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HYDROCATALYTIC REFINING OF LUBRICATING OILS AND CATALYST THEREFOR

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This invention relates to a process for refining or finish-treating lubricating oils or their fractions by hydrogenation under specific mild conditions, in the presence of a catalyst comprising molybdenum oxide on a siliceous support, wherein improvements in physical properties of the products are obtained without impairment of the inherent good qualities of the feed oil. More particularly, the process is one in which, through mild hydrogenation using a particular catalyst, improvements in such properties as steam emulsion number and reduction in neutralization number are obtained without reduction in the content of naturally-occurring inhibitors present in the lubricating oil feed.

Recent developments in the hydrogenation of petroleum show that it is adaptable for converting fuel oil to gasoline and gas oil, increasing the paraffinicity of kerosenes, burning oils, and lubricating oils, and converting all types of asphalts to distillate fuels. Until the last few years, commercial hydrogenation has been restricted to the use of highly purified hydrogen at pressures greater than atmospheric, temperatures below decomposition temperatures of the feed, and in the presence of powerful but sensitive catalysts of the type of reduced nickel. These processes are generally applicable to sulfur-free and arsenic-free materials, and accordingly are related primarily to the treatment of vegetable fats and oils. By using hydrogen alone and employing greatly increased pressures, both coal and petroleum oils can be highly liquefied, but because of their high contents of sulfur, oxygen compounds and ring-type compounds the resulting products are difficult to crack or further refine. With the advent of catalytic desulfurization, hydrogenation and reforming processes as applied to lighter stocks, and the development of sulfur resistant catalysts, the art has seen many developments in the field of flexible methods of treating and refining by the use of hydrogen.

Refining through the use of both chemical and physical means has long been known to enhance the utility and stability of waxes, lubricating oils and their fractions. In the application of hydrogenation as the refining method, the art lists a large number of metal compounds, particularly the oxides and sulfides of the metals of group VI and group VIII, paying particular attention to nickel, cobalt, iron, molybdenum, tungsten and chromium for these purposes. It is also recognized in the art that only through judicious application of refining methods can the inherent stability, color properties, or viscosity-temperature characteristics of a lubricating oil or wax be preserved, since many refining operations, including acid treatment, hydrogenation, solvent extraction, adsorption, thermal diffusion, extractive distillation, hydrodesulfurization, and chemical and clay treatments, remove desirable constituents along with the undesirable constituents. To overcome the shortcomings of the refining methods, it is common practice to incorporate various addends in the finished products and bring about new properties. Thus, it is common practice to apply refining methods to the extent of their worth as regards enhancement of viscosity, viscosity-index, color and carbon residue and then fortify the finished oil by the use of addends to offset deficiencies in oxidation stability, demulsibility, acid number, sludge resistance and the tendency to corrode metal parts which are directly or indirectly a result of the refining process.

Within the vast amount of art available on hydrogenation, hydrodesulfurization, destructive hydrogenation (hydrogenolysis) and related refining processes employing hydrogen to treat a wide variety of feed stocks, attention is generally directed to such matters and problems as the method of catalyst preparation or pretreatment, catalyst composition, removal or destruction of sulfur, oxygen and nitrogen compounds, removal or destruction of asphaltic or resinous compounds, the use of promoters in obtaining fluidizable catalysts, color stability in the product, removal of unsaturates and maintaining catalyst life or activity. These processes are generally conducted at temperatures above 750° F., employing pressures well above 500 lbs. per square inch, and as such inherently remove or transform both the undesirable and the desirable constituents therein. The art has now come to recognize that certain of the naturally-occurring sulfur, oxygen and nitrogen compounds that are destroyed or removed during these refining operations, have a decided effect upon the oxidation stability and sludge-forming propensities of the refined lubricating oils. A finished lubricating oil, consisting as it does of 10 to 40% of high boiling aromatic compounds, 25 to 80% of naphthenic hydrocarbons, and 15 to 75% of isoparaffinic hydrocarbons, along with various percentages of sulfur, oxygen and nitrogen compounds, represents a complex system for study. Although it is recognized that the stability of the lubricating oil in service, wherein it is subjected to highly complicated oxidation atmospheres catalyzed by the presence of metallic surfaces, which oxidation progresses as the extent of use is prolonged, may be improved by removing certain of the more unstable naphthenes, aromatics, or diphenyls, the organic sulfur compounds are responsible for much of the remaining resistance to oxidation the oil may have.

