United States Patent Office 2,921,025 Patented Jan. 12, 1960

2,921,025

HYDROCATALYTIC REFINING OF LUBRICATING OILS AND CATALYST THEREFOR

Le Roy W. Holm and Hillis O. Folkins, Crystal Lake, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application May 14, 1957
Serial No. 658,958

5 Claims. (Cl. 208—264)

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 consisting of moylbdenum oxide on an alumina support containing small amounts of silica, whereby improvements in physical properties of the products are obtained without impairment of the inherent good qualities of the feed. More particularly, the process is one in which, through mild hydrogenation at temperatures no greater than about 600° F. using a particular catalyst composition, the neutralization number of a lubricating oil can be reduced substantially to zero without affecting the natural oxidation resistance, viscosity and other properties of the feed, and over extended periods of time with no appreciable reduction in catalyst activity.

Recent developments in the hydrogenation of petroleum show that hydrogenation is adaptable for converting heavier oils 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 the decomposition temperature of the feed, and in the presence of powerful but sensitive catalysts of the type of reduced nickel. These processes were generally applicable to sulfur-free and arsenic-free materials and accordingly 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 liquefied to a high degree, but because of their high contents of sulfur and oxygen 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-resistanct catalysts, the art has seen many developments in the field of flexible methods of treating and refining by the use of hydrogen.

In the application of hydrogenation as a refining method, the art lists a large number of metal compounds, particularly the oxides and sulfides of group VI and group VIII metals, 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, 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 generallp 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, obtaining fluidizable catalysts, color stability in the product, removal of unsaturates and maintaining catalyst life or activity. Hydrogen processing is generally conducted at temperatures above 750° F., employing pressures well above 500 lbs. per square inch, and such processes inherently remove or transform both undesirable and desirable constituents. 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. 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 reduced by removing certain of the more unstable naphthenes or aromatics or diphenyls, it is the organic sulfur compounds that are responsible for any remaining resistance to oxidation the oil may have after such refining methods have been applied.

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 are not quantitative and the sulfur-rich extracts prove to be intractable and cannot 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. Differences in the activity of various sulfur compounds in reacting with peroxides, which are apparently present under oxidative conditions, is explainable on the basis of structure of the sulfur compounds and their ability to inhibit peroxide formation. However, such reaction products are also deleterious and contribute to sludge formation during use. 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 oxidation 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 may be refined by mild hydrogenation using a molybdenum oxide-alumina-silica catalyst under particular conditions of temperature and pressure to effect the greatest possible reduction in neutralization number of naphthenic acid content without adversely affecting the viscosity, viscosity index, steam emulsion number, or causing the destruction of the naturally-occurring, oxidation-inhibiting sulfur compounds, while at the same time maintaining prolonged catalyst life even though the catalyst is sensitive to the presence of sulfur compounds.

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 mild hydrotreating of lubricating oils, which catalyst contains a minor amount of an oxide of molybdenum incorporated in an alumina-silica support containing a predominate amount of alumina.

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 hourly space velocity of 1.5, and a hydrogen-to-oil mol ratio of 6.5 to 7.5, under a pressure of 500 p.s.i.g. and employing various molybdenum oxide-containing catalysts. The lubricating oil stock before treatment had the following characteristics:

API ° gravity	24.2
Refractive index n^{20}/D	1.4863
Molecular weight	370
Neutralization number (1948)	3.03
Vis. @ 100° F., SUS	241.3
Vis. @ 210° F., SUS	47.4
Viscosity index	76
Sulfur content, wt. percent	1.13
Steam emulsion No.	145
Boiling range, ° F.	720–930

The results of these experiments are shown in Table I. Results with a catalyst of this invention are compared to results with two well-known commercial catalysts in Table II.

The data further show that the catalyst composition is a critical factor with respect to cycle life. The results show that the combination of about 9 percent molybdenum oxide on a support consisting of 99 percent alumina and 1 percent silica is a very effective catalyst in reducing acid number when used at temperatures in the range of 550–600° F., and that its activity is still at a maximum after 161 hours of continuous processing. A similar composition, containing 9 percent molybdenum oxide on alumina alone, showed poorer acid reduction activity and had an active cycle life of only 7 hours.

Similarly, catalysts composed of lesser amounts of molybdenum oxide maintain high activity for acid removal for a much longer time when the alumina support contains minor amounts of silica.

