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COLOR IMPROVEMENT OF SULFUR-CONTAINING LUBRICATING OILS WITH A MORDENITE TYPE ZEOLITE

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U.S. Cl. 208—264 11 Claims

ABSTRACT OF THE DISCLOSURE

A lubricating oil is contacted with a catalyst comprising a Group VIII metal supported on a mordenite type zeolite in hydrogen form to yield a product oil of improved color with no significant change in sulfur content. The activity of the catalyst is enhanced if the zeolite is acid-treated to increase the silica-alumina mol ratio.

This invention is concerned with the hydrogen treatment of lubricating oil fractions. More particularly, it is concerned with the production of lubricating oils of improved color and stability.

The hydrofining of lubricating oils as a means for improving various properties of the oil is well known and has been practiced commercially for several years. In conventional hydrofining the lubricating oil is passed into contact with a sulfur resistant catalyst, that is a catalyst which is not poisoned by the presence of sulfur or sulfur containing compounds, for example, cobalt molybdate on alumina in the presence of hydrogen at elevated temperatures and pressures. Depending on the reaction conditions and the particular type of lubricating oil stock various characteristics of the oil such as color, viscosity index, viscosity and pour point may be improved. However, concurrently with the improvement of the properties to commercially accepetable levels, there is also an undesirable and unavoidable reduction in the sulfur content of the lubricating oils. This sulfur reduction is undesirable particularly in stocks having a naturally low sulfur content as the sulfur containing compounds act as natural oxidation inhibitors. Accordingly, it is desirable to retain as much sulfur as possible in the lube oil stock to maintain good oxidation stability and also copper-lead bearing protection. Unfortunately with conventional processes it has not been possible to hydrofine a lube oil stock to an acceptable color and color stability level without incurring an undesirable reduction in the sulfur content and it has therefore been necessary, after conventional hydrofining to add sulfur-containing compounds to the hydrofined oil to restore its oxidation stability. As a practical matter, the sulfur content of the lubricating oil should not be below 0.1% for most lubricating oil products and preferably, to maintain superior oxidation stability, should be maintained above about 0.2 weight percent.

According to the present invention, there is provided a process for improving the properties of a lubricating oil which comprises passing the lubricating oil in the presence of hydrogen into contact with a catalyst comprising a Group VIII metal supported on a base comprising a mordenite type zeolite in decationized form.

The lubricating oil stocks used in the process of the invention advantageously have a low wax content. Suitable charge stocks are those either of the naphthenic type or paraffinic stocks which have been subjected to a preliminary dewaxing treatment as for example by solvent dewaxing. Such dewaxed stocks ordinarily have a wax content of less than 5% and frequently have a wax content of less than 2%, sometimes as low as 1% by weight.

The hydrogen used in the process need not necessarily be pure hydrogen. However, the hydrogen should not contain more than about 40 volume percent impurities. Preferably, the hydrogenating gas contains at least 75% hydrogen. Suitable sources of hydrogen include catalytic reformer byproduct hydrogen, electrolytic hydrogen and hydrogen produced by the patial oxidation of hydrocarbonaceous material followed by shift conversion and scrubbing to produce a gas containing from 95–98 volume percent hydrogen.

The hydrofining temperature should be maintained between 200 and 700° F., preferably from 450–650° F. Pressures of 100–2000 p.s.i.g. may be used, satisfactory results having been obtained at pressures between 300 and 1000 p.s.i.g. The liquid hourly space velocity may range between 0.1 and 5.0 volumes of charge per volume of catalyst per hour, a space velocity of between 0.5 and 1.5 being preferred. The hydrogen should be present in an amount of at least 100 standard cubic feet per barrel of charge, the upper maximum being limited on a practical basis. Amounts in excess of 10,000 s.c.f.b. apparently are not justified commercially, good results having been obtained using hydrogen rates of 300–1500 s.c.f.b.

The catalysts used in the process comprise a decationized mordenite type zeolite alone or more preferably in conjunction with a Group VIII metal, particularly platinum, palladium and iron. Mordenite type zeolites such as mordenite, clinoptilolite, etc. are characterized by their structure and are made up of systems of essentially independent parallel channels which provide smaller void volumes than those zeolites containing systems of connecting cavities. They are also characterized by high silica:alumina mole ratios of at least 6.

Mordenite structures are characterized by parallel sorption channels of uniform cross-section. The sorption channels are parallel to the C-axis of the crystal and are elliptical in cross section. The sorption channels dimensions of sodium mordenite, based on crystallographic studies, have been reported as having a minor diameter of 5.8–5.9 A. and a major diameter of 7.0–7.1 A. and a free diameter of 6.6 A.; the hydrogen form of mordenite is believed to have somewhat larger pore openings with a minor diameter of not less than about 5.8 A. and a major diameter less than 8 A.

The effective working pore diameter of hydrogen mordenite prepared by acid treating synthetic sodium mordenite appears to be in the range of 8 A. to 10 A. as indicated by adsorption of aromatic hydrocarbons.

Mordenite does not selectively adsorb paraffin hydrocarbons and will not function as a molecular sieve for the separation of paraffins from aromatics by adsorption. On

the other hand, zeolite structures of the type represented by faujasite, a natural zeolite, and Type A, Type X and Type L synthetic zeolites, hereinafter for the sake of simplicity referred to as molecular sieves, are capable of selectively adsorbing particular hydrocarbon types from one another. For example, when a mixture of n-heptane and benzene, is contacted with a 5 A. molecular sieve at room temperature, n-heptane is selectively adsorbed. The 4–5 A. sieves quantitatively remove the straight chain paraffins from cyclic or aromatic components of the mixture. Some of the molecular sieves will also selectively separate normal from branched chain hydrocarbons.

It appears that the effectiveness of the mordenite type zeolite catalyst structures is not solely dependent upon the size of the pore opening. The synthetic mordenites have pore sizes as determined by crystallographic measurements, somewhere between those of Type A molecular sieves on the one hand, which are capable of admitting no hydrocarbons larger than normal paraffins into the unit cells, and the Type X and Y synthetic zeolites and faujasite, on the other hand, which admit also the larger molecules. Attempts to use modified Types A, X and Y molecular sieves having pore diameters larger than conventional Type A and smaller than the conventional Types X and Y as substitutes for mordenite in this process have not been entirely satisfactory as these other zeolites give a sulfur reduction in lube oils.

Mordenite has a chain type zeolite structure in which a number of chains are linked together into a structural pattern with parallel sorption channels similar to a bundle of parallel tubes. In contrast, the Type A and Type X and Type Y synthetic zeolites and faujasite have three dimensional crystalline cage structures having 4 to 6 windows or pore openings per unit cell through which access may be had to the inner cavity or unit cell of the zeolite.

Regardless of the particular reaction mechanism involved, it has been found that the hydrogen form of synthetic mordenite type zeolites having a sodium content of less than 5 weight percent, is exceptionally effective for improving the color of lube oils without appreciable desulfurization.

In addition to the crystal structure characteristics of mordenite which distinguish it from the three dimensional lattices characteristic of molecular sieve zeolites, mordenite types zeolites are characterized by relatively high silica contents; the sodium form of mordenite has a silica to alumina mol ratio of 10 and generally contains more than 80 mol percent silica, less than 10 percent alumina, and less than 10 percent soda (dehydrated basis). In contrast, the faujasites contain 55–72 percent silica and 14–24 percent of each alumina and soda, while Type A zeolite contains about 50 percent silica and 25 percent each of alumina and soda.

It is characteristic of the catalysts used in the present invention that they are not seriously affected by nitrogen or sulfur compounds contained in the feed stock.

Synthetic mordenite is usually produced in the sodium form, i.e. as a sodium alumino silicate. The hydrogen form, or decationized form, however, which may be produced by ion exchange of sodium in the mordenite with ammonium ions followed by heating, or calcining, to drive off ammonia, or by acid treatment of sodium mordenite, is an extremely effective catalyst as illustrated in the specific examples which appear hereinafter. Advantageously acid treatment is also used to remove some of the alumina from the zeolite structure and thereby increase the relative proportions of silica to alumina in the zeolite. The weight ratio of silica to alumina is in the range of 5–6 in natural or synthetic sodium mordenite. Acid treatment suitably is effected with dilute hydrochloric acid. Mordenite structures are acid stable. In contrast, the structures of faujasite, Type A, Type X and Type Y zeolites are readily destroyed by acid. Up to 70 percent of the sodium cations in the mordenite can be replaced with hydrogen by acid treatment, e.g., by treatment with dilute aqueous hydrochloric acid. Hydrogen mordenite prepared by treating synthetic sodium mordenite with hydrochloride acid, e.g. warm 3N to 6N hydrochloric acid, is a preferred catalyst. It is desirable to calcine the mordenite, with or without metal additions, by heating in air to a temperature above 500° F., preferably to 1000° F.

Decationized mordenite or calcined hydrogen mordenite alone is an effective catalyst for the color improvement of lube oils without simultaneous desulfurization. Hydrogen mordenite exhibits extremely long catalyst life in comparison with the three dimensional zeolite structures of the 5 A. type. Group VIII metals, particularly iron, palladium, platinum and rhodium have been found especially useful catalytic additions to hydrogen mordenite type zeolitic base structures. The catalytic metal may be incorporated in or on the zeolite base either by ion exchange or by impregnation techniques already well known in the art of catalyst manufacture. Hydrogen mordenite containing from 0.1 to 5 percent platinum or palladium or 1 to 10% iron by weight, preferably 0.5 to 2.5 percent of either platinum or palladium or 2 to 8% iron are effective catalysts for use in the process of this invention. Synthetic mordenite in hydrogen form having 1 to 2.5 percent by weight palladium incorporated thereon by impregnation has proven to be a very active and very rugged catalyst. This last mentioned catalyst is highly resistant to high temperatures, permitting regeneration of the catalyst by either oxidation techniques or high temperature hydrogen treatment.

Mordenite type base catalysts comprising 1 to 10 wt. percent, preferably from 1 to 5 percent by weight iron also are very rugged catalysts in that they are capable of operating for hundreds of hours in a hydrogen atmopshere without appreciable deactivation and are capable of withstanding high regeneration temperature.

The amount of Group VIII catalytic metal added to the mordenite base affects to some extent at least the activity and resistance of catalysts to deactivation. For example, a catalyst comprising 2 percent by weight palladium on hydrogen mordenite is more resistant to deactivation than a corresponding catalyst containing 0.5 weight percent palladium.

EXAMPLE 1

This example shows that hydrogen finishing a lube oil stock by conventional means to improve its color results in a significant reduction in the sulfur content. The charge is a solvent dewaxed wax distillate having the following characteristics.

Table 1

Viscosity, SUS, 100° F./210° F.	348/54
Viscosity index	90
Pour, ° F	10
Sulfur, wt. percent	0.10
Color, Lovibond	120/6"
Color stability,[1] Lovibond	160/½"

[1] Color after heating 24 hours at 220° F.

The catalyst in Runs 1 and 2 is a conventional hydrogenation catalyst containing 3% Ni and 15% Mo on an alumina support whereas the catalyst in Runs 3 and 4 contains 2% Pd on a decationized acid treated mordenite having a silica:alumina mole ratio of 13:1.

Reaction conditions and other data appear below.

TABLE 2

Run	1	2	3	4
Temperature, ° F	450	550	450	550
Pressure, p.s.i.g.	350	350	850	850
LHSV, v./v./hr.	0.74	0.74	0.46	0.47
Hydrogen, s.c.f.b.	6,000	6,000	6,000	6,000
Color, Lovibond 6"	55	30	25	10
Color stability, Lovibond 6"	75	45	40	10
Percent desulfurization	20	40	0	10

Although in Runs 3 and 4 the space velocity is lower and the pressure is higher than in Runs 1 and 2 both of which are conducive to greater desulfurization, actually the desulfurization in Runs 3 and 4 is lower than in Runs 1 and 2 while the color improvement is greater. Liquid yields in excess of 97 volume percent in both Runs 3 and 4 indicate the essential absence of cracking.

EXAMPLE 2

The charge in the example is a solvent dewaxed oil having the following characteristics:

Table 3

Viscosity, SUS, 100° F./210° F	865/78.2
Viscosity index	86
Pour, ° F	15
Sulfur, wt. percent	0.18
Color, Lovibond	45/½"
Color stability, Lovibond	50/½"

The catalyst contains 1% Pt on a decationized acid treated mordenite support having a nominal silica-alumina ratio of 10:1. Reaction conditions and other data appear below.

TABLE 4

Run Number	5	6	7
Temperature, ° F	450	550	600
Pressure, p.s.i.g	850	850	850
LHSV, v./v./hr	0.45	0.50	0.48
Hydrogen, s.c.f.b	8,000	5,800	8,100
Viscosity, SUS, 100° F./210° F	829/76.1	895/78.5	907/80.2
Viscosity index	84	83	86
Pour, ° F	15	10	5
Sulfur, wt. percent	0.18	0.16	0.15
Color, Lovibond	10/½"	70/6"	50/6"
Color stability, Lovibond	25/½"	170/6"	150/6
Liquid yields, vol. percent	97	98	96

EXAMPLE 3

This example shows variations in the reaction conditions using a catalyst containing 0.5% Pd on the same support as in Example 2. The charge is a wax distillate having the following characteristics:

Table 5

Color, Lovibond 6"	90
Sulfur, wt. percent	0.16
Pour, ° F.	40

Reaction conditions and other data are tabulated below:

TABLE 6

Run Number	8	9	10	11
Temperature, ° F	575	575	550	600
Pressure, p.s.i.g	1,500	400	850	350
LHSV, v./v./hr	0.70	0.71	0.53	0.74
Color, Lovibond 6"	10	10	20	10
Sulfur, wt. Percent	0.15	0.15	0.14	0.16
Pour, ° F	40	40	40	30

In each run there is a considerable improvement in color with no significant change in sulfur content.

EXAMPLE 4

This example shows the practical upper space velocity limit. The catalyst here is the same as that used in Example 1 and the charge is a solvent refined acid-treated wax distillate having the following characteristics:

Table 7

Color, Lovibond 6"	60
Sulfur, wt. percent	0.7
Pour, ° F.	−30

Reaction conditions and other data are tabulated below:

TABLE 8

Run Number	12	13	14
Temperature, ° F	625	625	625
Pressure, p.s.i.g	300	300	300
LHSV, v./v.hr	2.1	4.6	1.1
Hydrogen rate, s.c.v.b	5,000	5,000	5,000
Color, Lovibond 6"	20	50	20
Sulfur, wt. Percent	0.7	0.7	0.7
Pour, ° F	−20		−20

This example shows that at the relatively mild pressure of 300 p.s.i.g., a high space velocity of 4.6 v./v./hr. does not result in as much improvement as is commercially desirable.

EXAMPLE 5

The process has an entirely different effect on light hydrocarbon oils than on lube oils as shown in this example. The charge here is a West Texas kerosine having a sulfur content of 0.14 weight percent. The catalyst contains 1% palladium on a decationized acid-treated mordenite having a silica-alumina mole ratio of 8.5. Reactions and sulfur content of the product appear below.

TABLE 9

Run Number	15	16
Temperature, ° F	650	725
Pressure, p.s.i.g	1,500	1,500
LHSV, v./v./hr	1.0	1.0
Hydrogen rate, s.c.f.b	6,000	6,000
Sulfur, wt Percent	0.021	0.008

The above data show that the kerosine is substantially desulfurized.

EXAMPLE 6

In this example a comparison is made between hydrofining using commercially available catalysts and the hydrofining process of the invention. The charge is the same as that used in Example 1 and the reaction conditions: temperature 600° F., pressure 300 p.s.i.g., space velocity 0.5 and hydrogen rate 6000 SCFB. Results are tabulated below.

TABLE 10

Catalyst	Percent desulfurization	Color, Lovibond 6"
6% Ni 18% W on alumina	75	30
3% Ni 15% Mo on alumina	40	30
4% Ni 11% MoO_3 on alumina	69	35
3% Co 10% Mo on alumina	75	45
2% Pd on hydrogen mordenite	10	10

These data show the superiority of the process of this invention for color improvement without significant sulfur reduction.

The process of this invention may be combined with other known processes to produce lube oils of superior qualities. For example, to produce an oil of outstanding stability, the oil should be first acid treated. To produce an oil of exceptional stability and a predetermined sulfur content, a high sulfur oil may be acid treated, hydrofined as described in any of Examples 2, 3, 4 and 5 or Example 1, Runs 3 and 4 and then subjected to conventtional hydrofining over a conventional desulfurizing catalyst.

For an oil of exceptional color stability the oil may be hydrofined according to the present invention and then acid or clay treated. The product may then be conventionally hydrofined to reduce the sulfur content if this is desired.

The process of the present invention may be carried out in a reaction zone in which the catalyst is in the form of a fixed bed, a fluidized bed or a slurry. In the case of a fixed bed, the reactant stream may be up-flow or down-flow, the latter being preferred.

Various other modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and there-

fore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for improving the properties of a lubricating oil which comprises contacting a sulfur-containing lubricating oil under hydrogenation conditions at a temperature between 450–650° F., a pressure between 100 and 2000 p.s.i.g., a liquid hour space velocity between 0.1 and 5 in these presence of hydrogen with a catalyst comprising a Group VIII metal selected from the group consisting of a noble metal and iron, said metal being supported on a base comprising a crystalline mordenite type zeolite in hydrogen form and recovering from the hydrogenation product a lubricating oil of improved color and having substantially the same sulfur content as the lubricating oil charged to the hydrogenation zone.

2. The process of claim 1 in which said Group VIII metal is platinum.

3. The process of claim 1 in which said Group VIII metal is palladium.

4. The process of claim 1 in which said Group VIII metal is iron.

5. The process of claim 1 in which the lubricating oil is a solvent dewaxed lubricating oil.

6. The process of claim 1 in which the lubricating oil is an acid treated lubricating oil.

7. The process of claim 1 in which the hydrogenated lubricating oil is subjected to a subsequent clay treatment.

8. The process of claim 1 in which the hydrogenated lubricating oil is subjected to a subsequent desulfurization to produce an oil of predetermined sulfur content.

9. The process of claim 1 in which the mordenite type zeolite has been converted to the hydrogen form by acid treatment.

10. The process of claim 1 in which the hydrogenated lubricating oil is subjected to a subsequent acid treatment.

11. The process of claim 1 in which the lubricating oil is a naphthenic lubricating oil.

References Cited

UNITED STATES PATENTS

2,973,317	2/1961	Watson	208—271
3,044,955	7/1962	de Groot et al.	208—271
3,114,695	12/1963	Rabo et al.	208—217
3,163,594	12/1964	Arey, Jr. et al.	208—264
3,224,955	12/1965	Anderson	208—211

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,549,520 Dated December 22, 1970

Inventor(s) HERBERT C. MORRIS

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 39, "accepetable" should be --acceptable--.

Column 2, line 18, "patial" should read --partial--.

Column 6, lines 22-23, "Reactions" should read --React conditions, Table 8, line 4 "s.c.v.b." should read --s.c.f.b.--, Table 10, line 3, "4% Ni" should read --4% NiO--.

Signed and sealed this 17th day of August 1971.

(SEAL)
Attest:

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