Sept. 5, 1967 M. L. DIRINGER ETAL 3,340,181

TOW-STAGE HYDROTREATMENT FOR WHITE OIL MANUFACTURE

Filed Aug. 6, 1965 2 Sheets-Sheet 1

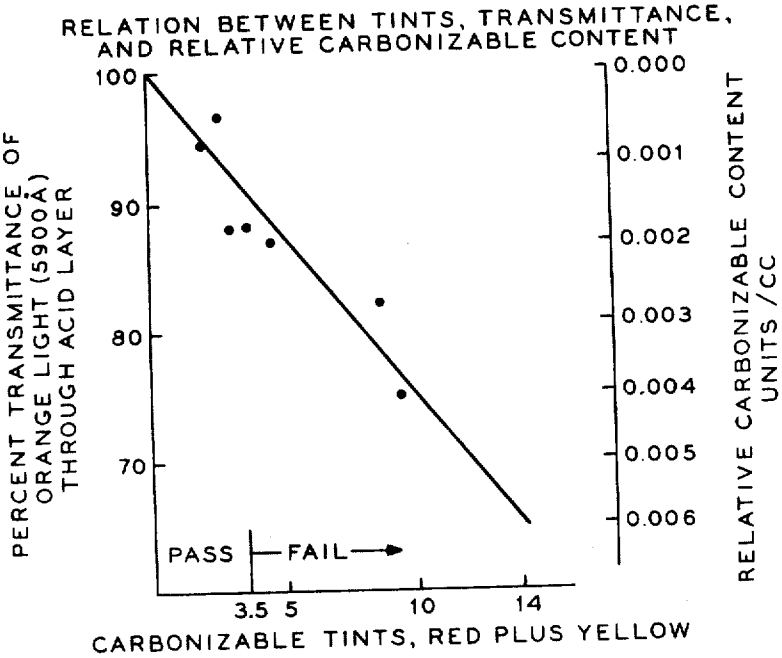


FIG. 1

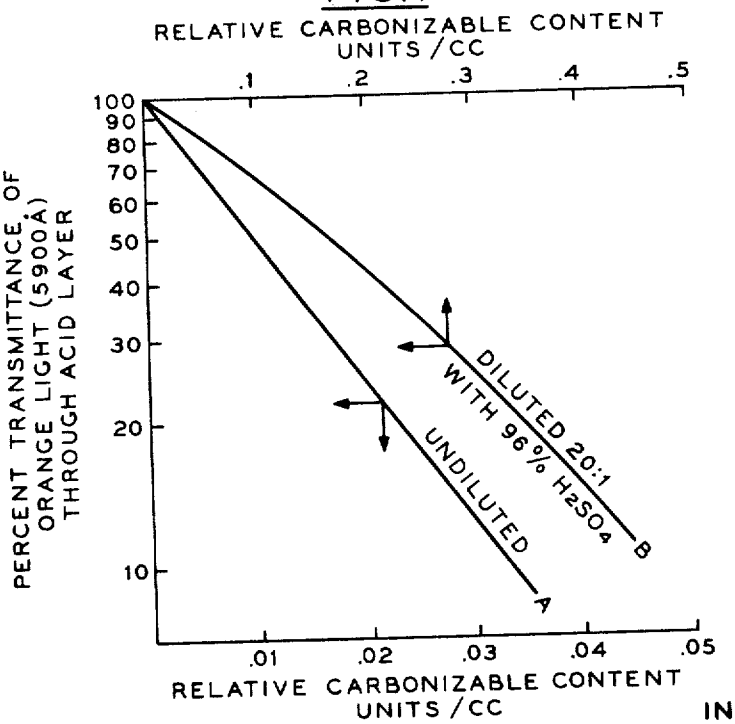


FIG. 2

INVENTORS
MONTY L. DIRINGER
CHAUNCEY R. HARE
BY Jack M. Whitney
P. E. Johnston
ATTORNEYS