The results of Table II show further the specificity of our catalyst composition for acid removal and long cycle life. A composition of 9% MoO_3 and 3% CoO on a support consisting of activated alumina containing 5% silica was evaluated for comparative purposes, and, at the same operating conditions as used for our preferred catalyst, showed poor activity, selectivity, and catalyst life. The cobalt molybdate catalyst reduced the acid number of a heavy residual lube oil to only about 0.5., and at the same time reduced the sulfur content by an appreciable amount. The results in Table II show the detrimental effect of this type of catalyst and emphasize the superiority of the specific catalyst compositions of our invention for the refining of lubricating oils.

Similarly, the use of Porocel (an activated bauxite containing about 84% alumina, 15% silica, and minor amounts of iron) as the catalyst for acid removal showed again the marked superiority of our catalyst for this particular purpose. The results in Table II obtained with Porocel also demonstrate its short active life compared to the catalysts of our invention.

TABLE I

Hydrotreating lubricating oil

Run No.	Catalyst Comp.			Temp. of treatment, ° F.	Characteristics of Product													
	Percent MoO_3	Base Comp. SiO_2	Base Comp. Al_2O_3		° API	Color	C.R.	$n^{20}D$	Mol. Wt.	Neut. No.	Vis., SUS 100° F.	Vis., SUS 210° F.	VI	Wt. Percent S	Steam Emulsion No.	Vol. Percent <718° F.	VI Lube Stock	Catalyst Life [1] hrs.	Catalyst Life [1] bbl./ton
1	3.0	0.09	99.1	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		
4	9.3		100.0	553	24.6	4+	0.06	1.4868	345	0.04	226.8	46.7	77	1.18	68		78	10	
5	8.9		100.0	550	24.7			1.4854	375	<0.03	214.4	46.2	81	1.05	92	1.4	78		
6	10.0	83.0	17.0	650	28.2			1.4712	320	0.16	96.6	39.1	100	0.75	35	13.3	91		
7	10.0	87.0	13.0	650	27.2			1.4786	300	0.16	114.6	40.6	99	0.85	76	10.0	87		
10	10.0	85.0	15.0	590						0.03									
11	9.0	1.0	99.0	555	24.7	2+	0.01		375	<0.03	214.4	46.2	81	1.1					
12	9.0	1.0	99.0	549	24.4	2	0.04			<0.03	230.0	46.8	78	1.10				>161	>2,900
13	9.0		100.0	550	24.7				370	0.09	228	47	78	1.11				7	
14	3.0		100.0	551	24.4	2	0.02		355	<0.03	225	47	77	1.2				<10	
15	3.0	87.0	13.0	551	25.7	+2	0.04		345	0.05	166	43.6	85	1.12				3.5	
16	3.0	5.0	95.0	554	24.7	+2	0.03		365	<0.03	219	46.3	78	1.2				>10	
17	7.5		100.0	550	24.2					[2] 0.05	241	47.4	77	1.11				<10	

[1] Length of service before Neut. No. reached 0.1 at which time regeneration was necessary.
[2] Neut. No. at end of 12 hours of operation.

From the results shown in Table I, it is seen that different compositions of molybdenum oxide on alumina-silica supports are effective catalysts for the neutralization of lubricating oil stocks and that the greatest effectiveness is obtained at temperatures of 600° F. or lower. It should be noted also that the greatest efficiency in acid neutralization is obtained over those catalyst compositions wherein the molybdenum oxide is incorporated into porous alumina supports containing minor proportions of silica.

The invention may be applied to any lubricating oil or fraction thereof. Both neutrals and bright stocks can be satisfactorily treated in accordance with the invention. The process also can be advantageously applied in the conversion of bright stocks into neutrals under hydrogen, but the process of the invention is best applied where the main object of the treatment is a reduction in the neutralization number of the lubricating oil without appreciably affecting the sulfur content and vis-

