

Jan. 29, 1974

M. C. KIRK, JR

3,788,976

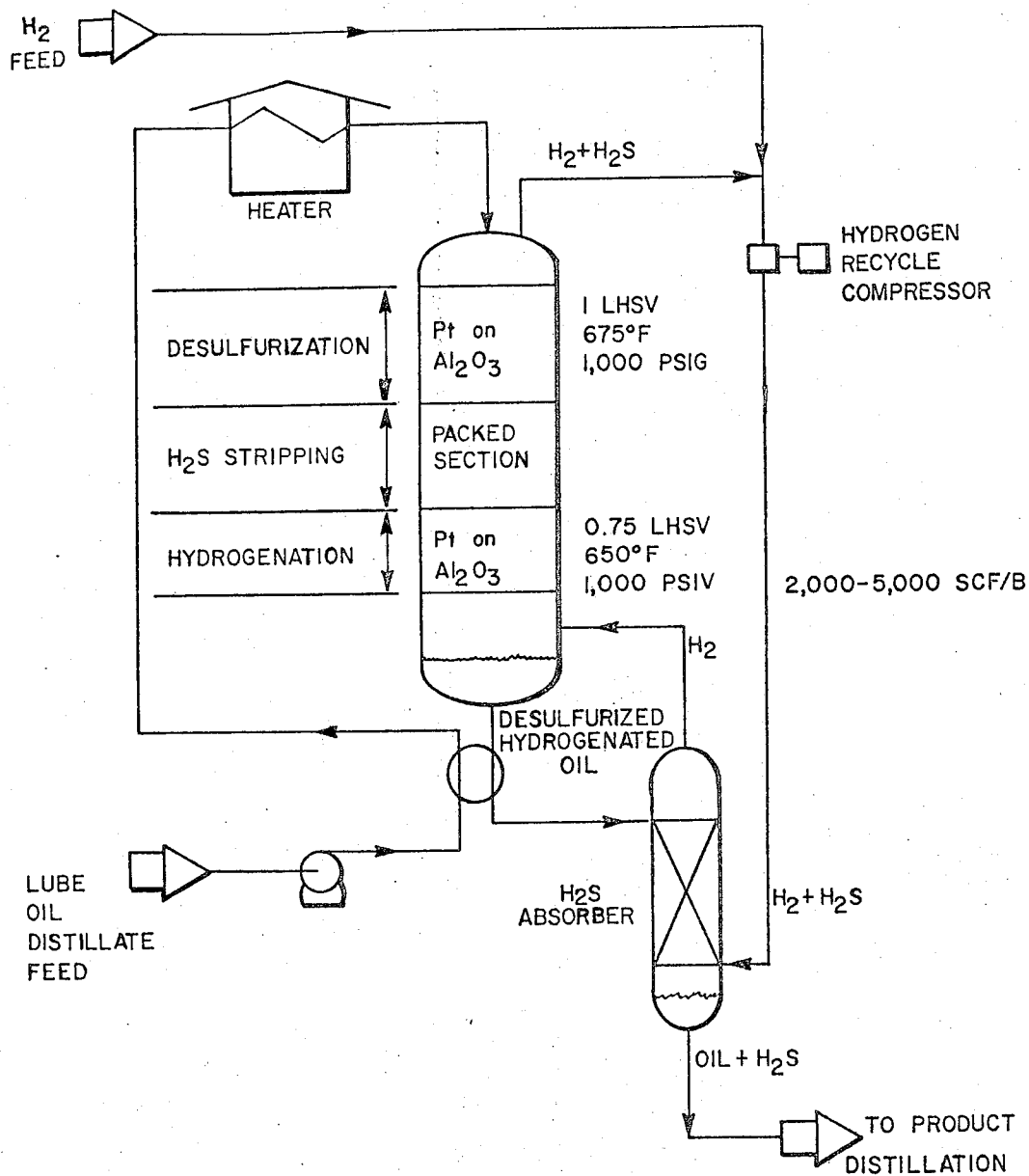
MULTI-STAGE PROCESS FOR PRODUCING HIGH UR OIL BY HYDROGENATION

Filed May 18 1972

3 Sheets-Sheet 1

FIG. 1

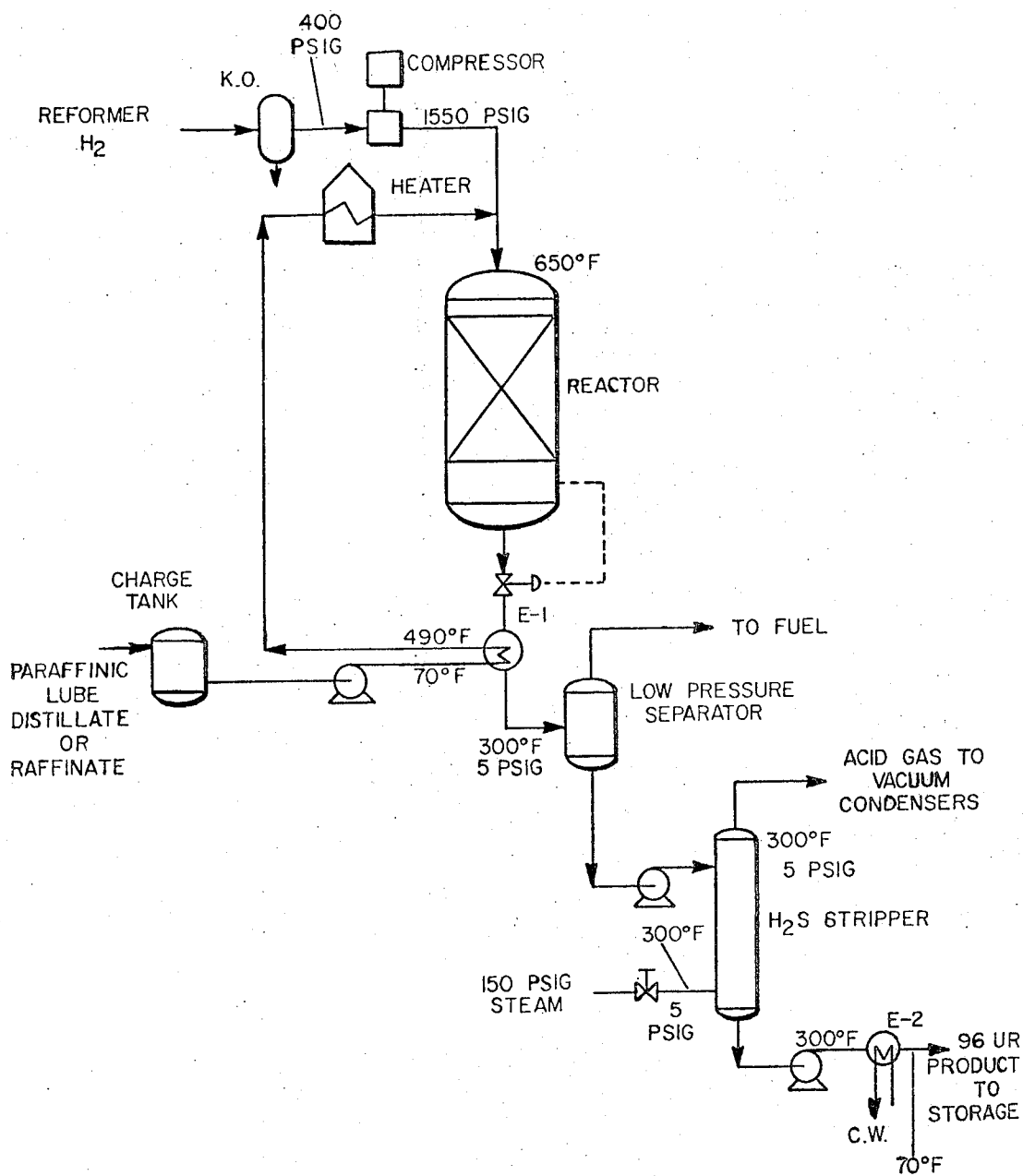
SINGLE STAGE SPRAY OIL-WHITE OIL HYDROGENATION PROCESS



3,788,976

3 Sheets-Sheet 2

TRICKLE PHASE 96 UR SPRAY OIL HYDROGENATION



Jan. 29, 1974

M. C. KIRK, JR

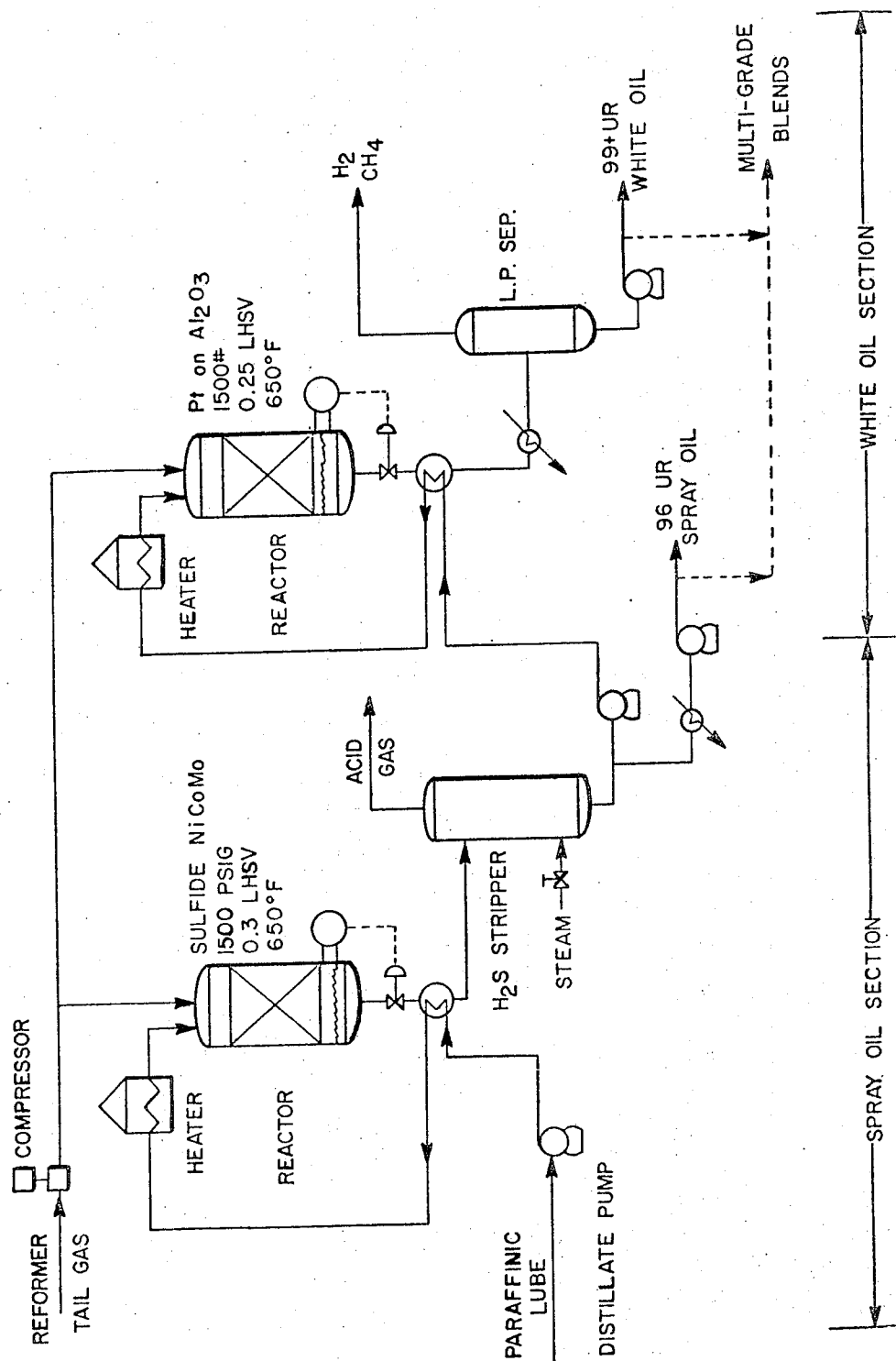
3,788,976

MULTI-STAGE PROCESS FOR PRODUCING HIGH UR OIL BY HYDROGENATION

Filed May 18 1972

3 Sheets-Sheet 3

FIG. 3
TWO STAGE SPRAY-OIL-WHITE OIL
HYDROGENATION PROCESS



1

2

3,788,976
MULTI-STAGE PROCESS FOR PRODUCING HIGH UR OIL BY HYDROGENATION
Merritt C. Kirk, Jr., Thornton, Pa., assignor to Sun Oil Company of Pennsylvania, Philadelphia, Pa.
Continuation-in-part of application Ser. No. 16,495, Mar. 4, 1970, now Patent No. 3,673,078, dated June 27, 1972. This application May 18, 1972, Ser. No. 255,874
The portion of the term of the patent subsequent to June 27, 1989, has been disclaimed
Int. Cl. C10g 23/04
U.S. Cl. 208—89

9 Claims

ABSTRACT OF THE DISCLOSURE

Refined mineral oils (useful as textile oils, white oils and agricultural spray oils) which have a viscosity in the lubricating oil range and a volume percent unsulfonated residue (UR) of at least 94.5 (typically at least 96) are produced from a dewaxed raffinate of a distillate oil, preferably a substantially wax-free distillate, obtained from a crude oil classified as paraffinic or mixed-base by ASTM viscosity-gravity constant (VGC). One preferred distillate is a de-waxed raffinate having a UR less than 93. A preferred process for producing such a refined mineral oil (with a UR of at least 96) comprises (a) introducing a mineral oil distillate of lubricating viscosity into a reaction vessel containing a first reaction zone, a second reaction zone and an intermediate zone between said first and said second reaction zones; (b) contacting said distillate in said first zone with a hydrogen-rich gas and a catalytic amount of a sulfur-resistant hydrogenation catalyst to desulfurize said distillate; (c) passing the distillate from said first zone to said intermediate zone containing therein a packing material which is substantially inert to hydrogenation and wherein the flow of hydrogen is countercurrent to the flow of distillate whereby hydrogen sulfide which was formed in said first zone is stripped from said distillate; (d) contacting the desulfurized distillate in said second zone with hydrogen and a hydrogenation catalyst; (e) said contacting steps in said first and said second zones being conducted at a temperature of about 550 to 750° F. and a pressure in the range of 500–6000 p.s.i.g.; and (f) withdrawing mineral oil product from said second zone having an unsulfonatable residue of at least 96.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 16,495, filed Mar. 4, 1970, now U.S. 3,673,078, issued June 27, 1972.

The disclosure of all of the following applications and patents is hereby incorporated herein by reference.

Serial No.	Filing date	Title/inventor
636,493 (now U.S. 3,681,279, issued 8-1-72).	5-5-67	Process for Preparing an Aromatic Oil and Non-Discoloring Rubber Composition Containing Said Oil—Mills-Dimeler-Kirk.
799,399 (now U.S. 3,594,307, issued 7-20-71).	2-14-69	Production of High Quality Fuel by Two Stage Hydrogenation—Kirk.
812,516 (now U.S. 3,619,414, issued 11-9-71).	2-19-69	Catalytic Hydrofinishing of Petroleum Distillates in the Lubrication Oil Boiling Range—Mills-Kirk-Olenzak.
828,746 (now U.S. 3,658,689, issued 4-25-72).	5-28-69	Isomerization of Waxy Lube Streams and Waxes—Steinmetz-Barmby.

TABLE—Continued

Serial No.	Filing date	Title/inventor
850,717 (now abandoned).	8-18-69	Hydrotreated Lube Oil and Process of Manufacture—Mills-Dimeler.
16,495 (now U.S. 3,673,078, issued 6-27-72).	3-4-70	Process for Producing High UR Oil by Hydrogenation of Dewaxed Raffinate—Kirk.
228,832	2-24-72	Hydrotreated Lube Oil and Process of Manufacture—Mills-Dimeler.

Of particular import is the disclosure in these applications of sulfur-resistant hydrogenation catalysts (particularly those containing sulfided oxides of Ni, Mo, Co, etc.), since such catalysts can be useful in practicing the present invention. The applications of Mills and Dimeler disclose a process for producing a technical white oil having an ultraviolet absorptivity in the 280–289 millimicron region less than 2.0 and having a viscosity in the range of 300–600 SUS at 100° F., said process comprising hydrogenating a paraffinic distillate having a viscosity in the range of 300–600 SUS at a temperature in the range of 550–600° F., at a hydrogen partial pressure in the range of 800–3000 p.s.i. and a total pressure in the range of 800–6000 p.s.i.g., in the presence of a hydrogenation catalyst comprising sulfides of nickel and molybdenum, and at a liquid hourly space velocity in the range of 0.1–1.0. The applications also disclose a process for producing a technical white oil having an ultraviolet absorptivity in the 280–289 millimicron region less than 1.5 and having a viscosity in the range of 50–300 SUS at a temperature in the range of 565–640° F., at a hydrogen partial pressure in the range of 800–6000 p.s.i. and a total pressure in the range of 800–6000 p.s.i.g., in the presence of a hydrogenation catalyst comprising sulfides of nickel and molybdenum, and at a liquid hourly space velocity in the range of 0.1–1.0. The Mills-Dimeler process can be used as a first stage in the present process (such a combined process being the invention of Kirk, Dimeler and Mills).

RELEVANT PATENTS AND PUBLICATIONS

In parent application Ser. No. 16, 495, filed Mar. 4, 1970, the following references were cited by the Examiner:

Patent No.	Issue date	Patentee	Class/sub
2,917,448	December 1959	Benther et al.	208/57
3,340,181	September 1967	Diringer et al.	208/143
3,392,112	July 1968	Bercik et al.	208/143
3,431,198	March 1969	Rausch (I)	208/143
3,459,656	August 1969	Rausch (II)	208/89

SUMMARY OF THE INVENTION

Refined mineral oils (useful as textile oils, white oils and agricultural spray oils) which have a viscosity in the lubricating oil range and a volume percent unsulfonated residue (UR) of at least 94.5 (typically at least 96) are produced from a dewaxed raffinate of a distillate oil, preferably a substantially wax-free distillate, obtained from a crude oil classified as paraffinic or mixed-base by ASTM viscosity gravity constant (VGC). One preferred distillate is a dewaxed raffinate having a UR less than 93. A preferred process for producing such a refined mineral oil (with a UR of at least 96) comprises

(a) Introducing a mineral oil distillate of lubricating viscosity into a reaction vessel containing a first reaction zone, a second reaction zone and an intermediate zone between said first and said second reaction zones;

(b) Contacting said distillate in said first zone with a hydrogen-rich gas and a catalytic amount of a sulfur-resistant hydrogenation catalyst to desulfurize said distillate;

(c) Passing the distillate from said first zone to said intermediate zone containing therein a packing material which is substantially inert to hydrogenation and wherein the flow of hydrogen is countercurrent to the flow of distillate whereby hydrogen sulfide which was formed in said first zone is stripped from said distillate;

(d) Contacting the desulfurized distillate in said second zone with hydrogen and a hydrogenation catalyst;

(e) Said contacting steps in said first and said second zones being conducted at a temperature of about 550 to 750° F. and a pressure in the range of 500–6000 p.s.i.g.; and

(f) Withdrawing mineral oil product from said second zone having an unsulfonated residue of at least 96.

At low gas recycle the preferred catalysts comprise sulfided oxides of nickel and molybdenum. The more preferred gas recycle is at least 500 s.c.f./bbl. and the preferred catalysts include nickel and the noble metal hydrogenation catalysts (e.g., Pt, Pd, Ru, Rh, Re) and alloys of 2 or more noble metals (e.g., PdRu, PtRe, PtRh, etc.).

For example, in the first stage or zone the catalyst is preferably substantially sulfur resistant (e.g., sulfided CoMo, NiMo, NiCoMo, PtS) under the reaction conditions and conditions are chosen so that the H₂S-free product oil has less than 10 p.p.m. sulfur. In the second stage or zone, the low sulfur product of the first stage or zone can be contacted with amore active (and more sulfur-sensitive) catalyst for saturation of aromatic rings (e.g., Pt, Pd, Ni, Rh, Re, Ru or alloys of two or more of these metals).

Lubricating oils with low unsulfonated residue (UR) and/or improved color and oxidation stability can be made by hydrotreating with conventional CoMo or NiMo desulfurization catalysts at 500–700° F., 0.2–3 LHSV, 200–3000 p.s.i.g., with or without recycle hydrogen. Although significant color improvement and reduction of unsaturates is obtained in such processes with sulfided Co and NiMo catalysts, their moderate activity limits the extent of improvement at conventional operating conditions. Higher operating temperatures compensate to some degree for activity, but above about 650–700° F., the products become unstable. In other words, the selectivity for color removal and stability decreases. Pt, Ni, Pd or similar metal catalysts are several orders of magnitude more active for hydrogenation, but are rapidly poisoned by sulfur in the feed (which can be as high as 0.2 wt. percent for lube boiling range distillates).

Lubes can be hydrotreated in a two-stage process where the feed (typically containing 100–2000 p.p.m. S) is desulfurized to less than 50 p.p.m. (preferably less than 10 p.p.m.) of sulfur in first reactor stage, H₂S is stripped from the product and hydrogenation occurs in a separate second reactor stage. The present invention relates to the accomplishment of both reaction stages in a single vessel in which a center zone of packing (which is preferably substantially inert as a hydrogenation catalyst) serves to strip H₂S from the product of the first stage. The net result is a simplified process employing a 3 zone reactor with common countercurrent gas flow, to yield a highly refined lube oil product of very light color (and which can have a high UR).

The volume percent unsulfonated residue (or UR) is an important test measurement in determining the suitability of a given refined mineral oil for use as an agricultural spray oil or as a technical white oil. The UR is determined by ASTM test method 483–63 and involves contacting the oil with 96% sulfuric acid and determining the volume of oil which does not react with the acid. In the range of 93.5 to 99 UR, the UR is approximately directly proportional to the total wt. percent of aromatics plus olefins in the oil. For example, a 93.5 UR oil has about 13.5% aromatics plus olefins, a 96 UR oil has 6.0% and a 99 UR oil has about 0.8% aromatics plus olefins.

Refined mineral oils (useful as textile oils, white oils and agricultural spray oils) which have a viscosity in the lubricating oil range and a volume percent unsulfonated residue (UR) of at least 94.5 are produced from a dewaxed raffinate of a distillate oil obtained from a crude oil classified as paraffinic or mixed-base by ASTM viscosity-gravity constant (VGC), the dewaxed raffinate having a UR less than 93. The preferred process involves contacting the dewaxed raffinate with a hydrogen rich gas and a catalytic amount of a sulfur-resistant hydrogenation catalyst at a temperature of about 550–750° F. (preferably 650–700° F.), a pressure in the range of 500–6000 p.s.i.g., preferably at least 1500 p.s.i.g., and a hydrogen recycle rate of about 200 to 10,000 s.c.f./bbl. of feed (preferably at least 500 for proper H₂S removal in the intermediate zone), said contacting being at a liquid hourly space velocity (typically 0.1–1.0, more preferably 0.2–0.6) sufficient to convert said dewaxed raffinate to a hydrogenated oil having a UR of at least 94.5. Preferably the feed hydrogen is in the range of 50–100% pure, and the partial pressure of hydrogen in the reactor inlet is at least 800 p.s.i.a. (more preferred at least 1200 p.s.i.a.).

At low gas recycle the preferred catalysts comprise sulfided oxides of nickel and molybdenum. When the gas recycle is at least 500 s.c.f. the preferred catalysts also include nickel and the noble metal hydrogenation catalysts (e.g., Pt, Pd, Ru, Rh, Re) and alloys of 2 or more noble metals (e.g., PdRu, PtRe, PtRh, etc.).

The contacting is in two or more stages or zones. In the first stage or zone the catalyst is substantially sulfur resistant (e.g., sulfided CoMo, NiMo, NiCoMo, PtS) under the reaction conditions and the product has less than 10 p.p.m. sulfur. In the second stage or zone, the low sulfur product of the first stage or zone is contacted with a more active catalyst for saturation of aromatic rings (e.g., Pt, Pd, Ni, Rh, Re, Rh).

In conducting such a lube oil hydrogenation process in a single reactor vessel having three zones, the same catalyst can be used in the top and bottom zones (e.g., sulfided NiMo oxides or Pt on Al₂O₃); however, it is preferred that one zone (e.g., the top zone in FIG. 3) contain a sulfur resistant hydrogenation-dehydrogenation catalyst (e.g., sulfided NiCoMo oxides) and the final zone (e.g., the bottom zone in FIG. 3) contain a more active, sulfur-sensitive hydrogenation-dehydrogenation catalyst (e.g., Pd on alumina or kieselguhr, which for 99+ UR product requires that the feed to the final zone contain less than 10 p.p.m. of sulfur). In the embodiment illustrated in FIG. 1, the top and bottom lines of the reactor are each loaded initially with the same catalyst (Pt on Al₂O₃). However, during operation, as illustrated in the figure, the Pt catalyst in the top zone becomes at least partially converted to sulfided Pt catalyst. This conversion to sulfide is caused by sulfur present in the feed stock to the first zone. In the bottom zone sulfide formation is not favored since H₂S-free, feed hydrogen first enters the reactor at this zone and also because the lube oil feed to the bottom zone is substantially free from sulfur and H₂S (e.g., typically, containing from 1–10 p.p.m. S).

The preferred feed stocks are distillate fractions, in the lubricating oil viscosity range (i.e., having a viscosity at 100° F. in the range of about 40 SUS to 12,000 SUS), of crude oils classified as paraffinic or mildly (or "relatively") naphthenic by the viscosity-gravity constant (VGC) classification system. In general, such fractions will have a VGC in the range of 0.790–0.849, a paraffinic fraction having a VGC of 0.819 or less, a relatively naphthenic fraction having a VGC in the range of 0.820–0.849 (e.g., see Bruins, Plasticizer Technology, vol. 1, p. 80, Reinhold Pub. Corp., New York). Preferably, but not necessarily, the distillate is subjected to further processing (such as extraction with an aromatic selective solvent and/or dewaxing) to reduce the aromatic content and/or reduce the pour point. The solvent extraction can

be by conventional methods, as with furfural, phenol, SO_3 , H_2SO_4 etc. The dewaxing can be by conventional methods (e.g., chilling, solvent dewaxing, etc.) or by isomerization as in U.S. 3,658,689 of Steinmetz and Barmby.

FIG. 1 is a schematic illustration of a hydrogenation process wherein a single reactor has three separate contacting zones. In the zone wherein fresh feed enters the reactor, the catalyst is preferably sulfur-resistant (e.g., sulfided Pt, sulfided NiCoMo, sulfided NiMo oxides, etc.). In the intermediate zone, there is preferably no hydrogenation or desulfurization catalyst but only inert contact material (e.g., ceramic rings, beads, inert pellets of clay, bauxite, glass, pebbles, etc.). In this intermediate zone the H_2S -containing product oil from the first zone is stripped of its H_2S content by the contact with the inert packing and with the H_2S -free hydrogen-containing gas from the third contact zone. In the remaining or second reaction zone the H_2S -free, desulfurized lube product from the intermediate zone is contacted with fresh hydrogen of 70–100% purity at a total pressure of at least 800 p.s.i.g. (preferably, 1200–5000 p.s.i.g.). The product from the second reaction zone can be a 96+ UR spray oil or a 99+ UR white oil (as from a paraffinic or mixed base feed) or if the feed is a naphthenic distillate or aromatic extract the product can be a non-discoloring rubber oil (e.g., see previously referred to copending application Ser. No. 636,493) or a refrigerator or transformer oil (e.g., see previously referred to copending application Ser. No. 812,516). This type of three zone vessel is also useful in preparing high luminometer number jet fuel utilizing the feeds and process conditions described in previously referred to copending application Ser. No. 799,499, now U.S. Pat. No. 3,594,307, issued July 7, 1971.

In the attached drawings, FIG. 2 is a schematic illustration of a process for producing hydrorefined lube having a UR of at least 94.5 (typically 96–98 UR) from 85–93 UR paraffinic (or mixed-base) lube distillate or raffinate (which is preferably dewaxed prior to the catalytic contacting). Preferably the feed stocks contain less than 900 p.p.m. sulfur. This process utilizes trickle phase hydrogenation (e.g., substantially all of the feed hydrogen is consumed in the reactor either by chemical reaction or by being contained in dissolved form in the reacting effluent). The preferred catalyst comprises sulfided oxides and metals of Co, Ni, and Mo (e.g., NiMo, CoMo, NiCoMo, NiW, etc.) preferably on a non-reactive carrier such as bauxite, alumina, kieselguhr, etc.

FIG. 3 of the drawings is a schematic illustration of a two stage process for producing 94.5+ UR spray oil and/or 99+ white oil from 80–93 UR paraffinic, naphthenic or mixed-base distillate or raffinates from extraction of such distillates with aromatic-selective solvents (e.g., phenol, furfural, "duo wol," etc.). Preferably the feed stocks contain less than 800 p.p.m. of sulfur and are dewaxed (e.g., by methyl-ethyl ketone solvent) prior to the catalytic contacting. In this two stage process, the preferred first stage catalyst is the same as that preferred in the process of FIG. 1. However, the preferred second stage catalyst is a highly active, sulfur sensitive metal (preferably on an inert carrier) such as Ni, Pt, Pd, Ru, Ir, Re, Rh and combinations of one or more such metals.

ILLUSTRATIVE EXAMPLES

Example I

Using the process shown in the attached in FIG. 2, a 70 SUS (at 100° F.) distillate fraction of a dewaxed raffinate obtained from a paraffinic lube distillate, the fraction having a UR of 92.5, was hydrogenated to produce a 96 UR product. A distillate fraction of a dewaxed raffinate obtained from a paraffinic lube distillate was preheated and mixed with reformer hydrogen that had been compressed to 1550 p.s.i.g. and passed over a sulfur resistant catalyst (such as the NiCoMo sulfide catalysts sold commercially as Filtrol 500–8 and Filtrol 500–10) at a liquid hourly space velocity of 0.3 to 0.4 volume per hour

per volume at a temperature of 650° F. The reactor effluent was cooled to 300° F. and degassed, with light hydrocarbons being removed in a low pressure separator. Hydrogen sulfide in the low pressure separator liquid was removed by steam in an H_2S stripper. Clean product of 96 UR was cooled and pumped to storage. Table 1 summarizes the reaction conditions and reports the properties of a typical 96+ UR oil produced by the process of this example. The feed contained 500 p.p.m. sulfur and the product contained less than 25 p.p.m. sulfur.

Example II

Both a 94+ UR spray oil and a 99+ UR white oil can be produced by the process shown schematically in FIG. 3. The first stage involves a spray oil section which is similar to that shown in FIG. 1 except that there is no low pressure separator. A product similar to the Example 1 product is obtained from the spray oil section. All or part of this product (which is preferably 96+ UR) can be transferred to the second stage, or the white oil section, and hydrogenated to produce a 99+ UR white oil.

In the attached Table II, Runs No. HPP-1–188 and HPP-1–191 represent, respectively the first and second stages of such a two stage hydrogenation process. In Table II a low and high temperature (575 and 600° F. respectively for HPP-1–191) are reported. These temperatures represent the lowest and highest temperatures observed by a series of thermocouples in various positions in the catalyst bed. In such a catalyst bed the most important temperature is the highest recorded temperature. Table II also reports a number of other single and double stage pilot plants runs.

In the two stage process of this example, the first stage hydrogenation was a trickle phase hydrogenation at zero hydrogen throughput. Only sufficient hydrogen was added to the trickle phase reactor to supply that consumed in chemical combination and that dissolved in the product (thus maintaining the operating pressure). In the second stage, or white oil section, H_2S -free feed 96 UR spray oil from the spray oil section was preheated and mixed with reformer hydrogen which had been compressed to 1500 p.s.i.g. and passed over a platinum on alumina catalyst at a liquid hourly space velocity of 0.25 and a temperature of 600° F. (although 650° F. is a more preferred temperature). The reactor effluent was depressured and cooled and passed to a low pressure separator where dissolved hydrogen and light hydrocarbon gases were removed. Liquid from the low pressure separator was a 99+ UR white oil (e.g., 99.9 UR with UVA of 1.06 at 260 millimicrons). The process of this example was effected with pure hydrogen at a rate of 10,000 standard cubic feet per barrel of feed. The preferred embodiment is to operate the white oil section in such a manner that the amount of hydrogen added is just sufficient for reaction plus solution losses. In this preferred operation hydrogen consumption rate, for the feed and conditions of this example, would be approximately 200 s.c.f./bbl. of which about 150 is reacted chemically with the feed and the remaining 50 s.c.f./bbl. is dissolved in the liquid effluent from the reactor.

Example III

A single stage spray oil-white oil hydrogenation process, as described schematically in FIG. 1, can be used to produce a 99+ UR white oil from an 85–92.5 UR dewaxed raffinate or lube distillate feed. The advantages of this process over that described in Example II are decreased capital equipment cost, increased thermal efficiency in operation and more efficient utilization of hydrogen. No intermediate separation is required from the spray oil section and the process requires less heating and cooling of the process stream.

For example, the raffinate is preheated and passed downflow to a desulfurization zone containing a fixed bed of Pt on aluminum catalyst (which is sulfided by the feed during the catalytic contacting). Countercurrent to the

feed flow is an upward flowing stream of hydrogen at a pressure of 1000 p.s.i.g. at a maximum contact temperature of 657° F.

Hot liquid product from the desulfurization zone (and which contains dissolved H₂S) flows downward to a packed section of inert ceramic rings where the H₂S is stripped from the liquid by up-flowing hydrogen from a lower hydrogenation zone. The up-flowing hydrogen rate is in the range of 2000 to 5000 s.c.f./bbl.

Desulfurized and stripped 94+ UR spray oil from the packed section flows downwardly into the lower hydrogenation zone, which contains a fixed bed of Pt on alumina catalyst. The operating conditions in the lower hy-

TABLE I.—HYDROGENATION OF DEWAXED RAFFINATE LUBE¹ OVER PRESULFIDED FILTROL 500-10 CATALYST

Conditions:	
Temperature.....	650° F.
Total pressure.....	1,500 p.s.i.g.
Feed gas purity.....	80 mol percent H ₂ .
LHSV.....	0.3-0.4 v./hr./v.
Product qualities:	
U.R.....	96.1 vol. percent (±0.2 vol. percent).
Aromatics.....	5.8-6.4 wt. percent.
Olefins.....	0.1 wt. percent.
Sulfur.....	1-8 p.p.m.
Gravity.....	34.6° API.
Color, Saybolt.....	30+.

¹ 0.81 VGC.

TABLE II.—HYDROGENATION OF DEWAXED RAFFINATE LUBE

Catalyst: Engelhard Rd-150, 0.6 wt. percent Pt on Al₂O₃, 200 cc., 176.5 gm.

	Run No. HPP-1-															Fresh Charge ¹
	187	188	189	190	191	192	193	194	195	196	197	198	199	200		
Operating conditions:																
Temp., ° F.:																
Low.....	585	650	665	620	575	550	550	620	665	675	625	550	690	640	-----	
High.....	675	715	700	650	600	575	575	650	700	700	650	580	750	700	-----	
Pressure, p.s.i.g.....	500	1,000	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	-----	
LHSV, v./hr./v.....	0.50	0.50	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.50	0.50	0.50	0.50	0.50	-----	
Charge stock.....	Fresh	Fresh	(2)	(2)	(2)	(2)	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	-----	
100% H ₂ /oil, s.c.f./b.....	0	0	10,000	10,000	10,000	10,000	10,000	10,000	10,000	5,000	5,000	5,000	0	0	-----	
Recycle, s.c.f./b.....	8,000	20,000	0	0	0	0	0	0	0	0	0	0	0	0	-----	
Product qualities:																
Aromatics, wt. percent:																
Mono.....	17.2	8.1	2.5	1.7	1.6	1.4	5.5	3.4	3.6	5.1	6.1	9.7	11.8	10.4	10.1	
Di.....	2.1	0.5								0.1	0.1	0.2	1.1	0.7	2.0	
Tri.....	0.7														0.4	
Total.....	20.0	8.6	2.5	1.7	1.6	1.4	5.5	3.4	3.6	5.2	6.2	9.9	12.9	11.1	12.5	
Olefins, wt. percent.....	2.2	1.6	0.2	0	0	0	0.4	0.3	0.6	0	0	0	1.7	1.0	2.0	
UR, vol. percent.....	92.5	94.9	97.8	98.4	99.9	98.8	96.5	97.1	97.3	96.7	96.0	94.9	93.6	93.0	92.5	
Yield, vol. percent of charge ²	92	103	100	100	99	102	100	100	101	102	102	102	100	104	-----	

¹ Fresh charge was obtained by solvent dewaxing of a furfural raffinate of a vacuum distillate fraction of a paraffinic crude oil. The fresh charge had had a viscosity of about 70 SUS at 100° F., a viscosity index of about 95 and a specific dispersion of about 100.

² Run 188 product.

³ Observed in pilot plant.

drogen zone are an LHSV of 0.75, a maximum temperature of 650° F. (a minimum of 640° F.) and 1000 p.s.i.g., with upward flowing hydrogen (85% pure at the inlet) at a rate of 2000 to 5000 s.c.f./bbl. Product liquid from the lower hydrogenation zone serves to absorb hydrogen sulfide from the hydrogen recycle stream. The H₂S-saturated product oil from the lower zone contains 99+ UR and is transferred to product distillation to remove H₂S and for adjustment of flash point and viscosity. Table III reports the properties of a typical product of this example and also reports the usual range of product properties which can be encountered in commercial scale operation.

Where the feed to the process of the present invention has not been dewaxed, it is sometimes advantageous to utilize in at least one contacting stage or zone a combination of a hydrogenation (e.g., Ni, Pt) or hydrosulfurization catalyst (e.g., NiMoSx, PtS) with a hydroisomerization catalyst (particularly an acidic alumino-silicate catalyst which is at least partially crystalline to X-ray and which can adsorb benzene). Such dual function, hydrogenation-hydroisomerization catalysts and their uses in converting wax to lubes are disclosed in copending application Ser. No. 828,746 of Ib Steinmetz and David S. Barmby, now U.S. Pat. No. 3,658,689, issued Apr. 25, 1972.

One feed which can be used in the process of the present invention (e.g., instead of a paraffinic raffinate or distillate) is a hydrocracked, high viscosity index paraffinic lube such as can be obtained by hydrocracking a distillate classified as paraffinic or mildly naphthenic by viscosity-gravity constant. The lube can be "stabilized" by solvent extraction. Such hydrocracked lubes (and stabilized lubes) are described, for example in application Ser. No. 178,193, filed Sept. 7, 1971 of Bryer et al. and the application filed Apr. 24, 1972 of Newingham et al., titled "Mist Lubrication With Oil Containing a Polymeric Additive."

TABLE III.—PROPERTIES OF PRODUCT FROM HYDROGENATION OF DEWAXED RAFFINATE LUBE

	Typical completely hydrogenated product	Usual range
SUS at 100° F. ¹	70.5	66-74
° API gravity ²	33.8	(³)
Unulfonated residue ⁴	99+	92-100
Pour point, ° F. ⁵	-20	(⁶)
Distillation at 10 mm. Hg., ° F., 50% ⁷	423	425±12
Color, Saybolt.....	30+	

¹ ASTM D445-61 and D446-63.

² ASTM D-287-55.

³ 33 minimum.

⁴ ASTM D483-61T.

⁵ ASTM D97-57.

⁶ 20 maximum.

⁷ ASTM D1160-61.

The invention claimed is:

1. A process for producing a refined mineral oil having a viscosity in the lubricating oil range and a volume percent unulfonated residue of at least 96, said process comprising

(a) introducing a mineral oil distillate of lubricating viscosity into a reaction vessel containing a first reaction zone, a second reaction zone and an intermediate zone between said first and said second reaction zones;

(b) contacting said distillate in said first zone with a hydrogen-rich gas and a catalytic amount of a sulfur-resistant hydrogenation catalyst comprising sulfided oxides of nickel and molybdenum or sulfided platinum to desulfurize said distillate;

(c) passing the desulfurized distillate from said first zone to said intermediate zone containing therein a packing material which is substantially inert to hydrogenation and wherein the flow of hydrogen is countercurrent to the flow of distillate whereby hy-

drogen sulfide which was formed in said first zone is stripped from said distillate;

(c) passing the desulfurized distillate from said first zone to said intermediate zone containing therein a packing material which is substantially inert to hydrogenation and wherein the flow of hydrogen is countercurrent to the flow of distillate whereby hydrogen sulfide which was formed in said first zone is stripped from said distillate;

(d) contacting the desulfurized distillate in said second zone with hydrogen and a hydrogenation catalyst; (e) said contacting steps in said first and said second zones being conducted at a temperature of about 550 to 750° F. and a pressure in the range of 500–6000 p.s.i.g.; and

(f) withdrawing mineral oil product from said second zone having a volume percent unsulfonated residue of at least 96.

2. The process of claim 1 wherein the flow of hydrogen in step (c) is sufficient to remove substantially all of the hydrogen sulfide from said desulfurized distillate.

3. The process of claim 1 wherein there is a gas recycle of at least 500 s.c.f./bbl.

4. The process of claim 1 wherein the catalyst in said second zone comprises Ni, Pt, Pd, Rh, Re, Ru, Ir or alloys thereof.

5. The process of claim 1 wherein said catalyst in said first zone comprises a sulfided member from the group consisting of nickel-molybdenum oxides, nickel-cobalt-molybdenum oxides, and cobalt-molybdenum oxides, on an inert carrier.

6. A process for producing a refined mineral oil having a viscosity in the lubricating oil range and a volume percent unsulfonated residue of at least 96, said process comprising

(a) introducing a mineral oil distillate of lubricating viscosity into a reaction vessel containing a first reaction zone, a second reaction zone and an intermediate zone between said first and said second reaction zones;

(b) contacting said distillate in said first zone with a hydrogen-rich gas and a catalytic amount of a sulfur-resistant hydrogenation catalyst to desulfurize said distillate;

(c) passing the desulfurized distillate from said first

zone to said intermediate zone containing therein a packing material which is substantially inert to hydrogenation and wherein the flow of hydrogen is countercurrent to the flow of distillate whereby hydrogen sulfide which was formed in said first zone is stripped from said distillate;

(d) contacting the desulfurized distillate in said second zone with hydrogen and a hydrogenation catalyst comprising Ni, Pt, Pd, Rh, Re, Ru, Ir or alloys thereof;

(e) said contacting steps in said first and said second zones being conducted at a temperature of about 550 to 750° F. and a pressure in the range of 500–6000 p.s.i.g.; and

(f) withdrawing mineral oil product from said second zone having a volume percent unsulfonated residue of at least 96.

7. The process of claim 6 wherein the flow of hydrogen in step (c) is sufficient to remove substantially all of the hydrogen sulfide from said desulfurized distillate.

8. The process of claim 6 wherein there is a gas recycle of at least 500 s.c.f./bbl.

9. The process of claim 6 wherein said catalyst in said first zone comprises a sulfided member from the group consisting of nickel-molybdenum oxides, nickel-cobalt-molybdenum oxides, and cobalt-molybdenum oxides, on an inert carrier.

References Cited

UNITED STATES PATENTS

2,917,448	12/1959	Beuther et al.	208—57
3,431,198	3/1969	Rausch	208—143
3,392,112	7/1968	Berick et al.	208—143
3,340,181	9/1967	Diringer et al.	208—143
3,459,656	8/1969	Rausch	208—89
3,673,078	6/1972	Kirk	208—89

DELBERT E. GANTZ, Primary Examiner

J. W. HELLWEGE, Assistant Examiner

U.S. Cl. X.R.

208—18, 143, 210, 264