Sept. 5, 1967 M. L. DIRINGER ETAL 3,340,181

TOW-STAGE HYDROTREATMENT FOR WHITE OIL MANUFACTURE

Filed Aug. 5, 1965 2 Sheets-Sheet 2

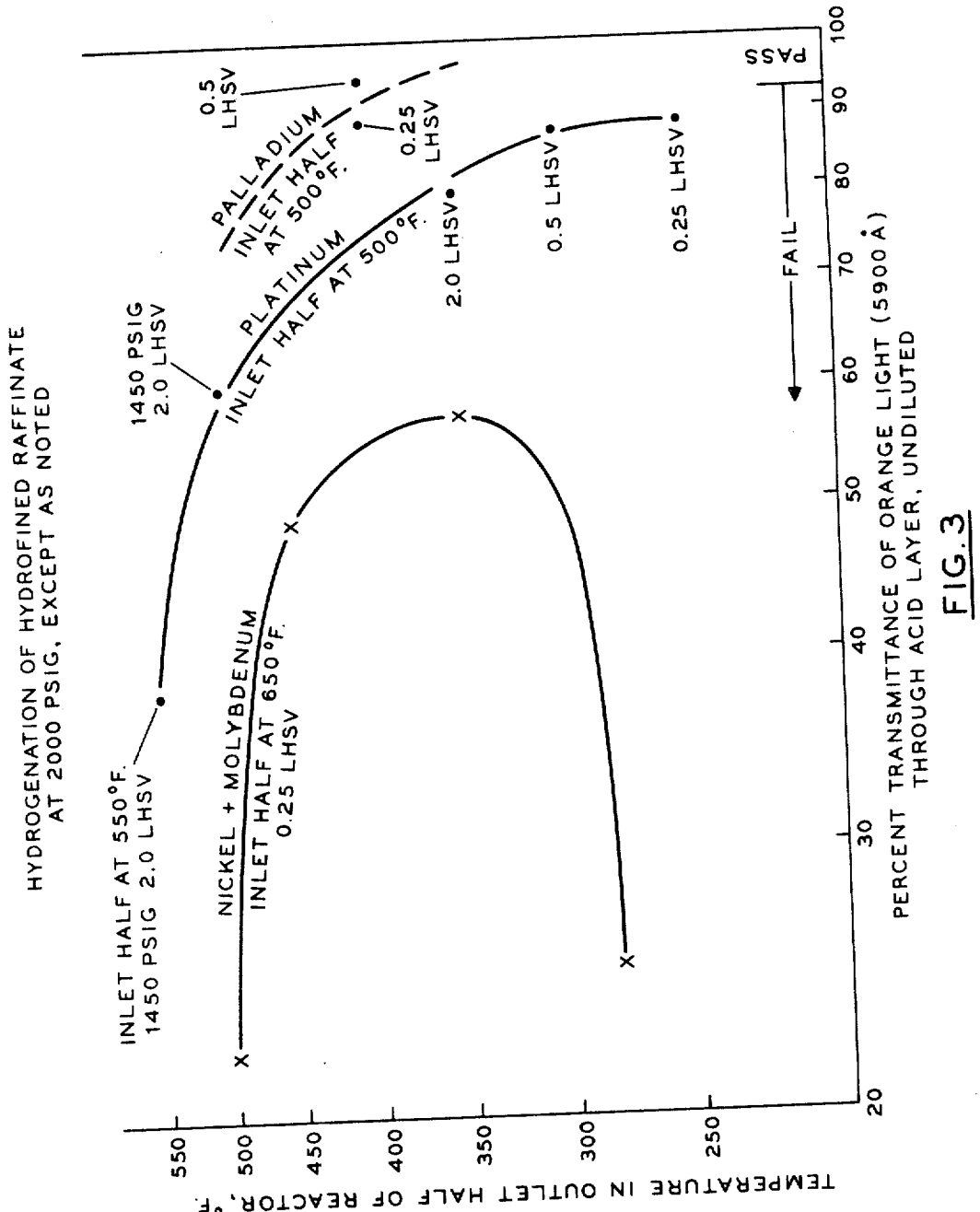


FIG. 3

INVENTORS
MONTY L. DIRINGER
CHAUNCEY R. HARE

BY P E Johnston
Jack M Whitney
ATTORNEYS

United States Patent Office 3,340,181 Patented Sept. 5, 1967

3,340,181

TWO-STAGE HYDROTREATMENT FOR WHITE OIL MANUFACTURE

Monty L. Diringer, Orinda, and Chauncey R. Hare, Berkeley, Calif., assignors to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

Filed Aug. 5, 1965, Ser. No. 477,395
8 Claims. (Cl. 208—210)

This invention relates to processes for treating hydrocarbon oils with hydrogen in the presence of solid catalysts. More particularly, the invention is concerned with a process for producing colorless mineral oil commonly referred to as white oil.

White oils are highly refined lube oil fractions, so-named because of their colorless, "water-white," appearance. Such oils find many uses where a premium is placed on quality features of uniform high purity, color, odor, and taste, for example in cosmetics. The oils must be essentially free of aromatic hydrocarbon species as indicated by an unsulfonated residue of 99–100%, preferably 100% as determined by ASTM method D–483–63. Besides having a color of +30 Saybolt (water-white) a particular specification for such oils is low absorbance of ultraviolet light in the wave lengths 2750, 2950, and 3000 Angstroms, as determined by ASTM method D–2008. In addition, the oils are desirably essentially free of carbonizable substances, the presence of which is detactable by contacting a sample of the oil with an equal volume of 95% H_2SO_4 for ten minutes at 212° F., with intermittent shaking, and then comparing the color of the oil layer with the original oil and comparing the color of the acid layer with a specific standard, as in ASTM method D–565–45. To pass the test the color of the oil layer must be unchanged and the acid layer must not be darker than the standard. To obtain numerical values the color of the acid layer may be measured with a Tintometer using Lovibond slides of the 510 (yellow) and 200 (red) series, the results being reported as yellow and red tints. In another method for obtaining a numerical indication of the relative content of carbonizable substances, the transmittance of orange light (5900 A.) through the acid layer is measured in a colorimeter relative to an empty tube.

With respect to the above, the following are typical desirable specifications for a white oil:

TABLE I

Ultraviolet absorbance at 2750 A.
=less than 0.300 (1 mm. cell)
Ultraviolet absorbance at 2950 A.
=less than 0.225 (10 mm. cell)
Ultraviolet absorbance at 3000 A.
=less than 0.180 (10 mm. cell)

Carbonizable substances, either:
Yellow tints=less than 2.3
and
Red tints=less than 1.2
or
Transmittance of orange light (5900 A.)
=at least 92%

Oils containing sufficient aromatics to have an unsulfonated residue significantly below 100% will not meet the ultraviolet absorbance and carbonizable substances specifications. An unsulfonated residue of 100%, however, provides no assurance that the ultraviolet absorbance and carbonizable substances specifications will be met, nor does a Saybolt color of +30. The ultraviolet absorbance test detects the presence of multiple-ring aromatics at trace concentrations lower than can be measured by sulfonation.

In the attached drawings, FIGURE 1 shows graphically the relationship between carbonizable tints and percent transmittance of orange light. Also shown is a scale for relative carbonizable content in arbitrary units per cc. Tints are not meaningful above 9.9 on the yellow scale or 3.9 on the red scale. Relative carbonizable content thus provides a means of describing oils which are off-scale for tints, and permits further extending the range of measurement, as shown in FIGURE 2.

In FIGURE 2, the curve labeled A shows relative carbonizable content on the lower scale versus percent transmittance of orange light through the acid layer, and is essentially an extension of the curve of FIGURE 1. The curve labeled B in FIGURE 2 is a similar plot for oils of high carbonizable content wherein the acid layer is diluted with 20 volumes of 96% H_2SO_4 per volume prior to reading percent transmittance. Relative carbonizable content is read from the upper scale for curve B, which was constructed on the basis that Beer's law applies and 100% transmittance corresponds to zero carbonizable content. These curves are presented to indicate how carbonizable contents shown in some of the examples hereinafter were determined when off-scale for yellow and red tints.

Reference to FIGURE 3 of the drawings will be made hereinafter in connection with the description of the invention. Briefly, FIGURE 3 summarizes results of several examples.

Heretofore white oils have been prepared by multiple treatment of suitable lube fractions with solvents, acids, and adsorbents. That is, more than one stage of extraction with phenol or other solvents for aromatics, in combination with more than one stage of treatment with sulfuric acid, plus at least a final clay percolation treatment, has been needed to produce product meeting such stringent purity specifications. In contrast, ordinary lube oils are usually given only a single solvent extraction, acid treatment, clay contacting, and dewaxing. Catalytic hydrofining has been applied in treating ordinary lube oils as a substitute for one or more of the conventional chemical treatments, but hydrofining treatments heretofore known are not capable of producing oil of white oil quality because of the above stringent requirements of essentially no aromatics, water-white color, low ultraviolet absorbance, and freedom from carbonizable substances.

It has now been found that oil of white oil quality can be produced from a hydrocarbon oil feed consisting essentially of solvent-refined and acid-treated naphthenic lube oil raffinate having an unsulfonated residue as low as 95%, or even lower, by a combination of treatment with hydrogen in the presence of a sulfactive hydrogenation catalyst and treatment with hydrogen in the presence of a noble metal hydrogenation catalyst.

In accordance with the present invention, a lube oil having an unsulfonated residue of at least 75% is passed with hydrogen at elevated pressure through a reaction zone to contact therein a sulfactive hydrogenation catalyst having denitrification activity at temperatures maintained in the range 600–900° F. until aromatics are essentially eliminated, and recovering a hydrofined oil having an unsulfonated residue of at least 98%. The hydrofined oil and hydrogen are then passed at elevated pressure through a reaction zone to contact therein a noble metal hydrogenation catalyst at temperatures maintained in the range 200–550° F. including a terminal temperature below about 450° F. until carbonizable substances are essentially eliminated, and recovering water-white oil having low absorbance in the ultraviolet at 2750, 2950, and 3000 A. It is most important that the final treatment with the noble metal hydrogenation catalyst be completed at a low temperature below about 450° F., preferably below 425° F., and still more preferably not substantially in excess of 400° F. to eliminate carbonizable substances and obtain low ultraviolet absorbance. It

has been found that even brief contact of the oil with the reaction zone steel internals at a final temperature of 450° F. causes degradation of the product. Thus, an initial portion of the contacting with the noble metal catalyst may be at elevated temperatures as high as 550° F., but the temperature at the reactor outlet must be substantially lower as indicated. Also, it appears that the average temperature in the over-all contacting with noble metal hydrogenation catalyst should be at least about 350° F.

The lube oil employed as feed to the process of this invention may be raffinate prepared by conventional solvent extraction and/or acid treating processes well known to those skilled in the art, if suitable straight run oil is not available. For example, the solvent refining may be carried out using SO_3, phenol, cresol, chlorese, nitrobenzene, furfural, and/or other suitable solvents or mixtures thereof for removing aromatic hydrocarbons and thereby increasing the unsulfonated residue of the raffinate. The acid treating is usually carried out using concentrated sulfuric acid, again for the purpose of removing sulfonatable materials and color bodies. The treatments are sufficiently severe in terms of solvent to oil ratio and acid to oil ratio to provide a raffinate having an unsulfonated residue of at least 75% preferably at least 90%. In the contacting with the sulfactive hydrogenation catalyst prior to contacting with the noble metal hydrogenation catalyst the unsulfonated residue is to be increased to at least 98%, and preferably to 99% or higher, which is difficult to accomplish if the unsulfonated residue of the raffinate feed is below about 90%. The yield loss becomes substantial if the unsulfonated residue of the feed must be raised from below 80% to the desired 99% by hydrofining.

The boiling range and viscosity of the feed oil will be selected depending on the particular grade of white oil desired to be produced. Thus, each white oil product has its own additional specifications in addition to ultraviolet absorbance and carbonizable substances, including such properties as gravity, flash point, viscosity, and pour point. The feed should have a slightly lower gravity and higher viscosity than desired in the white oil product, as some viscosity reduction and gravity increase will accompany the catalytic treatment with hydrogen. If dewaxing is needed to obtain the desired product pour point, the dewaxing is preferably carried out as part of the feed preparation because control of the catalytic treatments with hydrogen to achieve the final product specifications is complicated if a dewaxing step must be interjected or applied to the final product.

In addition to the small amount of aromatics indicated by the high unsulfonated residue of at least 75%, the feed will contain naturally-occurring sulfur and nitrogen compounds. In accordance with the present invention, these compounds are substantially completely eliminated in the contacting with sulfactive hydrogenation catalyst. The final product may have poor oxidation stability due to the elimination of natural inhibitors, but will exhibit improved response to inhibitor additives.

Aromatics and sulfur and nitrogen compounds are essentially eliminated from the feed to obtain a hydrofined oil having an unsulfonated residue of at least 98% by contacting the raffinate with hydrogen and a sulfactive hydrogenation catalyst in a reaction zone at elevated temperature and pressure. The contacting may be carried out in a variety of ways known in the art, using concurrent or countercurrent flow of oil and hydrogen, fluidized catalyst particles, gravitating catalyst particles, or fixed beds of particles. Most suitably, however, the feed oil and hydrogen are preheated to reaction temperature at elevated pressure and pass through a reactor containing one or more fixed beds of catalyst particles. The effluent of the reaction zone is then cooled to condense the normally liquid hydrocarbons and separate them from hydrogen-rich gas which can be recycled.

The sulfactive hydrogenation catalyst employed must have substantial denitrification activity as it is desired to eliminate substantially completely the organic nitrogen compounds contained in the feed. Suitable catalysts comprise combinations of the Group VI metals and compounds thereof, particularly the oxides and sulfides, with Group VIII metals and compounds thereof, particularly the oxides and sulfides. More particularly, catalysts comprising combinations of molybdenum and/or tungsten sulfide with nickel sulfide, alone or associated with porous refractory oxide materials are greatly preferred, especially such catalysts containing from 15 to 30 weight percent of molybdenum or tungsten associated with alumina-containing supports. The preferred supports or carriers comprise a major portion of alumina and a minor portion of silica. Pure alumina is a suitable carrier, however, as are various silica-magnesia composites. An exemplary preferred catalyst thus comprises nickel-molybdenum-alumina-silica wherein alumina is present in greatest concentration, molybdenum in the next greatest concentration, and silica and nickel are present in lesser concentrations of 5–5 weight percent. It is desired that the catalyst not be strongly acidic as a hydrocracking centrations of 5–15 weight percent. It is desired that activity and resistance to poisoning or deactivation by sulfur or nitrogen compounds.

Such catalysts, as is well known, may be prepared by a variety of methods including impregnation of nickel and molybdenum compounds on previously formed calcined supports, coprecipitation or cogellation of all ingredients simultaneously, and combinations wherein some of the ingredients are coprecipitated and others are later impregnated on the coprecipitate or cogel.

Conditions employed in the treatment of the oil feed with the sulfactive hydrogenation catalyst include elevated pressures of above 1000 p.s.i.g. and up to 4000 p.s.i.g. or higher. Temperatures of 600° F.–900° F., preferably 650°–800° F., are used, and the oil is passed through the catalyst particles, where a fixed bed is employed, at the rate of from 0.2 to 10 volumes of oil per hour per volume of catalyst (LHSV), preferably in the lower range of 0.3–2 LHSV. Hydrogen-rich gas circulation rate is in the range 2,000–20,000 standard cubic feet per barrel of oil, and hydrogen consumption in the reactions is usually in the amount of from 50 to 1,000 s.c.f./bbl. of oil, depending on the content of aromatics and the concentration of sulfur and nitrogen compounds in the feed.

As mentioned, the conditions used are selected so as to essentially eliminate aromatics and sulfur and nitrogen compounds to provide a hydrofined oil having an unsulfonated residue of at least 98%, and preferably 99% or higher. The concentration of nitrogen compounds is to be reduced to below 10 p.p.m., and more desirably to below 1 p.p.m. The concentration of sulfur compounds is to be lowered to below 100 p.p.m., and more desirably to below 50 p.p.m. The obtaining of a very high unsulfonated residue in the product while at the same time reducing the sulfur and nitrogen concentrations to very low levels is difficult to achieve in that the use of elevated temperatures to obtain conversion of the contaminating hetero organic compounds is somewhat inconsistent with attempting to completely saturate aromatics. This is one reason why the feed preferably has an unsulfonated residue of at least 90% to begin with, and to favor the hydrogenation pressures of at least 2000 p.s.i.g. are preferably employed.

Ammonia and hydrogen sulfide by-products are removed from the hydrofined liquid oil effluent of the first stage by water washing and/or hydrogen stripping, and the oil may also be given a simple fractionation to remove low boiling hydrocarbon by-products from the oil prior to contacting in the next reaction zone with the noble metal hydrogenation catalyst.

The following examples illustrate typical operating conditions and results obtained in the treatment with sulfactive hydrogenation catalyst.

Examples 1–3

The feedstock treated was a refined lube raffinate prepared by furfural extraction and sulfuric acid treating, having the inspections shown in the first column of Table II below, and selected for producing the type of white oil defined by the typical inspections in the last column. The catalyst employed was the sulfided nickel-molybdenum-alumina type, prepared by impregnation of alumina with Ni and Mo compounds. Operating conditions and hydrofined oil inspections are shown below.

TABLE II

	Example		
	1	2	3
Temperature, ° F	675	675	700
Pressure, p.s.i.g.	2,250	2,250	2,500
Space velocity, LHSV	0.5	1.0	0.5
H_2 flow rate, s.c.f./bbl.	4,500	4,500	4,000

	Feed	Hydrofined oil	Hydrofined oil	Hydrofined oil	Typical white oil
Inspections:					
Gravity, ° API	26.3	28.6	27.5	29.5	24.7–28.2.[1]
Aniline point, ° F	204.6	219.4	219.6	218.5	224.
Sulfur, p.p.m.	2,900	35	35	46	<1,000.
Nitrogen, p.p.m.	196	0.2	0.9	0.3	<1.
Unsulfonated residue, percent	95	99.2	99.6	99.0	100.
Flash, ° F	405	365	390	350	360 min.[1]
Viscosity, SSU at 100 ° F	407.5	278.6	333	205.7	330–350.[1]
Color, Saybolt	[2] 6	+3	+5	+19	+30.[1]
Pour point, ° F	−30	−45	−35	−30	0 max.[1]
Refractive index	1.4868	1.4817	1.4838	1.4790	1.4831.
Boiling range, IBP–EP, ° F	575–985	530–972	530–968	511–976	757–900.

[1] Typical specifications.
[2] ASTM.

The hydrofined oil products of Examples 1–3 above are all suitable for treating with a noble metal hydrogenation catalyst to prepare white oil in accordance with the invention, since all have unsulfonated residue values of at least 99%. In other tests it was demonstrated that hydrofined oil with an unsulfonated residue of 98–99% could be produced from dewaxed, solvent-refined, distillate raffinate feeds having unsulfonated residues as low as 78%. These tests are summarized in the following Table III.

TABLE III

	95% Boiling point, ° F.	Sulfur, p.p.m.	Nitrogen, p.p.m.	Unsulfonated residue, percent
Feed, phenol raffinate	786		180	82
Hydrofined oil		6	0.3	98.6
Feed, phenol or SO_2 raffinate	816	5,200	141	78
Hydrofined oil		4	0.1	99.6
Feed, duosol raffinate	1,000	1,700	112	92
Hydrofined oil		4	0.3	99
Feed, duosol raffinate	818	1,200	44	93.6
Hydrofined oil		3	0.1	98.8

The noble metal hydrogenation catalyst employed in the second stage contacting preferably comprises a minor amount of platinum or palladium associated with a strongly acidic carrier or support such as an active silica-alumina cracking catalyst. Palladium- or platinum-alumina hydrogenation catalysts may be employed to lesser advantage in the sense that such catalysts appear to be more sensitive to the small amount of organic sulfur in the hydrofined oil and do not retain high activity for as long as the noble metal silica-alumina catalysts.

Except for the temperature of operation, the conditions in the contacting with the noble metal hydrogenation catalysts are similar to those used in the contacting with sulfactive hydrogenation catalysts. Thus pressures of 1000–4000 p.s.i.g., preferably about 1500 p.s.i.g. or higher, space velocities of 0.2–10 LHSV, proferably 0.3–2 LHSV, and hydrogen throughputs of 2,000–20,000 s.c.f./bbl. of oil are employed. Lower temperatures of 200–550° F. are used, however, and if a temperature as high as 550° F. is employed, such should only be used in the initial portions of the contacting. The contacting must be completed at lower temperatures of below about 450° F., and preferably not substantially in excess of 400° F. Hydrogen consumption is small and difficult to determine separately from leakage and losses by solubility in the oil, as the unknown materials being hydrogenated are present in such small quantities.

The following examples illustrate results obtained at various operating conditions and with different catalysts in hydrogenating the hydrofined oil produced in Example 3 above. In these examples a reactor was employed in which the first half or inlet portion of the catalyst could be operated at a higher or lower temperature than the second half or outlet portion of the catalyst, and accordingly reference is made to the temperatures in the respective halves and to the average temperature.

Examples 4–6

These examples compare results obtained at similar operating conditions with different catalysts. In Example 4 the catalyst was a sulfided nickel-molybdenum-alumina-silica cogel sulfactive hydrogenation catalyst having high denitrification activity and only moderate, non-acidic, hydrocracking activity. In Example 5 the catalyst was 1.7% platinum on alumina. In Example 6 the catalyst was 2.0% palladium on a silica-alumina cracking catalyst support. Operating conditions and feed and product inspections are shown in Table IV below.

TABLE IV

	Example		
	4	5	6
Catalyst	Ni-Mo	Pt-alumina	Pd-silica-alumina
Temperature, average ° F	450	450	450
Inlet half/outlet half	500/400	500/400	500/400
Pressure, p.s.i.g.	2,000	2,000	2,000
Space velocity, LHSV	0.25	0.25	0.5
H_2 flow rate, s.c.f./bbl.	13,500	14,000	6,200

TABLE IV—Continued

	Feed [1]	Product	Product	Product
Inspections:				
UV absorbance at 2,750 A.	4.8	0.76	0.035	0.000
UV absorbance at 2,950 A.	15	0.14	0.000	0.000
UV absorbance at 3,000 A.	13	0.11	0.000	0.000
Carbonizable tints:				
Yellow	>9.9		1.7	1.3
Red	>3.9		0.6	0.6
Relative carbonizable content	0.14	0.022		

[1] Hydrofined oil of Example 3.

Referring back to the desired typical inspections for white oil previously set forth in Table I, it is seen that the products obtained using the noble metal platinum and palladium catalysts are acceptable. These products also meet the other typical specifications shown in Table II hereinabove. The product obtained using the sulfactive nickel-molybdenum catalyst is not acceptable. In other tests with the sulfactive catalyst it was found that a lower carbonizable content could be obtained by operating the inlet half of the reactor hotter and the outlet half cooler, but no conditions were found at which an acceptable product was obtainable. Some of these other tests are shown summarized in the attached FIGURE 3 of the drawings.

Referring now to FIGURE 3, the curve labeled "nickel+molybdenum" shows percent transmittance of orange light, as a measure of relative carbonizable content of the product, as a function of temperature in the outlet half of the reactor when the inlet half was at 650° F. As shown, the maximum transmittance, indicating minimum carbonizable content, at 350° F. outlet is still too high, and is higher at both 450° F. and 280° F. with the sulfactive catalyst. At 550° F. in the outlet half, the product carbonizable content was greater than the hydrofined oil feed (not shown because off-scale for FIGURE 3). Thus, the sulfactive hydrogenation or hydrofining catalysts are not capable of producing white oil meeting the specifications set forth.

Also in FIGURE 3, the curve labeled "platinum" shows results obtained in other tests with the 1.7% Pt on alumina catalyst at different conditions as indicated. In these tests the minimum specification of at least 92% transmittance at 5900 A. was not achieved. Example 5 of Table IV above showed that acceptable product was obtained at a terminal temperature of 400° F. That data, however, was obtained with fresh platinum-alumina catalyst whereas the data shown on FIGURE 3 was obtained with catalyst which had been used longer. The following Table V presents data showing how product quality declined with time on stream while treating the hydrofined raffinate with the platinum catalyst at 2000 p.s.i.g., 0.25 LHSV, at 450° F. (500° F. inlet half and 400° F. outlet half).

TABLE V

Pt-alumina catalyst age, bbls. feed/bbl. catalyst	8	23
Product inspections:		
UV absorbance at:		
2,750 A	0.035	0.112
2,950 A	0.004	0.032
3,000 A	0.000	0.030
Carbonizable tints:		
Yellow	1.7	7.2
Red	0.6	1.7

Referring again to FIGURE 3 of the drawing, the data points thereon labeled "palladium" represent tests with the palladium-silica-alumina catalyst of Example 6 at several space velocities, which tests were continued while producing acceptable product for considerably longer than could be done with the platinum-alumina catalyst. The following Table VI presents further data regarding these tests, carried out at 2000 p.s.i.g., 450° F. (500° F. inlet half and 400° F. outlet half) and at H_2 flow rates of 5,000–13,000 s.c.f./bbl.

TABLE VI

Pd-silica-alumina catalyst age, bbls. feed/bbl. catalyst	8	21	25	29
Space velocity, LHSV	0.25	0.5	1.0	2.0
Product inspections:				
UV absorbance at:				
2,750 A	0.000	0.000	0.002	0.009
2,950 A	0.000	0.000	0.000	0.000
3,000 A	0.000	0.000	0.000	0.000
Carbonizable tints:				
Yellow	1.9	1.3	1.4	2.8
Red	0.8	0.6	0.4	1.0

Thus the palladium-silica-alumina catalyst is considerably more effective for removing materials responsible for UV absorbance, and it retains activity for removing carbonizable substances longer than the platinum-alumina catalyst. In other tests with the palladium catalyst carbonizable tints became excessively high (1) when the entire reactor was operated at 550° F., (2) when the entire reactor was operated at 350° F., and (3) when the entire reactor was operated at 400° F. and the space velocity was 4.0 LHSV. At 350° F. throughout the reactor the catalyst appeared to lose activity rapidly and irreversibly. At 550° F. throughout, some cracking occurred.

Control of the operating conditions in the process of the invention to eliminate carbonizable substances is particularly important because off-test products cannot be effectively upgraded in this respect by such conventional clean-up operations as clay testing. For example, when off-test product having a relative carbonizable content of 0.007 and bromine number of 0.025 was treated with attapulgus clay at the rate of 10,000 gallons per ton, the carbonizable content did not change and the bromine number was lowered only to 0.022 (essentially unchanged). Absorbance in the ultraviolet wave lengths was improved, however.

Economic evaluations have shown that the two-stage treatment with hydrogen in accordance with the invention is a considerably less expensive route for producing white oil than the repeated chemical treatments heretofore used. This is the case regardless of whether the platinum or the palladium catalyst is used in the final hydrogenation. The silica-alumina supported catalyst is preferred because of its greater activity and stability. The lesser effectiveness of alumina as the carrier appears to be related to the presence of minor amounts of sulfur contaminants in the hydrofined raffinate. More complete removal of sulfur in the first stage hydrofining could make platinum-alumina more attractive for the second stage. In this respect it will be noted that white oils produced in accordance with the invention are characterized by low sulfur content of below 50 p.p.m,, whereas ordinary white oils will contain above 100 p.p.m. sulfur.

We claim:

1. A process for producing colorless oil which comprises providing a hydrocarbon oil feed consisting essentially of a refined lube oil having an unsulfonated residue of at least 75%, passing said oil and hydrogen at elevated pressure through a reaction zone to contact therein a sulfactive hydrogenation catalyst having denitrification activity at temperatures maintained in the range 600–900° F. until aromatics and sulfur and nitrogen compounds are essentially eliminated, recovering a hydrofined oil having an unsulfonated residue of at least 98%, passing said hydrofined oil and hydrogen at elevated pressure through a reaction zone to contact therein a noble metal hydrogenation catalyst at temperatures maintained in the range 200–550° F. including a terminal temperature below about 450° F., until carbonizable substances are essentially eliminated, and recovering water-white oil having low absorbance in the ultraviolet at 2750, 2950, and 3000 A.

2. The process of claim 1 wherein said feed has an unsulfonated residue of at least 90%.

3. The process of claim 1 wherein said hydrofined oil has an unsulfonated residue of at least 99%.

4. The process of claim 1 wherein the terminal temperature in the reaction zone wherein hydrofined oil is contacted with the noble metal hydrogenation catalyst is not substantially in excess of 400° F.

5. The process of claim 1 wherein the average temperature over-all during contacting the hydrofined oil with the noble metal hydrogenation catalyst is at least 350° F.

6. The process of claim 1 wherein said noble metal hydrogenation catalyst comprises platinum or palladium and a strongly acidic silica-alumina carrier.

7. A process for producing colorless oil which comprises: solvent treating a crude lube oil fraction containing aromatics and sulfur and nitrogen compounds with a solvent for aromatics to remove aromatics, and recovering a refined lube raffinate having an unsulfonated residue of at least 95%; passing said raffinate and hydrogen at elevated pressure through a reaction zone to contact therein a sulfided nickel-molybdenum sulfactive hydrogenation catalyst at temperatures maintained in the range 650–800° F. until aromatics and sulfur and nitrogen compounds are essentially eliminated, and recovering a hydrofined oil having an unsulfonated residue of at least 99%; passing said hydrofined oil and hydrogen at elevated pressure through a reaction zone to contact therein a noble metal hydrogenation catalyst comprising palladium associated with silica-alumina at temperatures maintained in the range 350–500° F. including a terminal temperature not in excess of 400° F., until carbonizable substances are essentially eliminated, and recovering water-white oil having low absorbance in the ultraviolet at 2750, 2950 and 3000 A.

8. White oil boiling between 500° and 1,000° F. and containing less than 50 p.p.m. sulfur and prepared by hydrogenating a hydrofined lube raffinate having an unsulfonated residue of at least 99% using a noble metal catalyst at an average temperature of 350–450° F. including a temperature not in excess of 400° F. during the last half of the contacting with the catalyst.

References Cited

UNITED STATES PATENTS

3,003,953	10/1961	Evans	208—254
3,006,843	10/1961	Archibald	208—264
3,121,678	2/1964	Behymer et al.	208—264
3,245,903	4/1966	Champagaat	208—264

DELBERT E. GANTZ, *Primary Examiner.*

S. P. JONES, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,340,181 September 5, 1967

Monty L. Diringer et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the two sheets of drawings, line 2, for "TOW-STAGE", each occurrence, read -- TWO-STAGE --; column 1, line 28, for "detactable" read -- detectable --; column 3, line 25, after "75% insert -- and --; column 4, line 22, beginning with "centrations of" strike out all to and including "nitrogen compounds." in line 26, same column 4, and instert instead -- centrations of 5-15 weight percent. It is desired that the catalyst not be strongly acidic as a hydrocracking catalyst, but rather that it have higher hydrogenation activity and resistance to poisoning or deactivation by sulfur or nitrogen compounds. --; column 6, line 2, for "proferably" read -- preferably --; column 7, TABLE IV- Continued, fourth column, line 2 thereof, for "0.000" read -- 0.004 --; column 8, line 30, for "products" read -- product --.

Signed and sealed this 29th day of October 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents