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[54] **LUBE OIL IMPROVEMENT**

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[51] **Int. Cl.** **C10g 23/02**

[58] **Field of Search** 208/264, 143

[56] **References Cited**

UNITED STATES PATENTS

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3,472,763	10/1969	Cosyns et al.	208/143
3,493,517	2/1970	Jaffe	208/254 H

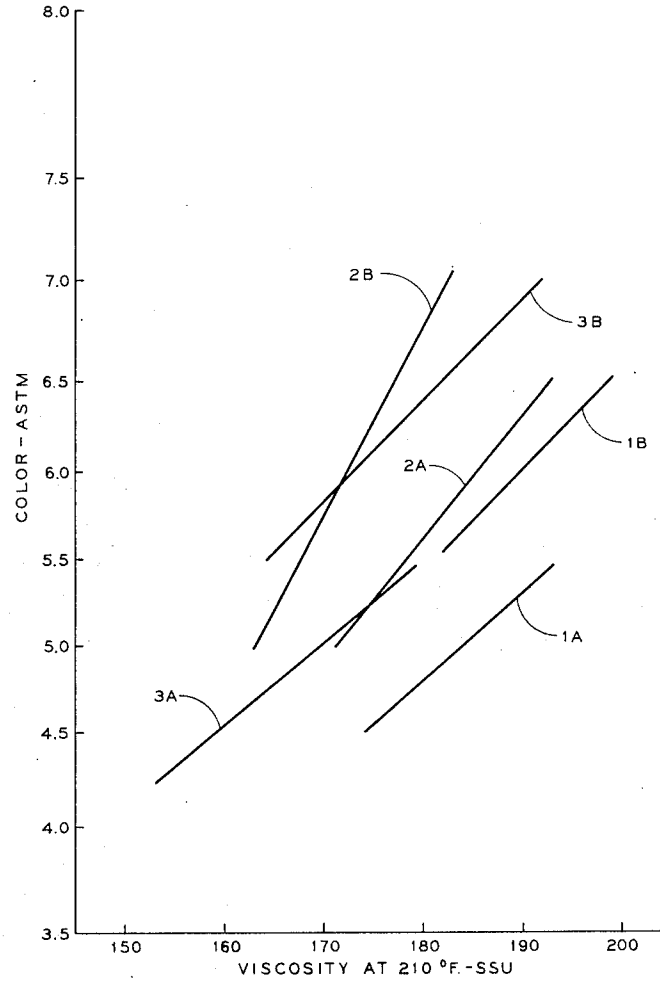
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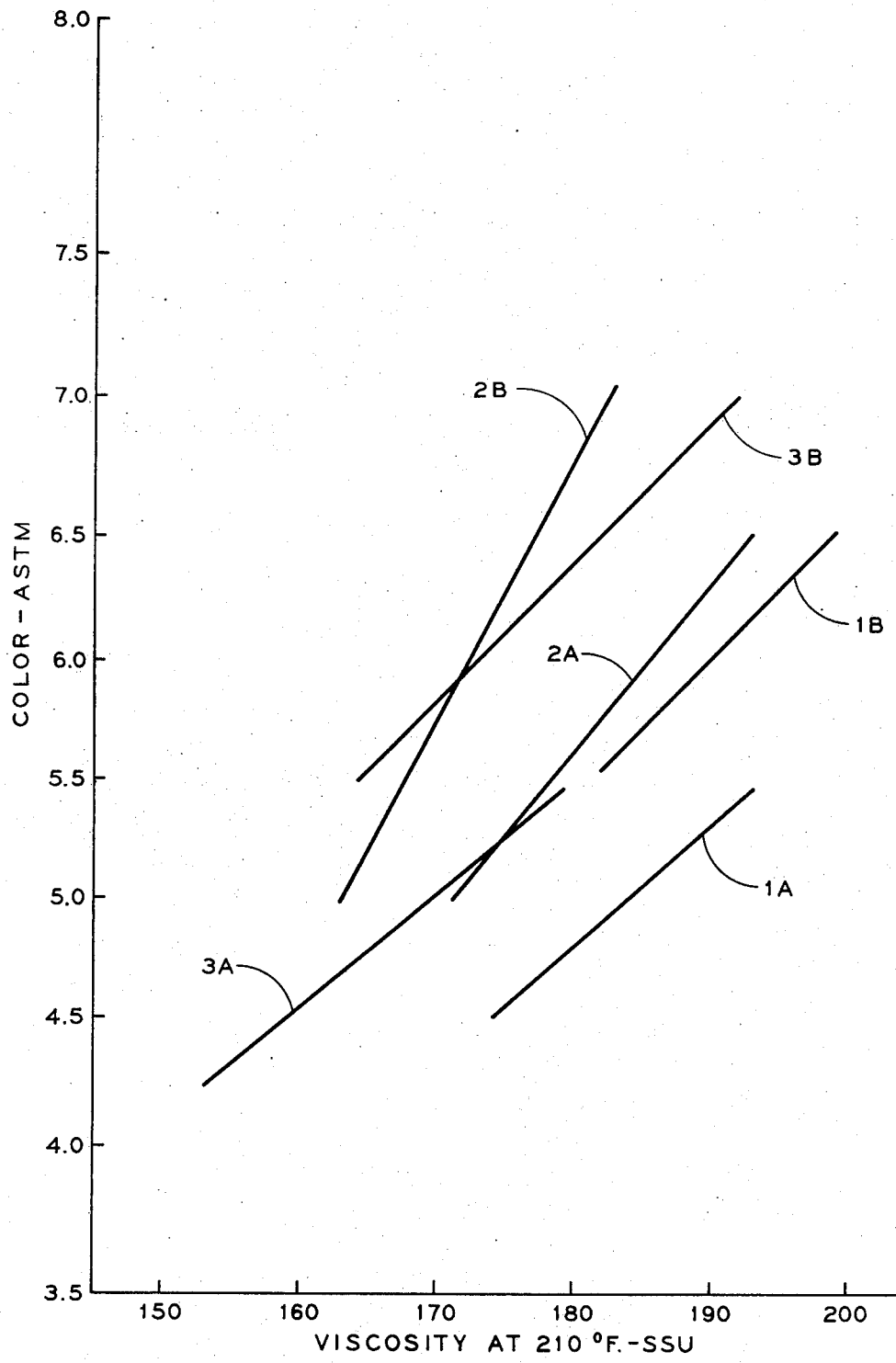
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[57] **ABSTRACT**