Attempts have been made to isolate the sulfur compounds naturally present in lubricating oil fractions, as by the formation of mercuric chloride addition compounds, or by selective adsorption on fuller's earth, but the results were not quantitative and the sulfur-rich extracts proved to be intractable and could not be separated or purified by ordinary chemical means. In many instances, it has been reported that the sulfur-containing fractions did not inhibit the oxidation of the sulfur-free oils. The sulfur compounds themselves must be as complicated as the mixtures of hydrocarbons from which they are extracted. Research on the oxidation inhibition qualities of synthesized sulfur compounds has indicated that monosulfides are good inhibitors; those sulfur compounds in which the sulfur is a part of a ring are somewhat more active, but mercaptans and disulfides are not as active on an equivalent sulfur basis as the corresponding monosulfides. These differences are partly attributed to the influence of the rate of reaction of the sulfur compounds with peroxides formed or present in oil, and it is generally accepted that the rate of oxygen adsorption of oils may be proportional to the peroxide concentration. Those oils which contain natural antioxidants, or agents capable of reducing peroxides, will not build up high peroxide concentrations with consequent high oxidation rates. Sulfur compounds in their reaction with the peroxides are oxidized to deleterious products in the oil. The refiner, therefore, is faced with the dilemma of refining lubricating oils to improve their flow characteristics while still trying to retain a sufficient concentration of natural sulfur compounds to prevent the development of appreciable concentrations of peroxides and consequent high oxida-

tion rates, and at the same time maintaining the content of sulfur compounds sufficiently low so that upon oxidation the concentration of deleterious oxidation products is innocuous.

In accordance with the present invention, it has been discovered that lubricating oils, their fractions, and base stocks can be refined by mild hydrogenation using a molybdenum oxide-silica-alumina catalyst, under particular conditions of temperature and pressure, to enhance the viscosity, viscosity-index, color and other related properties without adversely affecting the steam emulsion number or destroying the naturally-occurring oxidation-inhibiting sulfur compounds, while at the same time attacking the oxygen-containing compounds to the extent that the content of naphthenic acids is reduced sufficiently to meet the required neutralization number.

Accordingly, a first object of this invention is to provide a process for refining or finishing lubricating oil fractions and lubricating oil base stocks.

Another object of this invention is to provide a superior catalyst composition and method of its utilization for improving the properties of lubricating stocks by mild hydrogenation.

A third object of the invention is to provide a catalyst for the mild hydrotreating of lubricating oils, which catalyst contains a minor amount of an oxide of molybdenum incorporated on a silica-alumina support containing a predominant amount of silica.

Still another object is to provide a process for preparing neutrals or lubricating oil stocks of lower density and other improved properties from heavier stocks such as deasphalted oils and bright stocks.

These and other objects of the invention will become apparent as the description thereof proceeds.

In order to demonstrate the invention, a series of experiments were conducted in which a 241 viscosity neutral lubricating oil stock was treated to mild hydrogenation at different temperature levels at a liquid volume hour space velocity of 1.5, hydrogen-to-oil mol ratio of 6.5 to 7.5, and under a pressure of 500 p.s.i.g., employing various molybdena-containing catalysts. The lubricating oil before treatment had the following characteristics:

°API gravity	24.2
Color NPA	3½
Refractive index N_D^{70}	1.4863
Molecular weight	370
Carbon res. (Conradson)	0.02
Neutralization number	2.88
Vis. @ 100° F., SUS	241.3
Vis. @ 210° F., SUS	47.4
Viscosity index	76.3
Sulfur content, wt. percent	1.13
Steam emulsion No.	145
Initial boiling point, °F.	718

