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HYDRO-REFINING METHOD FOR LUBRICATING OILS AND WAX USING NICKEL MOLYBDATE OR SILVER MOLYBDATE ON ALUMINA

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This invention relates to a method of refining or finish-treating lubricating oils, waxes and their fractions by hydrogenation under specific mild conditions in the presence of a catalyst comprising silver molybdate and/or nickel molybdate. More particularly, this invention relates to a method of decolorizing and stabilizing lubricating oils and waxes and their semi-finished fractions without affecting the other properties thereof by treatment with hydrogen at 450 to 650° F., 150 to 1000 lbs. per square inch pressure, using hydrogen circulation rates of 800 to 4000 s.c.f./bbl. in the presence of a catalyst comprising 2 to 30 weight percent of silver molybdate or nickel molybdate or mixtures thereof supported on alumina.

It is known in the art that the heavier fractions of crude oil, such as lubricating oils and waxes and their fractions are enhanced in utility and stability by refining through both chemical and physical means. Lubricating oils and waxes are commonly subjected to various treatments for the purpose of increasing their stability during use and storage, enhancing their utility by bringing about changes in certain physical properties and, equally important, producing good yields of finished products which have acceptable color, odor and general appearance. It is essential that these refined products retain their enhanced and augmented properties after they leave the producer and while they are being used. For many purposes, even slight changes in low-temperature fluidity, oxidation stability, viscosity index, emulsibility, color, penetration and the like, after finishing or during storage and use, spells the difference between success and failure of a given refining or finishing operation or sequence of operations. This invention has as one of its purposes the provision of a refining process or finishing process which is applicable to lubricating oils and waxes and their fractions wherein the above objectives may be accomplished.

The art teaches that various addends may be incorporated in refined petroleum products to overcome shortcomings in inherent properties, further augment desirable physical and chemical properties, and bring about new properties. Because of their cost, the necessity of close control of their use, differences in effectiveness and the desirability of attaining a stable and uniform level of good oxidation resistance, or color, or viscosity or other properties in the product, it is equally desirable that the use of additives be minimized or eliminated. Another object of this invention is to provide a process for finishing lubricating oils and waxes and their fractions which, in whole or in part, eliminates the necessity of further fortification by the use of additives.

It is also recognized in the art that only through judicious application of refining methods can the inherent stability, color properties, or viscosity-temperature properties of a lubricating oil or wax be maintained, since many refining operations, including acid treatment, hydrogenation, solvent extraction, adsorption, thermal diffusion, extractive distillation, chemical and clay treatments, remove desirable constituents as well as undesirable constituents. The higher fractions of petroleum contain the more complex hydrocarbons along with various significant amounts of oxygen, sulfur and nitrogen compounds. This means that removal or transformation of one or more of these types of compounds may bring about a desirable change in the finished product for one purpose and a highly undesirable change for another purpose. The oxidation-inhibiting properties of the naturally occurring sulfur compounds is a good example of this phenomenon, for which there is ample evidence and considerable discussion in the prior art. A lubricating oil which has been severely refined to a very low sulfur content is not as stable to oxidation, nor as resistant to wear, as the same oil which has not been as severely refined and which contains small amounts of residual, naturally occurring sulfur compounds. Nitrogen and oxygen compounds have similar but lesser effects, although certain natural acidic or phenolic bodies have been shown to be exceptions to this rule. The natural sulfur compounds seem to be the principal agents responsible for the stability of straight mineral lubricating oil. The art has also established that the rate of oxidation of refined lubricating oils, though initially more stable in some respects, is accelerated during use, and the rate of oxidation of unrefined oils or less severely refined oils tends to slow down during use. Recognizing the desirability of maintaining any inherent stability or resistance to oxidation, or resistance to emulsification, that may be present in a refined oil or wax ready for finishing or decolorization, this invention provides a finishing step which does not deleteriously effect any inherent stability or other desirable property. A further object of the invention is to provide a refining or finishing process for lubricating oils and waxes involving mild hydrogenation under certain conditions using a particular catalyst.

