pa., and John R. Strausser, Baytown, Tex., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware  
Filed Dec. 8, 1964, Ser. No. 416,817  
10 Claims. (Cl. 208—264)

This invention relates to a method of producing lubricating oil stocks of improved stability and especially to a method of treating high naphthene content oils having a viscosity in the transformer oil range of mild catalytic hydrogenation followed by clay treating.

Transformer grade oils are highly refined petroleum fractions of low viscosity boiling in the light lubricating oil range. Transformer grade oils of acceptable quality must have a relatively low viscosity, usually not greater than about 85 SUS, to facilitate removal of heat from transformers by convection, a relatively high flash point so as to minimize fire hazard and evaporation losses, and a very low pour point to assure fluidity in cold weather. In view of their use in electrical apparatus, transformer grade oils should have a relatively high dielectric strength. Moreover, such oils should be relatively free from acid, alkali, moisture, dirt and harmful sulfur compounds which could corrode or injure the metal parts. Finally, transformer grade oils of acceptable quality must exhibit a high degree of stability against the formation of deposits formed by deterioration under service conditions. Formation of deposits in transformer oils is undesirable since such deposits tend to collect on the transformer windings, thereby causing overheating, and a decrease in dielectric constant, eventually to the point of complete failure of the oil.

It has been previously proposed to produce lubricating oils of various grades from a wide range of stocks by catalytic hydrogenation of the raw distillate base stocks with a variety of hydrogenating catalysts at relatively high catalyst bed temperatures, so as to insure maximum removal of trace elements such as sulfur, nitrogen and oxygen which are present in the oils as small parts of compounds that impart undesirable characteristics to oils intended for use in transformer service.

It has now been found that when lubricating oil base stocks, particularly high naphthenic content lubricating oil distillates, are catalytically hydrogenated in the presence of the restricted group of hydrogenating catalysts whose use is disclosed herein, exceptionally high yields of oils of remarkable stability and quality can be obtained and that still further benefits in these respects are obtainable by the use in conjunction with such catalysts of exceptionally low catalytic hydrogenation temperatures and/or a clay filtering treatment. Accordingly, the present invention, based on the foregoing discovery, relates to a process for manufacturing lubricating oil base stocks in improved yields and of improved quality. The process of this invention includes the steps of contacting suitable lubricating oil distillates with hydrogen, in the presence of a catalyst comprising at least one hydrogenating component selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent (preferably 4 to 16 percent) by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the

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atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4 and, (b) a combination of about 5 to 40 percent (preferably 10 to 25 percent) by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:0.1 to 5 (preferably 1:0.3 to 4) of said hydrogenating component being composited with an alumina support. Preferred feed stocks for the purposes of this invention are high naphthenic lubricating oil distillates having a viscosity in the transformer oil range and whose properties prior to further refining render the oils unsuitable for use under transformer service conditions, but other lubricating distillates can be used. An example of a preferred base stock is a distillate derived from a coastal crude oil having a viscosity of about 55 SUS at 100° F., and containing about 80 percent naphthenes, about 20 percent aromatics, and that is free from alkanes. However, other transformer oil base stocks having a viscosity at 100° F. of about 50 to 85 SUS, a pour point not greater than about -40° F., and that contain about 12 to 25 percent by volume of aromatic constituents and up to as much as 5 percent alkanes can be used. Specific examples of preferred catalysts are those containing about 2 percent nickel, 1.5 percent cobalt and 10 percent molybdenum supported on alumina, or 6 percent nickel and 19 percent tungsten supported on alumina, these catalysts being preferably employed in sulfided form, although they also may be employed in the oxide form with good results. These catalytic hydrogenating components can be used with a variety of porous bases or supports which may or may not have catalytic activity of their own. Examples of such supports are alumina, bauxite, silica gel, as well as aluminas stabilized with small amounts of silica. Halogens, such as fluorine or chlorine, can be present in the support in combined form in amounts ranging up to 0.2 or 0.5 percent by weight or more. Other suitable supports can also be used. These catalyst components can be prepared in known manner. In accordance with the present process, especially advantageous results are obtained when the hydrogenation treatment is carried out at an average catalyst bed temperature of about 575° to 645° F., especially 600° to 635° F., and under a combination of conditions effective to produce appreciable consumption of hydrogen but no substantial cracking. However, the process can be carried out at higher temperatures, up to 750° F. with acceptable results. It is preferred to employ reaction pressures in the range of 1000 to 1800 p.s.i.g., but other pressures in the range of about 600 to 3000 p.s.i.g. can be used with good results. The oil is preferably contacted with the catalyst in a ratio of about 1.5 to 3 volumes of liquid per hour per volume of catalyst, but other ratios in the range of about 0.5 to 4 liquid volumes per hour per volume of catalyst can be used. The hydrogen-containing gas to oil ratio employed in the hydrogenation reaction is preferably in the range of about 1000 to 3000 s.c.f./bbl., but other ratios can be used, for example, the gas to oil ratio can be as low as 500 s.c.f./bbl. or as great as 4000 s.c.f./bbl. with good results. Very satisfactory results have been obtained with hydrogen of about 80 to 85 percent purity that has been generated in a platinum reforming reaction, but the hydrogen employed in the process need not be of this purity and, in fact, can be as low as 70 percent hydrogen or less, for example, 60 percent.