The results of these experiments are shown in the following table:

From the results shown in the table it is seen that in runs No. 3, 6 and 7 the products have increased viscosity index and exhibit properties which show controlled hydrocracking. Reference is made to the last three columns of the table which show the amount of material boiling below the initial boiling point of the charge, the viscosity index of the product fraction having an initial boiling point of 718° F. (the initial B.P. of the charge), and the initial boiling point of the hydrogenated product. Although all of the runs were conducted at a low space velocity of 1.5, the data at 650° F. indicates that this temperature is the highest temperature desirable for the reaction. The acid reduction was not as good at 650° F. as that obtained at 550° F., and at the higher temperature, desulfurization is becoming appreciable. At these higher temperatures the controlled hydrocracking is increased and therefore the active cycle life of the catalyst is shorter. This necessitates intermittent catalyst regeneration in order to maintain catalyst activity at the maximum if charge stocks are employed wherein substantial lowering of viscosity is desired. Otherwise, the catalyst will perform to quantitatively remove acids but the extent of controlled hydrocracking will be reduced. It should be noted also that at 650° F. the improvement in steam emulsion characteristics has passed the optimum, although results are obtained which are still far superior to those obtained under any conditions over catalysts composed of molybdenum oxide on alumina, or molybdenum oxide on alumina which has only small amounts of silica incorporated therein.

In another series of runs, several catalysts were tested over a longer period of time in order to determine their relative efficiencies for removing acids from the 241 viscosity neutral lubricating oil stock used in the runs presented in Table I. Before making these runs the catalysts tested were calcined and reduced at around 800° F. Runs were made at a pressure of 250 p.s.i.g., and at temperatures of around 570° F. The charge rates were at a LVHSV of 1.3 and the hydrogen charge rate was 3000 cubic feet per barrel of charge. After 15 hours on stream, the acid numbers as shown in Table II were obtained. These results clearly show the superiority of the catalyst of our invention under conditions of mild or incomplete pretreatment or regeneration procedures. Under more complete regeneration procedures at temperatures of around 1000° F., complete acid removal is obtained over each of the catalysts for prolonged cycles of operation. The data thus show that the catalyst of our invention is less dependent upon precise regeneration procedures than are other compositions.

The data show that catalysts containing 3.0 to 10% MoO_3 on silica-alumina, high-surface-area supports containing around 83 to around 90 percent silica are far superior to other catalyst compositions when used in the temperature range of 550–650° F., and that beyond these temperature ranges the catalysts still function although they are relatively less superior at higher temperatures.

TABLE I

Hydrotreating lubricating oil

Run No.	Catalyst Composition			Temp. of treatment, ° F.	Characteristics of Product											IBP, ° F., overhead
	Percent MoO_3	Base Comp.			° API	Color	C. R.	n_D^{20}	Mol. Wt.	Neut. No.	Vis., SUS		VI	Wt. Percent S	Steam Emulsion No.	Vol. Percent <718° F.	VI Lube Stock	
		SiO_2	Al_2O_3								100° F.	210° F.						
1	3.0	------	100.0	550	24.4	--------	--------	1.4862	355	<0.03	225	46.6	77	1.21	90	--------	--------	--------
2	3.0	5.8	94.2	550	24.7	1½+	0.03	1.4850	365	<0.03	219	46.3	78	1.21	109	--------	--------	--------
3	3.0	87.0	13.0	550	25.7	+2	0.04	1.4821	345	0.05	166.4	43.6	85	1.12	18	7.6	82	357
4	9.3	------	100.0	550	24.6	4+	0.06	1.4868	345	0.04	226.8	46.7	77	1.18	68	--------	78	--------
5	8.9	1.0	99.0	550	24.7	2+	0.01	1.4854	375	<0.03	214.4	46.2	81	1.05	92	1.4	78	665
6	10.0	83.0	17.0	650	28.2	+2	0.01	1.4712	320	0.16	96.6	39.1	100	0.75	35	13.3	91	355
7	10.0	87.0	13.0	650	27.2	+4½	0.01	1.4786	300	0.16	114.6	40.6	99	0.85	76	10.0	87	365