TABLE II

Hydrogenation of distillate and residual lube oil stocks

Run No.	Catalyst	Charge Oil	LHVSV	Hydrogen Rate, s.c.f./bbl.	Reactor Pressure, p.s.i.g.	Reactor Temp., ° F.	Length of Run, hrs.	Yields, Vol. Percent (of chg.)
1	Same as Run 12, Table I.	No. 5, Table III.	1.0	2,600	250	543	147	99.5
2	do	No. 6, Table III.	1.4	1,900	250	541	20	100
3	do	do	1.8	1,100	100	600	17	100
4	Cat. No. 20-3, cobalt molybdate.	do	1.6	1,900	250	553	8	98.1
5	do	do	1.5	1,700	250	600	4	100
6	Porocel	No. 4, Table III.	1.0	2,600	250	579	40	100

Run No.	Product Specifications								
	Vis., SUS		VI	1948 N.N. ASTMD	° API	Sulf.	Con. Carbon Res., Wt., Percent	Flash, ° F.	Eff., Oper. hrs.[1]
	@ 100	@ 210							
1	228.6	46.8	78	<0.03	24.4	1.13	0.04	420	147
2	3,600	181.1	90	<0.03	21.7	1.17	2.1	560	20
3	3,600	180	91	<0.03	21.6	1.17	1.9	575	17
4				0.8					0
5				0.45		0.85			1
6	3,000	166.2	94	0.5	23.0	1.02	1.5	580	<12

[1] Hours of continuous operation during which product Neut. No. was below 0.10.

cosity, and without producing gas or gasoline. The invention will find use where reduction of steam emulsion number is the primary object in the development of steam turbine oils. The following table sets forth the physical properties of some lubricating oils that may be benefited by applying the mild hydrogenation reaction of this invention.

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

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

TABLE IV

Temperature	450–600° F.
LVHSV	0.5–2.0.
Hydrogen/HC mol. ratio	5.0–10.
Pressure	100–500 p.s.i.g
H_2 rate	1000–4000 s.c.f./bbl.

By operating within the conditions set forth in Table IV using the catalyst compositions of this invention, lubricating oil distillates, bright stocks, and residual oils can be improved with respect to their VI, color, neutralization number, demulsibility, and reduction in the 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 the corrosion within the extraction system and also economies are obtained in the finishing clay contacting treatments. The catalyst composition is subject to very little variation; in general, from about 5 to 10 weight percent of molybdenum oxide must be present and the alumina support must contain from between about 90 to 99.95% alumina, which means that the silica content can vary between 0.05 to 10%.

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 said content of acidic compounds is reduced without affecting the content of naturally-occurring sulfur compounds and without deleteriously affecting the viscosity, viscosity index and steam emulsion number of said mineral lubricating oils which consists in subjecting said mineral lubricating oils to contact with hydrogen at a temperature

of between about 550° and 600° F. in presence of a catalyst selected from the group consisting of an alumina base containing about 94.2 wt. percent alumina and about 5.8 wt. percent silica with about 3.0 wt. percent molybdenum oxide, an alumina base containing about 99.0 wt. percent alumina and about 1.0 wt. percent silica with about 9.0 wt. percent molybdenum oxide and an alumina base containing about 95.0 wt. percent alumina and about 5.0 wt. percent silica with about 3.0 wt. percent molybdenum oxide, and recovering a hydrogenated lubricating oil characterized by having a neutralization number (1948 method) of below about 0.03, the original content of naturally-occurring sulfur compounds, without impairment of the physical properties thereof.

2. The process in accordance with claim 1 in which said catalyst is an alumina base containing about 94.2 wt. percent alumina and about 5.8 wt. percent silica with about 3.0 wt. percent molybdenum oxide.

3. The process in accordance with claim 1 in which said catalyst is an alumina base containing about 99.0 wt. percent alumina and about 1.0 wt. percent silica with about 9.0 wt. percent molybdenum oxide.

4. The process in accordance with claim 1 in which said catalyst is an alumina base containing about 95.0 wt. percent alumina and about 5.0 wt. percent silica with about 3.0 wt. percent molybdenum oxide.

5. The process in accordance with claim 1 in which the lubricating oil is a neutral oil having a viscosity at 100° F. of about 240, a viscosity at 210° F. of about 47, a steam emulsion number of about 145, a neutralization number of about 2.88, and a sulfur content of about 1.13 weight percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,437,532	Huffman	Mar. 9, 1948
2,486,361	Nahin et al.	Oct. 25, 1949
2,654,696	La Porte	Oct. 6, 1953
2,706,167	Harper et al.	Apr. 12, 1955