It is well known in the art that oils and waxes may be beneficiated by treatment at elevated temperatures with hydrogen using catalysts known to promote the hydrogenation reaction. For this purpose 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 chromium, molybdenum, tungsten, iron, cobalt, and nickel. Many references are made to the use of oxides of molybdenum, either alone or admixed with other components, such as alkali metals, alkaline earth metals, oxides and sulfides; these are promoted with iron, cobalt or nickel for the purpose of hydrogenating organic materials. Mixtures of oxides and molybdenum oxide are used to promote the hydrogenation of glyceride oils. In the prior art investigations molybdate salts of various metals are designated as superior hydrogenation catalysts. The present invention is based upon the finding that for the purpose of decolorizing and stabilizing lubricating oils and waxes without deleteriously affecting the other properties thereof, silver molybdate and nickel molybdate are outstanding in their properties and are not the equivalent of the large group of catalytic materials disclosed in the prior art.

Accordingly, it becomes a primary object of this invention to provide a process for the refining of lubricating oils, waxes and their fractions under certain mild conditions of hydrogenation using silver molybdate and/or nickel molybdate as the promoting material.

A second object of this invention is to provide a process for decolorizing lubricating oils and waxes by hydrogenation at 450 to 650° F. in the presence of a silver molybdate-alumina catalyst and/or a nickel molybdate-alumina catalyst.

A third object of this invention is to provide a process for decolorizing lubricating oils and waxes in high yields

without deleteriously affecting such properties as viscosity, viscosity index, gravity, emulsibility, penetration and general stability during use and during storage.

A further object of this invention is to provide a process for decolorizing and finish-treating lubricating oils and waxes possessing natural resistance to oxidation and deterioration under conditions such that these inherent stability properties of the oils and waxes, or fractions of either, are not destroyed or altered appreciably.

These and further objects of this invention will become apparent or be described as the description of the invention proceeds.

In order to demonstrate this invention, the results of a number of experiments will be presented in which a comparison is made of different catalytic agents in hydrotreating several lubricating oils and a microcrystalline wax. In Table I are shown the results of treating an SAE 30 oil having the following characteristics:

SAE 30 oil:	
Carbon Res., Conradson, weight percent	0.73
Color, ASTM (NPA)	4½
Flash, C.O.C., ° F.	445
Fire, C.O.C., ° F.	495
Flash, P.M., ° F.	435
Vis. SUS at 100° F., secs	604
Vis. SUS at 130° F., secs	263.0
Vis. SUS at 210° F., secs	67.9
Viscosity index	93
Gravity, ° API	27.0
Refractive index, N^{20}/D	1.4920
Bromine number	1.6
Total sulfur, weight percent	0.67
Steam emulsion number	792

temperatures, on the other hand is an effective decolorizing agent and silver molybdate carries the ASTM color down to +3. Furthermore, it is apparent that the other product characteristics of the finished oil, such as VI, gravity, steam emulsion number are equivalent to, if not better than, those produced by the commercial catalyst or cobalt molybdate. In finishing lubricating oils the color of the hydrogenated product will vary somewhat with the grade of neutral oil. Light neutrals should have an ASTM color of about 1, while bright stocks should have an ASTM color of about 5, with the other neutrals having colors between these two extremes.

The problem of improving the color of waxes, particularly microcrystalline wax, is more difficult than improving the color of lubricating oils. Clay contacting or other contacting methods are capable of producing ASTM colors slightly darker than 1½ to meet a color specification of 2. Careful control of the contacting method may bring about a product color of about 1½+. Percolation methods are not capable of yielding products which meet these color specifications. The invention is further illustrated by reference to the data in Table II showing the results obtainable in hydrogenating microcrystalline wax having the following characteristics:

Color, ASTM (NPA)	+4½
Melting point, ° F.	179
Penetration at 77° F.	17
Penetration at 100° F.	27
Penetration at 120° F.	84
Total sulfur, weight percent	0.14

This microcrystalline wax was obtained from a Mid-Continent residuum having the following characteristics: boils above about 900° F.; ° API, 12.5; SUS at 210–1425; pour, +90° F.; and S, 2.1%; by treating same by propane deasphalting, phenol extracting and methyl ethyl ketone dewaxing.

TABLE I

Hydrotreating SAE 30 base oil

Exp. No.	Catalyst	Reaction Conditions				Product Characteristics											
		Temp., ° F.	Press., p.s.i.g.	LVHSV	H_2 Rate, ft.³/bbl. (STP)	Carbon Res.	Color	Flash, COC	Fire, COC	Vis. at 100° F.	Vis. at 130° F.	Vis. at 210° F.	V.I.	Grav., API	R.I.	Br. No.	Tot. Sulf.	Steam Emul. No.
1	"A"	550	250	1.0	5,700	------	+4	460	510	------	------	------	------	------	1.4920	2.0	0.63	54
2	12.2 weight percent cobalt molybdate on alumina.	600	250	1.8	2,800	0.55	+4½	445	510	562	247.2	66.1	94	27.5	1.4910	1.7	0.57	120
3	15.8 weight percent nickel molybdate on alumina.	450	250	1.0	5,700	------	3½+	------	------	------	------	------	------	27.1	1.4910	------	0.55	86
4	------do------	550	250	1.0	5,700	------	+3	------	------	------	------	------	------	27.4	1.4900	------	0.42	46
5	------do------	600	250	1.1	5,500	------	+3½	------	------	------	------	------	------	27.3	1.4902	------	0.34	54
6	16.7 weight percent silver molybdate on alumina.	600	250	1.2	5,100	0.48	+3	450	500	565	248.7	66.2	94	27.3	1.4910	1.9	0.52	57

From the results of Table I, it is apparent that a commercial catalytic hydrogenation catalyst (catalyst "A") when used under mild conditions of 550° F. and 250 p.s.i.g. gives a product which is fair as far as physical properties are concerned but is ineffective in removing color bodies. Similarly, cobalt molybdate ordinarily used in hydrotreating of lubricating oils, although being equal to commercial catalyst "A" in other respects, only reduces the color to +4½ as determined by ASTM Method D155–45T. Nickel molybdate, at even lower

In carrying out the hydrogenation experiments in Table II, the following conditions were used:

Temperature	550° F.
Pressure	500 p.s.i.g.
LVHSV	1.1.
Hydrogen charge rate	2,500 ft.³/bbl.
Recovery	100%.

TABLE II

Hydrogenation of a microcrystalline wax

Run	Catalyst	Yield, bb./ton	Color, ASTM (NPA)	M.P. °.F	Product Characteristics, Penetration at—			Total S, weight percent
					77° F.	100° F.	120° F.	
7	15.8 weight percent nickel molybdate on alumina, prepared from aluminum nitrate.	44.0	1+	178	17	29	97	0.08
8	12.2 weight percent of cobalt molybdate on alumina	14.7	4+	179	16	27	87	0.12
9	16.7 weight percent silver molybdate on alumina	40.0	1+	180	11	20	87	0.10
10	Catalyst "B"	(40.1)	(+2½)	(179)	(12)	(30)	(92)	(0.09)
11	Catalyst "S"	48.7	+2	181	12	29	95	
12	Alumina (alone)	36 0	+2½	181	12	30	98	
13	Activated carbon	46.3	3½	180	16	29	89	
14	Fuller's earth	68.1	+2	179	12	30	116	
15	Equilibrium bauxite	33.8	+2	179	19	30	116	
16	15.3 weight percent silver molybdate on silica	58.9	+4	177	14	27	81	0.13
17 [1]	25.0 weight percent copper molybdate on alumina	56.3	+1½	177	12	26	82	0.10
18 [1]	10.0 weight percent copper dichromate on pumice	44.3	4+	177	14	24	81	0.12

[1] Conducted at 550° F., 500 p.s.i.g., LVHSV of 1.4, H_2 charge rate 2,000 ft.³/bbl. (STP), recovery 100%.

In accordance with the results of Table II, it is seen that under the conditions specified, nickel molybdate and silver molybdate are outstanding in their ability to decolorize microcrystalline waxes. A comparison of experiments 7 and 9 with experiment 16 shows that alumina is the best carrier for silver molybdate and nickel molybdate. Those products which have ASTM colors of +2 or 2½+ are not commercially desirable. The process of hydrogenation at low temperatures in accordance with this invention is capable of continuous commercial production of 1+ color microcrystalline waxes, which is not possible using contacting or percolation methods.

The process of hydrogenation in accordance with this invention may be conducted on a batch or continuous basis using any type of reactor or series of reactors known to the art. A mixture of melted wax (or the lubricating oil) and hydrogen gas is fed to the hydrogenation reactor containing the catalyst. This mixture is preferably preheated to the reaction temperature of 450 to 650° F. and the reactor is maintained at 150 to 1000 lbs. per square inch pressure during the passage of the melted wax or lube oil therethrough. Unconsumed hydrogen is separated from the products and may be recycled through the hydrogenation reactor. Hydrogen circulation rates of 800 to 4000 s.c.f/bbl. are used.

In preparing a catalyst to be used in accordance with this invention, the alumina carrier may be prepared by precipitating the oxide of aluminum from an aqueous solution of a water-soluble aluminum salt such as the chloride, nitrate, sulfate, etc. This aqueous solution is treated with ammonia, carbon dioxide or acid to precipitate an aluminum compound. The precipitate is washed several times with water to remove any water-soluble impurities and then dried. The water-washing may be carried out both before and after the drying process which is carried out at 100° to 500° F. After thorough drying the prepared carrier is calcined at higher temperatures in the order of 700° to 1200° F. and may then be extruded, pilled, pelleted or otherwise shaped, granulated, or powdered. The alumina carrier is next impregnated with nickel and/or silver molybdate by immersing the carrier in a suitably concentrated aqueous solution of the nickel and silver salts and ammonium molybdate. Excess unabsorbed aqueous solution is removed by decantation, filtration or by centrifuging, and the impregnated carrier is dried at temperatures of from 100° to 1200° F. This drying is preferably carried out in stages, as is taught in the prior art, that is, by heating to 100° to 500° F. in the first stage and 750° to 1200° F. in the second stage. The heating or calcining may be accompanied by the use of an oxidizing atmosphere suitable to maintain the nickel and silver in the form of oxides associated or combined with the molybdena in the form known as molybdate salts.

The catalysts may be prepared by suspension of a hydrous alumina gel in distilled water, adding aqueous solutions of water-soluble salts of nickel and/or silver, as above mentioned, and ammonium molybdate, and precipitating these metals from the suspension in the form of combined oxides by adjusting the pH through the addition of a suitable base to a value above about 7.0. The suspension is agitated during the precipitation to bring about dispersion of the precipitated oxides in the alumina gel. The resulting mixture is gelatinous and is water-washed and dried, as above, to complete the catalyst preparation.

The catalysts may also be prepared by powdering an alumina carrier, calcining the powder and impregnating with water-soluble salts of nickel or silver or mixtures of same, under conditions to form nickel molybdate and/or solver molybdate. The alumina may be activated prior to impregnation. By each of these methods of preparation, the amount of silver molybdate or nickel molybdate is maintained within about 2 to 30 weight percent based on the total catalyst weight. Catalysts containing about 15.8 weight percent of nickel molybdate or about 16.7 weight percent of silver molybdate are superior for decolorizing waxes and lubricating oils.

The foregoing complete disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing materially from the scope or spirit of the claims:

What is claimed is:

1. The method of decolorizing a mineral lubricating oil without impairing the natural resistance to oxidation and deterioration due to naturally-occurring sulfur compounds contained therein and simultaneously improving the steam emulsion characteristics thereof which consists in contacting said mineral lubricating oil with hydrogen at a temperature of about 450° to 600° F. in the presence of a catalyst selected from the group of an alumina base containing about 15.8 weight percent of nickel molybdate and an alumina base containing about 16.7 weight percent of silver molybdate, and recovering a hydrogenerated lubricating oil characterized by improved color and reduced steam emulsion number.

2. The method in accordance with claim 1 in which the temperature is about 450° F., the catalyst is an alumina base containing about 15.8 weight percent of nickel molybdate.

3. The method in accordance with claim 1 in which the temperature is about 550° F. and the catalyst is an alumina base containing about 15.8 weight percent of nickel molybdate.

4. The method in accordance with claim 1 in which the temperature is about 600° F. and the catalyst is an alumina base containing about 15.8 weight percent of nickel molybdate.

5. The method in accordance with claim 1 in which

the temperature is about 600° F. and the catalyst is an alumina base containing about 16.7 weight percent of silver molybdate.

6. The method of decolorizing a microcrystalline wax without impairing the penetration, melting point, and natural resistance to oxidation and deterioration due to naturally-occurring sulfur compounds contained therein which consists in contacting said microcrystalline wax with hydrogen at a temperature of about 550° F. in the presence of a catalyst selected from the group of an alumina base containing about 15.8 weight percent of nickel molybdate and an alumina base containing about 16.7 weight percent of silver molybdate, and recovering

a hydrogenated microcrystalline wax of improved color, and having substantially the same melting point, penetration, and content of said sulfur compounds.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,915,448 December 1, 1959

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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 3 and 4, Table I, fourteenth column thereof, in the sub-heading under "Product Characteristics", for "V.L." read -- V.I. --; column 6, line 37, for "solver" read -- silver --; line 61, for "hydrogenerated" read -- hydrogenated --.

Signed and sealed this 14th day of June 1960.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

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