TABLE II

Run No.	Catalyst Composition, percent			Neutralization Number (1948)
	MoO_3	SiO_2	Al_2O_3	
8	9.0	1.0	99.0	0.12
9	9.0	0.3	99.7	0.15
10	10.0	83	17	0.06

The superiority in the prescribed temperature range is readily seen by comparing the catalysts of runs 3 and 5 of Table I. The catalyst of run 3 produces an increased API gravity, preferred controlled hydrocracking, and increased viscosity characteristics. On the other hand, the catalyst of run 5 does little more than effect acid removal. Steam emulsion characteristics are vastly improved with the catalyst of run 3, whereas in run 5 the improvement is of far lesser magnitude.

In order to show the influence of temperature on the properties of products obtained over these catalysts, a run was carried out at 700° F. using 241 viscosity neutral lubricating oil stock as the charge and maintaining other operating conditions the same as in the above runs. Using the 10 percent MoO_3 on a silica-alumina support, containing 17 percent alumina, a product of the following properties was obtained during a run of 19 hours duration:

	Charge	Product
Neut. No. (1948)	1.51	.03
Color	8+	6+
Sulfur	1.15	1.13

Considerable controlled hydrocracking was achieved.

Thus the data show that the combination of about 10% MoO_3 on 87% SiO_2 and 13% Al_2O_3 as the catalyst, used at temperatures of 550–650° F., gives the best results. Other catalyst compositions, even when used at the critical temperature range, either fail to give the required reduction in neutralization number, reduce the naturally-occurring sulfur compounds, or unduly influence the steam emulsion number of the product.

The invention may be applied to any lubricating oil or fraction thereof. Both neutrals and bright stocks may be satisfactorily treated in accordance with the invention. The process may be advantageously applied to the conversion of bright stocks into neutrals by mild hydrogenation, and may be applied where the main object of the treatment is a reduction in the viscosity of the lubricating oil and an increase in viscosity index without affecting the sulfur content and without producing gas or gasoline. The invention also finds use where reduction of steam emulsion number is the primary object, as in the development of steam turbine oils. The following Table III sets forth the physical properties of some lubricating

TABLE III

Hydrogenation charge oils

No.	Description	SUS Viscosity		VI	Neut. No.	° API	Total Sulfur, Wt. Percent	Conradson C.R., Wt. Percent
		@ 100° F.	@ 210° F.					
1	Heavy deasphalted oil	2,900	165.6	96	0.80	22.9		1.87
2	Medium neutral distillate	243.2	47.4	74	2.9	24.2	1.13	0.11
3	do	242.1	47.4	76	2.9	24.0	1.13	0.05
4	Heavy deasphalted oil	3,200	170.7	93	0.85	22.5	1.10	2.0
5	Medium neutral distillate	243.8	47.5	75	3.03	24.3	1.15	0.07
6	Heavy deasphalted oil		181	87	1.6	21.6	1.23	2.23
7	Neutral distillate	241.3	47.4	76	3.03	24.2	1.13	
8	Heavy deasphalted residuum		177.2		1.51	21.7	1.14	1.96
9	do		175.8		1.64		1.23	2.0
10	Solvent-refined neutral dist		37.5	90	0.15	34.0	0.12	0.01
11	do	200	46.0	90	0.30	28.5	0.45	0.02
12	do	800		90	0.35	27.0	0.60	0.25
13	Solvent-refined bright stock	2,400	153.0	100	0.25	26.5	0.45	0.60
14	do	3,300	170.0	90	0.45	24.3	0.75	1.2

°API gravity	25.3
Vis., SUS @ 100° F	197.0
Vis. SUS @ 210° F	45.2
Viscosity index	80.0
Neut. No. (1948)	<0.03
Sulfur, wt. percent	0.87
Color, NPA	2½

It is thus seen that while these results are equal or superior to those obtained over catalysts consisting of molybdenum oxide on supports consisting essentially of alumina, the results are inferior to those obtained over the same preferred catalysts at lower temperatures, i.e., runs 3, 6 and 7 of Table I, and that by operating at the higher temperatures much of the superior activity of the preferred catalysts is lost.

The efficiency of these catalysts for other stocks also has been demonstrated. A deasphalted oil was processed over a catalyst composed of 10 percent molybdenum oxide on a support of 83/17 SiO_2/Al_2O_3 to remove acids at 595° F., 250 p.s.i.g., a LVHSV of 1.5, and a hydrogen rate of 2400 cubic feet per barrel of charge. The following results were obtained:

oils that may be benefited by applying the mild processing with hydrogen according to this invention.

In general, the operating conditions used in treating lubricating oils to obtain the desired results are as follows:

TABLE IV

Temperature, ° F	500–650
LVHSV	1.0–5.0
Hydogen/HC mol. ratio	5.0–10
Pressure, p.s.i.g	250–600

By operating within the conditions set forth in Table IV using a catalyst composition consisting of about 3% molybdenum oxide, about 87% silica and 13% alumina with trace amounts of Na_2O, Fe_2O_3 and other trace materials, lubricating oil distillates, bright stocks, and deasphalted residual oils can be improved with respect to their VI, color, neutralization number, demulsibility, and content of carbon residue, resins and oxygenated compounds, without impairment of the naturally occurring sulfur content. In addition to this, where subsequent refining operations are to be employed, such as extraction, it will be found that there is a decrease in corrosion with-

in the extraction system and economies are obtained in the finishing clay-contacting treatments. The catalyst composition is subject to very little variation; in general, a minimum of about 2.5 to 3.5 weight percent of molybdenum oxide must be present with the upper limit at about 10 weight percent and the siliceous support must contain between about 83 and 90% silica, which means that the alumina content can vary between 10 and 17%.

What is claimed is:

1. The process of refining mineral lubricating oils having natural resistance to oxidation and deterioration due to the content of naturally-occurring sulfur compounds therein and containing acidic compounds whereby the viscosity and viscosity index characteristics of said lubricating oils are enhanced, the steam emulsion number reduced and the content of said acidic compounds reduced without affecting the content of said naturally-occurring sulfur compounds which consists in subjecting said mineral lubricating oils to contact with hydrogen at a temperature of between about 550° and 650° F. in the presence of a catalyst selected from the group consisting of a silica base containing about 87.0 wt. percent of silica and about 13.0 wt. percent of alumina with about 3.0 wt. percent of molybdenum oxide, a silica base containing about 83.0 wt. percent silica and about 17.0 wt. percent of alumina with about 10.0 wt. percent of molybdenum oxide and a silica base containing about 87.0 wt. percent silica and about 13.0 wt. percent alumina with about 10.0 wt. percent of molybdenum oxide, and recovering a hydrogenated lubricating oil characterized by having an improved viscosity index and

reduced neutralization number without reduction of said naturally-occurring sulfur compounds and without impairment of the physical properties thereof.

2. The process in accordance with claim 1 in which said catalyst consists in a silica base containing about 87.0 wt. percent of silica and about 13.0 wt. percent of alumina with about 3.0 wt. percent of molybdenum oxide.

3. The process in accordance with claim 1 in which said catalyst consists in a silica base containing about 83.0 wt. percent of silica and about 17.0 wt. percent of alumina with about 10.0 wt. percent of molybdenum oxide.

4. The process in accordance with claim 1 in which said catalyst consists in a silica base containing about 87.0 wt. percent of silica, and about 13.0 wt. percent of alumina with about 10.0 wt. percent of molybdenum oxide.

5. The process in accordance with claim 1 in which the mineral lubricating oil is selected from the group consisting of heavy deasphalted oil, medium vis. distillate oils, solvent-refined neutral distillates and solvent-refined bright stocks.

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