A process for improving the ASTM color of lube stocks which comprises contacting crude lube stock, at a temperature between 400° and 850°F., a pressure between 100 and 3000 psig, and in the presence of gaseous hydrogen, with a hydrofining catalyst having a mean pore diameter of at least 140 A. Preferred hydrofining catalysts include compositions containing Group VIB or Group VIII metals and a refractory support and dispersed metal phosphate particles such as titanium phosphate.

2 Claims, 1 Drawing Figure





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LUBE OIL IMPROVEMENT

BACKGROUND OF THE INVENTION

The present invention relates to lube oil hydrofining using solid catalysts.

Through the years numerous refining methods for lubricating oils have been used. Many of these include low-pressure fractionation, solvent extraction, solvent dewaxing, acid treating, and clay treating. Such lubricating oil treatments are discussed in Kirk-Othmer *Encyclopedia of Chemical Technology*, volume 10, The Interscience Encyclopedia, Inc., New York, pp. 147–153 (1953).

More recently, hydrofining has been used as a means for improving the quality of raw lubricating oil stocks. Such hydrogenation processes have been used generally to improve the color and stability of the oil and employ suitable hydrogenation catalysts. Typical catalysts for such hydrofining are nickel-tungsten sulfide, cobalt molybdate, nickel molybdate, cobalt sulfide, molybdenum sulfide, cobalt oxide and molybdenum oxide. These catalytic materials are generally supported on a suitable carrier or support, such as alumina, magnesia, silica, or silica-alumina.

U.S. Pat. No. 3,560,370, titled "Manufacture of Lubricating Oil with the Use of New Catalysts," is directed to a hydrocracking process for the conversion of feedstocks such as deasphalted vacuum residuum to lube oil stocks. The effluent from the hydrorefining or hydrocracking process of U.S. Pat. No. 3,560,370 is distilled to separate light fractions such as naphtha and gas oil from the lube oil fraction. The lube oil fraction is dewaxed using a conventional solvent such as methylethylketone with toluene. The lube oil may then be combined with various additives, for example, viscosity improvers such as polyisobutenes or methacrylic polyesters, to obtain an end product such as transformer oils or transmission fluids.

U.S. Pat. No. 3,483,119, titled "Hydrofining Process and Techniques for Improving the Color Properties of Middle Distillates," is directed to mixed phase or vapor phase hydrofining for color enhancement of middle distillate lube oil fractions.

Expanded catalysts, that is catalysts of an increased mean pore diameter size, for use in various reactions such as hydrotreating or hydrodesulfurization are described in U.S. Pat. No. 3,393,148 ("Cobalt and Molybdenum on Alumina Having 100 to 200 A. Pore Diameters") and U.S. Pat. No. 3,383,301 ("Resid Desulfurization with Catalysts Whose Pore Volume Is Distributed Over Wide Range of Pore Sizes"). On the other hand, U.S. Pat. No. 3,549,520, titled "Color Improvement of Sulfur-Containing Lubricating Oils with a Mordenite-Type Zeolite," is directed to the use of mordenite-type catalysts having pore or cage openings with a diameter of about only 7 A. to 10 A. for improving the color of lubricating oil feedstocks.

SUMMARY OF THE INVENTION

According to the present invention a process is provided for improving the ASTM color of lube stocks which comprises contacting crude lube stock, at a temperature between 400° and 850°F., a pressure between 100 and 3000 psig, and in the presence of gaseous hydrogen, with a hydrofining catalyst having a mean pore diameter of at least 140 A.

The present invention is based upon the unexpected finding that hydrofining catalysts with mean pore diameters above about **140** A. markedly improve the rate of color removal from lubricating oil stocks compared to similar smaller pored hydrofining catalysts.

The pore diameter of catalysts used in accordance with the present invention should be above at least about 140 A. whereas the mean pore diameter of typical hydrofining catalysts is usually below about 100 A. Hydrofining catalysts with mean pore diameters above 160 A. are particularly preferred for use in the process of the present invention. The hydrofining catalyst should also have good hydrofining activity, such as is conventionally achieved by using catalysts with surface areas above 100 m^2/g and hydrogenation metals such as Ni and W or Co and Mo.

Pore diameters referred to herein are mean pore diameters which may be calculated as follows:

$$\text{Pore diameter (A.)} = [4 \times \text{Pore Volume (cc/g)}]/[\text{Surface Area } (m^2/g)] \times 10^4$$

The pore size of the catalyst can be calculated by various methods, usually assuming the pores in the catalyst can be treated as approximately cylindrical. Pore size distribution can be obtained, for example, by capillary condensation methods as described, for example, by E. P. Barrett, L. G. Joyner, and P. H. Halenda in the *Journal of the American Chemical Society*, Vol. 73, p. 373 (1951). Larger pore sizes, usually in the range of 100 A. and larger, are frequently determined by a pressure porosimeter method described, for example, by H. L. Ritter and L. C. Drake in *Industrial and Engineering Chemistry*, Vol. 17, p. 782 (1945).

Various methods can be used to obtain the hydrofining catalyst of larger than average pore diameters for use in the hydrofining or hydrotreating step of the present invention. For example, commonly assigned application Ser. No. 774,203, filed Nov. 7, 1968 now abandoned, discloses that optimum catalyst properties, including increased pore sizes may be obtained by adding titania or recycle catalyst fines to the catalyst during the process of forming a catalyst. Also, commonly assigned Ser. No. 778,332, filed Nov. 22, 1968 now U.S. Pat. No. 3,577,353, discloses a process for producing catalysts of increased pore size obtained by extracting the catalyst with an alcohol, such as methanol, during manufacture of the catalyst particles.

Johnson and Mooi, in the *Journal of Catalysis*, 10, 342–354 (1968), discuss pore distribution in alumina catalysts. In their discussion, reference is made to treating alumina gels with methanol to exchange methanol for water in the alumina gels. The catalyst obtained upon drying and calcining had larger pore sizes than for those catalysts which were not treated with methanol to replace water prior to drying and calcining.

A particularly preferred method for producing catalysts with larger average pore diameters is described in commonly assigned application Ser. No. 3,239 now U.S. Pat. No. 3,657,151. The expanded (or increased pore size) catalyst production process described in Ser. No. 3,239 comprises (a) forming a hydrogel comprising at least one inorganic compound (which is typically converted to an oxide upon subsequent calcination), (b) adding a detergent to the hydrogel, and (c) carrying out at least part of the drying of the hydrogel after the detergent is added to the hydrogel.

Particular hydrofining catalysts which can advantageously be expanded in accordance with the above process include composites comprising discrete substantially insoluble metal phosphate particles (e.g., titanium phosphate or zirconium phosphate) surrounded by a continuous phase matrix comprising at least one solid oxide (e.g., alumina or silica-alumina) and at least one hydrogenating component selected from Group VIB metals (e.g., molybdenum or tungsten) and compounds thereof, and Group VIIIB metals (e.g., nickel or cobalt) and compounds thereof. Particularly preferred catalyst composites for production in expanded form for use in the process of the present invention are described in more detail in U.S. Pat. No. 3,493,517, the disclosure of which patent is incorporated by reference into the present specification. The hydrofining catalysts to which U.S. Pat. No. 3,493,517 is directed are particularly preferred for use in the process of the present invention for reasons including the following:

1. the hydrofining catalyst containing metal phosphates in a continuous phase matrix of other catalyst components as described in U.S. Pat. Nos. 3,493,517 and 3,546,105 can be readily expanded using methods such as the use of a high molecular weight detergent as described in Ser. No. 3,239 and/or by steaming;
2. the metal phosphate particles in the catalyst to which U.S. Pat. No. 3,493,517 is directed appear to contribute both to larger pore sizes of the catalyst composite and to enhanced hydrofining activity for the catalyst;
3. the phosphate catalysts also allow the use of a lower temperature and/or a higher space velocity to achieve a given amount of color enhancement for the crude lubricating oil feedstock compared to other catalysts. A result which is related to the latter-mentioned feature is the achievement of a relatively high viscosity for the product lube oil while still achieving substantial color improvement for the crude lube oil feedstock.

The term "hydrofining catalysts" is used in the present specification to mean a catalyst comprising Group VI and/or Group VIII metals or metal compounds and a refractory base material such as alumina and/or silica. Catalysts such as the well-known cobalt-molybdenum on alumina are typical hydrofining catalysts. The Group VI and Group VIII metals usually are in the form of oxides or sulfides in the finished catalyst. The hydrofining catalysts used in the process of the present invention should have a surface area of at least 100 m^2/g. (as determined, e.g., by the BET N_2 adsorption method), and preferably a surface area of at least 150 m^2/g.

The crude lubricating oil stocks (crude lube stocks) treated in accordance with the process of our invention can be of the type well-known in the art which boils generally in the gas oil or heavy gas oil range and above. Thus, for example, such crude lubricating oil stocks usually boil predominantly above about 600° or 650°F. and include stocks ranging from middle distillates to untreated residues obtained from vacuum or atmospheric towers. The process of the present invention is particularly advantageously applied to color improvement for crude lube stocks derived from the bottoms of a vacuum distillation column. Preferably the vacuum bottoms fraction which is fed to the process of the present invention is either subjected to aromatics removal and/or dewaxing before the vacuum distillation step or after the vacuum distillation step. Thus, for example, a reduced crude can be treated by a Duo-Sol extraction process to remove aromatics followed by a methylethylketone dewaxing process to remove paraffins to obtain a so-called "whole oil" or "whole dewaxed oil" which is then vacuum disti led into various vacuum distillate neutral cuts and a vacuum bottoms cut. The vacuum bottoms cut is particularly advantageously treated by the process of the present invention for color enhancement. The vacuum bottoms cut is frequently called "bright stock" and usually has an ASTM color of above 8.

The process of the present invention typically eliminates greater than 95 percent of the color bodies present in a heavy lube stock. For lubricating oil stocks ("lube stocks") of a relatively clear color before hydrofining it is of course more difficult to obtain a given percentage reduction in color bodies. Usually the color body reduction is at least 50 percent using the process of the present invention and for bright stocks the reduction is usually higher, above 80 percent and typically 95 percent or more.

The color of lubricating oils is generally measured using a standard colorimeter as described in ASTM method number D-1500. The color of the sample is compared with standard colored glasses which cover a range of colors from 0.5 (very light) to 8.0 (very dark). The sample is then given the color number equivalent to the glass which most closely resembles it. If the sample is darker than the number 8 color, it is diluted with a standard kerosene in the ratio: 15 volumes sample to 85 volumes kerosene. Nonhydrofined bright stock usually requires a double dilution to bring it on scale. A relative color body concentration scale can be formulated by successively diluting a dark sample in a controlled fashion and measuring each ASTM D-1500 color. This is useful since it gives an indication of the fraction of color bodies removed in a given process.

EXAMPLE AND DESCRIPTION OF THE DRAWING

The drawing is a graphical presentation of ASTM color of hydrofined lube stocks versus viscosity of the hydrofined lube stocks.

The data upon which the graph is based are tabulated in Table I below.

Included in the data which is tabulated is a comparison between a relatively large pored catalyst for crude lube oil color enhancement in accordance with the present invention and a smaller pored catalyst which is substantially the same catalyst except for a smaller average pore diameter and a larger surface area. Generally greater surface area enhances the activity and the ability of a catalyst to perform a given function in hydroconversion service. However, as can be seen by comparing curves 1*a* and 1*b* to curves 2*a* and 2*b*, a large pored (curves 1*a* and 1*b*) catalyst achieved substantially greater color enhancement for the crude lube oil feedstock than did the small pored (curves 2*a* and 2*b*) catalyst of identical composition. Both of the catalysts as indicated in Table I contained nickel and molybdenum. Also, both of the catalysts were prepared by cogelation of nickel and molybdenum compounds together with aluminum compounds and by dispersing metal phosphate particles, specifically titanium phosphate particles, in the gel before final treatment of the catalyst particles by calcination.

TABLE I

Total pressure=1,950 p.s.i.g. Hydrogen rate=5,000 s.c.f./b. (once-through)

Feed: gravity, color, viscosity	Catalyst							Hydrofining run data						First order rate const. HR-1 color[1]
		Metals, weight percent		Pore area, m.²/g.	Mean pore diam., A.	Mesh size	Bulk dens., g./ml.	Run No.	LHSV	Cat. temp., ° F.	Product Color body conc.	Product Vis. at 210° F. SSU	
	Type and number	Ni	Mo										
23.9° API color body conc. 672. ASTM D1500 color 4.5, double dilute	Cat. 1 (large pore)	9.0	18.8	165	160	1/16" whole extr	0.71	491-363	1.05	676	25.6	193	3.44
									1.03	698	16.2	174	3.82
									1.40	676	41.0	199	3.97
									1.50	700	25.6	182	4.91
									0.97	671.5	41.0	193	2.74
	Cat. 2 (small pore)	9.0	19.0	274	96	do	0.69	491-366	0.97	698	20.5	171	3.37
									1.55	698.5	51.2	183	3.99
									1.56	724	20.5	163	5.45
									0.99	701	25.6	179	3.24
	Cat. 3	2.8	13.0	178	137	do	0.72	491-365	1.04	724	16.2	153	3.87
									1.40	698	51.2	192	3.62
									1.45	724	25.6	164	4.76

[1] (Color Rate Constant) = (LHSV)·ln $\frac{\text{Feed Color Body Concentration}}{\text{Product Color Body Concentration}}$ where feed and product colors are obtained from ASTM D-1500 color. Concentration numbers are relative to a number 1 ASTM D-1500 color.

In general it is desirable to achieve a catalyst which will move the curve in the drawing as far towards the lower right-hand corner as possible as this represents maintaining a high viscosity while still achieving substantial color improvement for the crude lube oil feedstock.

Usually, the lube oil feedstock is stripped after the hydrofining treatment to remove light cracked products. Catalyst 1 in lube oil hydrofining service was advantageous not only in achieving substantial color improvement while avoiding substantial reduction of viscosity, but also in that only a relatively low amount of cracking to light products occurred with Catalyst 1 while obtaining the substantial color improvement.

Suitable operating conditions for the lube oil hydrofining color improvement process in accordance with the present invention include a temperature between about 400° and 850°F., a pressure between about 100 and 3000 psig, a hydrogen rate of about 500 to 15,000 standard cubic feet per barrel of feed (recycle hydrogen gas included) and a liquid hourly space velocity of about 0.2 to 5.0.

Although various embodiments of the invention have been described, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or scope of the present invention. It is apparent that the present invention has broad application to color enhancement of crude lubricating oil stocks using hydrofining catalysts of expanded pore size. Accordingly, the invention is not to be construed as limited to the specific embodiments or example discussed but only as defined in the appended claims.

What is claimed is:

1. A process for improving the ASTM–1500 color of lube stocks which comprises contacting crude lubricating oil stock, at a temperature between 400° and 950°F., a pressure between 100 and 3000 psig, and in the presence of gaseous hydrogen with a Group VI OR Group VIII hydrofining catalyst cogelled with an alumina gel having dispersed therein discrete insoluble metal phosphate particles and having a mean pore diameter of at least 140 A. and a surface area of at least 100 m^2/g.

2. A process in accordance with claim **1** wherein the crude lube stock is a vacuum distillation bottoms product.

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