Following hydrogenation in the manner indicated above, the treated oil is advantageously subjected to a

clay finishing treatment, utilizing clays of a kind normally used in clay finishing, such as fuller's earth, bauxite, Millwhite, Attapulgis or Filtrol, which can be previously activated for filtering and decolorizing purposes by roasting at temperatures of the order of 400° to 900° F. For purposes of the present invention, filtration to a clay life of 100 barrels of oil per ton of clay has been found satisfactory, but filtration to a clay life of as much as 250 barrels or more per ton can also be carried out. Normally, clay treating will be carried out at ambient atmospheric temperatures, but moderately elevated temperatures, e.g., up to the temperature of the oil as it leaves the stripping tower preceding the clay treater, can be used if desired. The present invention includes the foregoing combination of steps as well as novel subcombinations thereof.

The figure is a flow diagram illustrating schematically a suitable apparatus combination for carrying out the process.

The invention will be more easily understood by detailed reference to the drawing. Referring then to the drawing. Referring then to the figure in detail, the raw oil charge is introduced to the unit by way of line 1. As indicated, charge stocks useful for purposes of the present invention include high naphthenic distillate oils having viscosity, pour point and distillation characteristics in the transformer oil range. Preferably, the charge stocks of this invention will contain no alkanes, but a small amount of alkanes, perhaps as much as up to 5 percent alkanes, can be tolerated. In addition, the high naphthene distillate oil charge stocks of this invention can contain up to about 25 percent aromatics, the balance being substantially all naphthenes. A high naphthenic content coupled with substantial freedom from alkanes is important with transformer oil stocks in order that the pour point requirements for transformer oils can be met. The transformer oil grade distillate fractions utilized in the present invention will normally be such as to impart to the oil a flash point (open cup) of not less than 275° F., and such as to produce a viscosity at 100° F. of about 50 to 85 SUS, and a viscosity at 32° F. of not more than 280 SUS. These high naphthene distillates are obtained from crude petroleum oils from the coastal fields of Texas and Louisiana. Examples of other crude oils from which most of the pour test naphthenic distillates used in the present invention can be obtained are Bachaquero, Taparito and Tia Juana crude oils, all of which are produced in western Venezuela. The invention is especially useful in connection with high naphthenic distillates of the character indicated which are relatively high in sulfur and nitrogen content, as in accordance with the present method it has been found possible to produce transformer grade oils from crude oils that hitherto have been considered unsuitable as a source of transformer oil stocks. However, other lubricating oil stocks that are not of transformer grade can be used. For example, steam turbine engine lubricating oil stocks can be used.

The charge stock from line 1 is combined with a hydrogen-rich recycle gas stream from line 2, and after partial preheating in heat exchanger 4 by indirect heat exchange with the product flowing through line 6, the hydrogen-oil mixture passed by way of line 8 to furnace 10 for preheating to the required temperature. The preheat temperature should be somewhat less than the desired average catalyst bed temperature in view of the exothermic nature of the reaction. Thus, when an average catalyst bed temperature of about 625° F. is desired, the preheat temperature of the hydrogen-oil feed, as measured at the reactor inlet, may be in the range of about 590° to 615° F.

The recycle hydrogen stream from line 2 need not be pure hydrogen, and excellent results have been obtained with recycle gas stream containing 85 to 92 percent hydrogen. In fact, operations using as low as 70 percent

hydrogen in the circulating gas have shown no adverse effects on product quality, and even lower hydrogen purities, for example, as low as 60 percent hydrogen, are considered useful in the invention. In order to maintain the desired hydrogen to oil ratio, the circulating gas rate will normally be maintained in the range of about 500 to 4000 s.c.f. (standard cubic feet) per barrel of oil feed, and preferably in the range of about 1000 to 3000 s.c.f. per barrel. Good results have been obtained when using the 85 to 92 percent purity hydrogen referred to above by the use of recirculating gas rates of about 2000 s.c.f./bbl. Somewhat higher circulating gas rates may be desirable with lower hydrogen purities and conversely, lower circulating gas rates can be used with higher hydrogen purities.

The preheated hydrogen-oil mixture passes from preheater 10 through line 12 into reactor 14. Reactor 14 is packed with a stationary bed of a supported catalyst containing an active hydrogenating component that is effective to hydrogenate and desulfurize the charge stock under the reaction conditions utilized, such component being selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent (preferably 4 to 16 percent) by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4 and (b) a combination of about 5 to 40 percent (preferably 10 to 25 percent) by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:0.1 to 5 (preferably 1:0.3 to 4). The catalysts disclosed herein are highly important for purposes of this invention as it has been found that equivalent results are not obtainable with common hydrogenation catalysts. Especially effective catalysts for the purposes of this invention are those comprising molybdenum and at least two members of the iron group metals. Examples of satisfactory supports are alumina, alumina stabilized with a small amount of silica such as 2 to 10 percent silica, bauxite, and the like. In the modification illustrated in FIGURE 1 involving a downflow reactor, the catalyst particles will normally be in the form of a stationary bed or beds of granules, pellets, balls, cylinders or the like. Preferred catalysts for the purposes of this invention comprise alumina composited with nickel, cobalt and molybdenum, but other combinations of iron group metals and molybdenum such as iron, nickel and molybdenum and iron, cobalt and molybdenum, as well as combinations of nickel and tungsten can be used. The catalysts of this invention can be employed in sulfided or unsulfided form. At the same operating conditions, the colors and yields of the hydrofinished products have been found to be about the same when using either unsulfided or sulfided catalysts. However, use of the catalyst in sulfided form is preferred, as the activity of these catalysts as additionally measured by carbon residue and iodine number reductions in the product is superior to that of the unsulfided catalysts. When the use of a sulfided catalyst is desired, the catalyst can be presulfided, prior to contact with the charge stock, by contact with a sulfiding mixture of hydrogen and hydrogen sulfide at a temperature in the range of about 550° to 650° F., at atmospheric pressure, although elevated pressures can be used. The exact proportions of hydrogen and hydrogen sulfide are not critical, and mixtures containing very high proportions of hydrogen sulfide can be used. When the unused hydrogen and hydrogen sulfide utilized in the presulfiding operation is recycled through the catalyst bed, any water formed during presulfiding is preferably removed prior to recycling through the catalyst bed. Alternatively, the catalyst can be sulfided by contact at the hydrogenation process conditions disclosed with a hydrocarbon oil containing at least about 0.2 percent sulfur or more, which hydrocarbon oil may comprise the lubricating distillate feed.

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Specific examples of catalysts whose use is included by the present invention are as follows:

	1	2	3	4	5
Support.....	Alumina	Alumina	Alumina	Alumina	Alumina
Catalyst.....	Yes	Yes	Yes	Yes	Yes
Ni, percent.....	5.27	7.20	00.5	0.98	0.0
Co, percent.....	0	0	10.4	0	0.98
Fe, percent.....	0	0	0	0.93	0.93
Mo, percent.....	0	0	8	8	8
G, percent.....	14.24	22.95	0	0	0

As previously indicated, an important operating variable for purposes of the present invention is the average catalyst bed temperature. For the purposes of this invention, the average catalyst bed temperature can be any temperature sufficient to effect the desired extent of removal of trace elements such as sulfur and nitrogen, but which will not be so great as to adversely affect the yield and stability of the finished oil. It has been found that temperatures in the range of about 575° to 645° F., especially about 600° to 635° F., are suitable for the herein-disclosed high naphthenic charge stocks in conjunction with the particular catalysts of this invention.

Space velocities in the range of about 0.5 to 4, preferably about 1.5 to 3, volumes of liquid per hour per volume of catalyst can be used. Space velocities in the upper portion of the range indicated are economically advantageous from the standpoint of capital investment in view of the corresponding smaller reactor volumes required. However, when the degree to which the average catalyst temperature concurrently can be raised is limited, as in the present instance, some sacrifice in quality as regards product color, desulfurization and the like may accompany the use of such higher space velocities.

For purposes of the reaction to be effected in the present process, reactor pressures in the range of about 500 to 3000 p.s.i.g. can be used, with pressures in the range of about 1000 to 2000 p.s.i.g. being preferred. To a certain extent, the reaction conditions employed in the catalyst bed are interrelated. Thus, the more severe treating conditions of temperature and pressure would normally be more useful in connection with higher space velocities. Conversely, less severe conditions of temperature and pressure will normally be more useful with space velocities in the lower part of the range disclosed. By way of example, excellent results are obtainable at an average catalyst bed temperature of 600° F., an operating pressure of 1000 p.s.i.g. and at a space velocity of 1.5 liquid volumes of oil per hour per volume of catalyst; similarly, good results are also obtainable at an average catalyst bed temperature of 640° F., a reaction pressure of 1735 p.s.i.g. at a space velocity of 3 liquid volumes of oil per hour per volume of catalyst.

The treated oil passes out of reactor 14 into line 6 from which it passes in indirect heat exchange with incoming feed in heat exchanger 4. The hydrogenated product, partly cooled to about 70° to 150° F., then passes through line 18 into high pressure separator 20 where the initial separation of unreacted gas and liquid at a relatively high pressure is effected. Separated gas, comprising principally unreacted hydrogen, is recycled to feed line 1 by way of line 2 after recompression to the desired reactor pressure in compressor 24. Make-up hydrogen-rich gas is added to line 2 by way of line 26. Since hydrogen consumption in reactor 14 is relatively small, only small amounts of make-up hydrogen are required.

Partly degassed oil from high pressure separator 20 is passed into low pressure separator 30 by way of line 28 for decompression and further separation of gas from liquid. The gas removed from liquid product in low pressure separator 30 is removed from the system by way of line 32 for use as fuel gas or the like. Degassed liquid from low pressure separator 30 is removed by way of line 34 and reheated in heat exchanger 36 by indirect heat

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exchange with hot, stripped oil passing through line 38, and then introduced into furnace 42 by way of line 40 for further heating preparatory to steam stripping under vacuum. Heated oil from furnace 42 passes through line 44 to the upper section 46a of vessel 46, wherein the hydrogenated oil is steam stripped under a partial vacuum of about 150 mm. Hg absolute pressure to remove light hydrocarbons, dissolved gases and substantially all of the hydrogen sulfide dissolved therein. Stripping of hydrogen sulfide from the oil prior to clay treating is important so that all hydrogen sulfide may be removed from oil prior to any possible contact thereof with air to insure that none of the hydrogen sulfide will be converted to free sulfur. If any free sulfur is formed, the finished product will not pass corrosive sulfur test specifications. Stripping of other trace components, such as ammonia and light hydrocarbons, is also desirable prior to clay treating, inasmuch as these materials tend to reduce clay life. Stripping at relatively low temperatures, preferably at about 325° to 600° F., and for relatively short contact times, is desirable to prevent degradation of products. Stripping steam in amounts of about 1.1 to 49 pounds per barrel of oil can be used with good results.

Steam and stripped hydrogen sulfide pass out of stripper 46a through line 48, through water cooled heat exchanger 50 and into conventional vacuum jets contained in vessel 52. Steam condensate and hydrogen sulfide pass out of vessel 52 through line 54 into hydrogen sulfide stripper 56 where hydrogen sulfide and steam condensate are separated. Steam condensate is removed from stripper 56 by way of line 60, and hydrogen sulfide is removed by way of line 58.

Steam stripped oil passes from stripper 46a by way of line 47 to vacuum drying section 47b maintained under a partial vacuum of about 50 mm. Hg absolute pressure, where the water content of the oil is reduced to a maximum of about 25 p.p.m. Vaporized water leaves drying section 47b by way of line 47a. Vacuum drying is important not only for the purpose of minimizing the harmful effect of water on the electrical properties of the oil, but also in comparison to drying in the subsequent clay treating step, as water tends to reduce clay life.

Vacuum stripped and dried oil from vessel 46 passes through line 38 through heat exchanger 36, where it is cooled by indirect heat exchange with partly degassed liquid from low pressure separator 30, into line 62 and thence into clay treating tower 64 and out product line 66. In actual operation, the stripped oil may be stored in tanks prior to clay treating. The clay treating operation of the present invention is carried out in a conventional manner. Thus, the stripped, hydrofinished oil can be percolated through clays normally used in clay finishing processes, usually of a size sufficient to pass a 16 to 90 mesh screen, examples of which are fuller's earth, bauxite, Millwhite, attapulug clay or Filtrol, that may have been activated for clay percolation and decolorizing purposes by roasting at temperatures on the order of 400° to 900° F. Although moderately elevated temperatures, for example, up to 100° F. or even higher, can be used during clay finishing, too high a temperature is undesirable as such temperatures may result in color degradation of the final product. Normally, we prefer to effect clay finishing at ambient atmospheric temperatures. Elevated pressures can be used to speed up the flow of oil through the clay treating bed, but such pressures are not necessary. Normally, we prefer to utilize the clay to an extent of about 100 liquid volumes of oil per volume of clay prior to regeneration or replacement, but good results have been obtained with oil:clay treating ratios of greater than 200 volumes of oil per volume of clay. When the treating ratio of oil to clay has reached the desired limit, the clay is either discarded or regenerated in conventional manner, as by burning. Preferably, the spent clay will be washed with naphtha and stripped prior to regeneration by combustion. As is known, the optimum regeneration condi-

tions for the finished clay will depend upon the nature of the particular adsorbent employed.

In a specific embodiment of the invention, a high naphthenic distillation oil, derived from a coastal (Texas) crude oil, was charged to a catalytic hydrogenation treatment involving a single reactor, wherein the average reactor temperature was 600° F., the operating pressure was 1000 p.s.i.g., the space velocity was 1.5 liquid volumes of oil per hour per volume of catalyst, and the gas circulation rate was 2000 s.c.f./bbl. The catalyst employed was 1/2 inch diameter extrudates of nickel, cobalt and molybdenum on an alumina support. A typical sample of the fresh catalyst was found to have about 2.4 percent nickel, 1.28 percent cobalt, and 9.85 percent molybdenum, and about 0.03 percent chlorine. The catalyst was prepared by impregnation of the alumina support with water-soluble salts of the metals and calcining. The catalyst was sulfided by contact at reaction conditions with a West Texas furnace oil (containing 0.8 percent sulfur). A typical sample of this catalyst had a density of about 51.2 lbs./cu. ft. A typical sample of the naphthenic distillate charge stock had the following inspections:

Gravity, ° API	26.3
Viscosity:	
32° F.	245
100° F.	55.2
Interfacial Tension, 77° F., dynes/cm.	37.2
Flash, OC: ° F.	285
Pour point: ° F.	<-55
Color, ASTM D1500	L 1.0
Carbon Residue	0.09
Hydrocarbon Type Analysis:	
Alkanes	0.0
Non-condensed cycloalkanes	44.5
Condensed cycloalkanes	35.0
Benzene	16.3
Naphthalene	4.2

The product was then stripped to remove H<sub>2</sub>S with nitrogen equivalent to 11.1 pounds of steam per barrel of oil charged. The temperature at the top of the stripping tower was 277° F., 450° F. in the flash zone and 485° F. in the bottom of the tower. The stripped oil was then filtered through Triple A Attapulug clay in a proportion of 50 barrels of oil per ton of clay. The results of these runs, before and after clay filtering, are shown on the following page.

Inspections	Unfiltered	Clay Filtered (50 bbl./ton)
Gravity, ° API	27.1	27.3
Viscosity, SUV: Sec.:		
32° F.	299.5	58.3
100° F.	58.9	325
Flash, OC, ° F.	315	325
Pour Point, ° F.	<-75	<-75
Color, ASTM D156	+19	+30
Sulfur, Percent	<0.05	<0.05
Nitrogen, Basic, p.p.m.	17	<5
Dielectric Strength, ASTM D877	37.0	46
Interfacial Tension, ASTM D971	47.0	
Oxidation Test, ASTM D943: Time to 15 i.f.t., hr.	40	72
Sludge Test	1.072	0.178
Rotary Bomb Oxidation Test: ASTM D2112, min.	40	100
Sligh Oxidation No.²	3	4
Water, p.p.m.	41	29

<sup>1</sup> This test is conducted by contacting a sample of the oil for 24 hours in a closed bomb at 284±5° F. and an initial pressure of 180 lbs./sq. in. The oil is then allowed to stand in the dark for 20-24 hours, mixed with precipitate in naphtha and centrifuged to separate sludge. The results are reported as percent sludge by weight of the oil sample.

<sup>2</sup> In accordance with this test a measured sample of oil is subjected to an oxygen atmosphere at 392° F. for 2 1/4 hours. The solution is filtered and the weight of precipitate is reported in milligrams as the sligh oxidation number.

From the foregoing test it will be seen that the oil treated in accordance with the present invention, that is, the hydrogenated, stripped and clay filtered oil, is markedly superior with respect to flash point, color, nitrogen content, dielectric strength, stability and water content, as compared with the non-clay treated oil.

In contrast, when the same oil was catalytically hydrogenated at an average catalyst bed temperature of 500° F., but at otherwise identical conditions and compared with the oil obtained by treating at 600° F., the oil treated at the average catalyst temperature of 600° F. was found to be markedly superior with respect to color, sulfur, nitrogen content, heat stability and water content. The comparison of these results on the respective hydrogenated, unfiltered oils is set forth below:

Inspections	Hydrogenated Oil	
	600° F.	500° F.
Color, ASTM D156	+19	+3
Sulfur, percent	<0.05	0.10
Nitrogen, Basic, p.p.m.	17	58
Heat Stability:¹		
Copper, 240° F.:		
Hr. to 1 Color Inc.	48	24
Hr. to 2 Color Inc.	120	60
Water, p.p.m.	41	60

<sup>1</sup> This test is carried out by determining the time required for an oil sample at 240° F. and in contact with a copper strip to increase its ASTM color by one and two numbers.

The advantageous results flowing from observance of an average catalyst bed temperature not exceeding 645° F. in the hydrogen finishing step of the herein-disclosed process were demonstrated by subjecting to the conditions of the ASTM D2112 Rotary Bomb Stability test described earlier herein two samples of clay treated transformer oil heat had been hydrofinished at average reaction temperatures of about 633° F. and 662° F., respectively, over a catalyst having a typical composition consisting essentially of 2.3 percent nickel, 1.4 percent cobalt and 9.2 percent molybdenum, in sulfided form, on an alumina base, at a reactor pressure of 1000 p.s.i.g., a space velocity of 1.5 liquid volumes of charge per volume of catalyst per hour, and with a gas circulation rate of about 2400 s.c.f./bbl. of charge. The oil that had been processed at an average reactor temperature of 633° F. had an induction period of 48 minutes before the pressure drop prescribed in the test had occurred, whereas the oil that had been processed at the higher temperature of 662° F. exhibited an induction period of only 41 minutes.

The importance of the preferred upper hydrogenating temperature limit of the herein-described process was further demonstrated by a comparison of the properties of two unfiltered samples of an oil of the same kind used in the preceding runs, that had been catalytically hydrogenated, using the catalyst described above, at average catalyst bed temperatures of 628° F. and 702° F., respectively, at a pressure of 1000 p.s.i.g., a space velocity of 0.5 liquid volumes of oil per hour per volume of catalyst, and at a circulating gas volume ratio of about 2200 s.c.f./bbl. of oil. The results obtained in these runs are as follows:

Inspections	Hydrogenated Oil	
	628° F.	702° F.
Yield of Hydrofinished Oil Stripper Bottoms, Percent by Volume of Charge	95.8	87.5
Hydrogen Consumption, s.c.f./bbl. Oil	188	198
Oil Inspections:		
Gravity, ° API	27.2	28.0
Viscosity at 100° F., SUS	59.2	55.7
Flash Point, OC, ° F.	325	280
Pour Point, ° F.	<-75	<-75
Color, ASTM D155-45	-1	1.5
Sulfur, percent	0.04	<0.04
Carbon Residue, Conradson, percent	0.01	0.02
Heat Stability, 240° F., Hr.¹	72	4

<sup>1</sup> Time required for ASTM color of oil to increase by one number at 240° F. in contact with a copper strip.

From the foregoing comparison it will be seen that the oil treatment at a representative average catalyst bed temperature within the range disclosed herein is less costly to produce in terms of hydrogen consumption and relative volumes of oil recovered, as compared with treatment of the same oil at a representative temperature within the range heretofore proposed. In addition, the oil

treated in accordance with the present invention is markedly superior to the oil treated at the higher temperature with respect to flash point, color, carbon residue, and stability.

Similar results were obtained with a catalyst comprising 6 percent nickel and 19 percent tungsten on an alumina base, such catalyst having been calcined and presulfided as described above. In a run carried out on a Texas distillate oil having a viscosity of about 60 SUS at 100° F., at 1000 p.s.i.g., an average catalyst bed temperature of 675° F., a space velocity of 1.8 liquid volumes of oil per hour per volume of catalyst and at a recycle hydrogen-gas rate of 4180 s.c.f./bbl. of oil, a yield of only 85.0 percent by volume of charge was obtained, hydrogen consumption was 61 s.c.f./bbl. of oil, and a sludge content of 5.0 percent on the unfiltered oil was observed after 24 hours exposure to oxygen at 284° F. and 180 p.s.i.g. In contrast, the same catalyst when used in accordance with this invention to treat a Texas oil having a viscosity of about 55 SUS at 100° F., at a temperature of 632° F., a space velocity of 3.0 liquid volumes of oil per hour per volume of catalyst, and a recycle hydrogen rate of 1902 s.c.f./bbl., a yield of 98.8 percent by volume of charge was obtained. The hydrogen consumption was only 130 s.c.f./bbl., and the sludge content of the unfilterable oil under the same test conditions as used above was only 0.512 percent.

The importance of the herein-disclosed class of catalysts has been demonstrated experimentally by a comparison of a representative member of the class of catalysts disclosed herein with a typical commercial hydrofinishing catalyst. Thus, separate samples of a lubricating oil charge stock having a viscosity in the transformer oil range were subjected to parallel hydrofinishing operations carried out at 1000 p.s.i.g. pressure, an average reaction temperature of 639° to 642° F., and a space velocity of 1.5 liquid volumes of charge stock per volume of catalyst per hour. The catalyst employed in the run typifying the present invention was carried out using a catalyst having a composition of about 2.3 percent nickel, 1.4 percent cobalt and 9.2 percent molybdenum on an alumina base. The typical, commercial hydrofinishing catalyst was a cobalt molybdate catalyst containing 2.6 percent cobalt and 7 percent molybdenum on an alumina base. Greater activity of the catalyst typifying the present invention was evidenced by a 51° F. temperature rise through the catalyst bed, as compared with a temperature rise of only 16° F. for the cobalt molybdate catalyst. The relatively greater activity of the catalysts characterizing the present process was also evidenced by higher API gravity, lower sulfur content, lower nitrogen content, and greater heat stability for the products obtained with such catalyst. These comparative properties for the untreated charge stock are set forth in the following table, wherein the catalyst of this invention is indicated as Catalyst A.

Inspections	Charge Stock	Catalyst A Product	Commercial Catalyst Product
Gravity, ° API.....	26.5	27.2	26.8
Sulfur, percent.....	0.13	0.05	<0.05
Basic Nitrogen, p.p.m.....	43	12	31
Heat Stability—Copper, 240° F.: Hr. to 1 Color Inc.....	-----	48	48
Hr. to 2 Color Inc.....	-----	120	96

The importance of the conjoint use of the catalysts whose use is included by the present invention together with clay treatment has been shown by a comparison of the color and sludge-forming tendencies before and after clay filtering of separate samples of the oils obtained with the typical, commercial cobalt molybdate alumina catalyst and the nickel, cobalt, molybdenum-alumina catalyst as described in the immediately preceding portion of this description. Clay filtration was carried out at ambient temperatures to a throughput not greater than 100

barrels of oil per ton of clay in each case. The results of these runs are presented below:

	Catalyst A Product		Commercial Catalyst Product	
	Before Clay Filtering	After Clay Filtering	Before Clay Filtering	After Clay Filtering
Color, ASTM D156.....	+4	+5	+1	+1
Oxidation Test, ASTM D1314				
Sludge, Percent After—				
72 Hours.....	<0.01	0.01	0.02	0.02
168 Hours.....	0.01	0.01	0.05	0.08
336 Hours.....	0.05	0.08	0.12	0.27

From the foregoing results it is apparent that the catalysts whose use is included by the present invention produce lighter color products and that clay treating further enhances the color of the oil. In contrast, the oil produced with the typical commercial hydrofinishing catalyst is initially of darker color and no further improvement in color was obtained with clay treatment. In addition, clay filtering did not significantly harm the ASTM D1314 sludge-forming tendencies of the oil produced with the catalyst of the present invention, whereas clay treating adversely affected the corresponding sludge-forming tendencies of the oil produced with the typical commercial hydrofinishing catalyst.

Although the invention has been described in terms of certain specific embodiments, it will be appreciated that many variations thereof can be practical with good results. Thus, the catalyst bed can be separated in a plurality of reaction vessels with or without intermediate quench, and separate heaters may be used for the oil feed and the recycle gas in order to reduce heater residence time and minimize the possibility of thermal cracking prior to contact of the oil with catalyst. Similarly, other operating conditions and other catalysts disclosed herein can be used with good results. For example, nickel tungsten on alumina catalysts, either in sulfided or non-sulfided form, can be used. In addition, while the properties obtained in lubricating oil base stocks in accordance with the present invention are especially desirable in transformer oil stocks, such properties as light color, stability, non-sludge-forming tendencies and low nitrogen and sulfur content are also desirable in other lubricating oil base stocks. Hence, the use of other lubricating oil charge stocks, such as turbine oil stocks, crankcase oil stocks and diesel lubricating oil stocks, is also included by the present invention.

Obviously, other modifications and variations of the herein-disclosed invention may be resorted to without departing from the spirit or scope thereof. Accordingly, only such limitations on the invention should be imposed as are indicated in the appended claims.

We claim:

1. A process for producing lubricating oil stocks of improved stability, comprising contacting a lubricating oil distillate stock with hydrogen, in the presence of a catalyst comprising a hydrogenating component selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the ratio of each iron group metal to molybdenum is less than about 0.4, and (b) a combination of about 5 to 40 percent by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:0.1 to 5, said hydrogenating component being composited with an alumina support, said contacting being carried out at an average catalyst temperature of about 575° to 750° F., at a space velocity of about 0.5 to 4 liquid volumes of oil per volume of catalyst per hour, and at a pressure of about 500 to 3000 p.s.i.g., the combination of conditions being so selected as to effect appreciable hydrogen consumption but no substantial cracking, and clay treating the hydrogenated oil.

2. The process of claim 1 where the hydrogenating component is a sulfided combination of nickel, cobalt and molybdenum.

3. The process of claim 1 where the hydrogenating component is a sulfided combination of nickel and tungsten.

4. A process for producing lubricating oil stocks of improved stability, comprising contacting a lubricating oil distillate stock with hydrogen, in the presence of a catalyst comprising a hydrogenating component selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the ratio of each iron group metal to molybdenum is less than about 0.4, and (b) a combination of about 5 to 40 percent by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:01 to 5, said hydrogenating component being composited with an alumina support, said contacting being carried out at an average catalyst temperature of about 575° to 645° F., at a space velocity of about 0.5 to 4 liquid volumes of oil per volume of catalyst per hour, and at a pressure of about 500 to 3000 p.s.i.g., the combination of conditions being so selected as to effect appreciable hydrogen consumption but no substantial cracking, and clay treating the hydrogenated oil.

5. The process of claim 4 where the hydrogenating component is a sulfided combination of nickel, cobalt and molybdenum.

6. The process of claim 4 where the hydrogenating component is a sulfided combination of nickel and tungsten.

7. A process for producing transformer grade oils of good stability and good yields comprising contacting a high naphthene oil that is substantially free from alkanes and that has viscosity characteristics in the transformer oil range, with hydrogen, in the presence of a catalyst comprising a hydrogenating component selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the ratio of each iron group metal to molybdenum is less than about 0.4, and (b) a combination of about 5 to 40 percent by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:01 to 5, said hydrogenating component being composited with an alumina support, said contacting being carried out at an average catalyst temperature of about 575° to 645° F., at a space velocity of about 0.5 to 4 liquid volumes of oil per volume of catalyst per hour, and at a pressure of about 500 to

3000 p.s.i.g., the combination of conditions being so selected as to effect appreciable hydrogen consumption but no substantial cracking, and clay treating the hydrogenated oil.

8. The process of claim 7 where the hydrogenating component is a sulfided combination of nickel, cobalt and molybdenum.

9. The process of claim 7 where the hydrogenating component is a sulfided combination of nickel and tungsten.

10. A process for producing transformer grade oils of good stability and good yields, comprising contacting a distillate oil having an aromatics content not greater than about 25 percent, an alkanes content not greater than about 5 percent, the balance being substantially all naphthenes, and having a flash point not less than 275° F., a viscosity at 100° F. of about 50 to 85 SUS, and a viscosity at 32° F. of not more than about 280 SUS, with about 500 to 4000 s.c.f./bbl. of a hydrogen-containing gas containing at least 60 percent hydrogen, with a catalyst comprising a hydrogenating component selected from the group consisting of sulfides and oxides of (a) a combination of about 4 to 16 percent by weight molybdenum and at least two iron group metals where the iron group metals are present in such amounts that the ratio of each iron group metal to molybdenum is less than about 0.4, and (b) a combination of about 10 to 25 percent by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:03 to 4, said hydrogenating component being composited with an alumina support, said contacting being carried out at an average catalyst temperature of about 575° to 645° F., at a space velocity of about 1.5 to 3 liquid volumes of oil per volume of catalyst per hour, and at a pressure of about 1000 to 1800 p.s.i.g., the combination of conditions being so selected as to effect appreciable hydrogen consumption but no substantial cracking, stripping the hydrogenated oil at a temperature of about 325° to 600° F. to remove hydrogen sulfide, and clay treating the stripped hydrogenated oil in a proportion not exceeding about 250 barrels of oil per ton of clay.

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SAMUEL P. JONES, *Primary Examiner*.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,369,999

February 20, 1968

Robert E. Donaldson et al.

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

Column 1, line 14, for "of" read -- by --; column 4, line 31, for "1:03" read -- 1:0.3 --; column 5, in the table, first column, line 2 thereof, for "Catalyst" read -- Catalyst Sulfided --; same table, first column, line 7 thereof, for "G, percent" read -- W, percent --; same table, fourth column, line 3 thereof, for "00.5" read -- 0.05 --; same table, fourth column, line 4 thereof, for "10.4" read -- 1.04 --; column 7, line 4, for "distillation" read -- distillate --; column 8, line 28, for "heat" read -- that --; same column 8, second table, second column, line 7 thereof, for "-1" read -- 1 --; column 9, line 15, for "61" read -- 261 --; line 26, for "unfilterable" read -- unfiltered --; column 9, line 52, after "properties" insert -- , together with the corresponding properties --; column 11, lines 18 and 47, for "1:01", each occurrence, read -- 1:0.1 --; column 12, line 29, for "1:03" read -- 1:0.3 --.

Signed and sealed this 17th day of June 1969.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents