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3,072,564

HYDROFINING PROCESS

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The present invention is concerned with the production of light oils of the highest quality. More particularly, this invention pertains to the hydrofining of light distillate oils in order to improve color and odor and reduce the aromaticity thereof.

The problem of refining and stabilizing light distillate oils is a difficult one. These oils are widely used as lubricating, diluent or solvent oil in specialty services such as in textiles, and textile processing, disinfectants and sprays for household and agricultural products. Numerous processes have been proposed for improving the quality of such light distillate oils such as extraction, clay treating, acid and caustic washing, hydrogenation and hydrofining and combination operations involving hydrotreating and treatment with an adsorbent such as bauxite, silica gel or activated carbon.

These processing schemes have not proved to be entirely satisfactory for a variety of reasons such as low yields or low quality or lack of uniformity in the products. Hydrofining processes which would have the potential of offering substantial commercial advantages in comparison with acid treatment of no waste acid disposal problem and no undesirable by-product formation have not proved entirely satisfactory either because of insufficient improvement in the properties of the oil or the catalyst life of the more active catalysts has been too short to be commercially attractive.

It is the object of this invention to provide a process for treating light distillate oils with hydrogen in the presence of a solid catalyst to form products possessing excellent color, odor and stability characteristics.

It is also the object of this invention to prepare light distillate oils of high color, low sulfur content and low aromaticity eminently suitable for specialty services in textiles, disinfectants, sprays and the like by a hydrofining treatment.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that light distillate oils particularly suited for specialty services can be prepared by hydrofining the same first at a high temperature to lower the sulfur content and reduce the aromaticity of the oil and then in a second stage at low temperatures for decolorization. It has been found that other hydrofining conditions being the same, color improvement decreases with increasing temperature and sulfur reduction and reduction in aromaticity increases with increasing temperature. Accordingly, in order to attain color improvement as well as sulfur and aromatics reduction a combination of process conditions is required.

The light distillate oils which are advantageously treated in accordance with the present invention are petroleum hydrocarbon fractions having an initial boiling point of at least 425° F. and an end point of about 700° F. but boiling mainly in the range of from about 550-650° F. A typical oil feed is one having the following inspections:

Gravity, ° API	38.5
Flash, ° F.	290
Color, Saybolt	14
Viscosity, SSU at 100° F.	41
Sulfur, weight percent	0.26
Aniline point, ° F.	182

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Distillation (10 mm.):

IBP	200 (428)
5	300 (550)
10	312 (563)
50	333 (589)
95	360 (623)
F.B.P.	370 (635)

The hydrofining of the distillate oil can be effected in any suitable reactor. In view of the fact that the catalyst retains its activity for prolonged periods of time, fixed bed reactors are entirely satisfactory. If a temperature gradient is provided in a single reactor vessel, suitable means such as cooling coils or other suitable heat transfer means are required to maintain the reaction mixture at the desired temperature levels in the respective reaction zones. If the reactor system comprises two vessels in series, suitable cooling means can be arranged between the two vessels or the second vessel may be provided with suitable heat transfer means to maintain the desired temperature in the second vessel.

The catalysts used for hydrofining light distillate oils in accordance with this invention are cobalt molybdate or mixtures of cobalt oxide and molybdenum oxide dispersed upon an alumina support or carrier. In general, such catalysts are prepared by first forming adsorptive alumina particles in any suitable way and then compositing molybdenum oxide and cobalt oxide therewith. The molybdenum oxide can be added as a slurry or as a solution of ammonium molybdate. The cobalt oxide is most conveniently added as a salt such as cobalt nitrate or acetate, salts which are readily decomposed to cobalt oxide and volatile materials. The cobalt oxide and molybdenum oxide can be provided in equimolar amounts or a molecular excess of one over the other may be used. Suitable catalysts contain from about 5 to about 25 wt. percent of cobalt oxide and molybdenum oxide with the ratio of the former to the latter in the range of from about one to five to about five to one. Other catalysts which may be used include molybdenum oxide or sulfide on alumina containing about 5 to 15 wt. percent molybdenum oxide or sulfide and also nickel-tungsten sulfide, preferably dispersed upon an alumina support. In order to improve the activity of the hydrofining catalysts, it is preferred to sulfide the same prior to use as by treating with a suitable sulfiding agent such as hydrogen sulfide, carbon disulfide, ethyl mercaptan, sour gas oil (1.0-3.0 wt. percent sulfur) or the like, preferably in the presence of hydrogen. The amount of sulfur added is preferably at least 25% of the stoichiometric quantity necessary to convert the catalytic metal oxides to the corresponding sulfides.

The hydrofining treatment is usually effected at pressures above about 200 p.s.i.g., preferably at about 600 p.s.i.g. Higher pressures of up to about 5000 p.s.i.g. can also be used but ordinarily the higher cost of equipment to withstand such pressures and the higher cost of operation at higher pressures makes it uneconomic to use pressures above about 1000 p.s.i.g.

The temperature in the first hydrofining stage or pass is between about 450 and 650° F., preferably at about 500-550° F. The temperature in the second hydrofining stage or pass is between about 150-250° F., preferably about 175-225° F. The feed rate in each of the hydrofining stages is about 1/2 to 4 v./v./hr., preferably about 2 v./v./hr. Hydrogen or hydrogen-rich treat gas is supplied with the distillate oil feed at rates of from 50 to 2000 s.c.f. per barrel of liquid feed, but preferably at a minimum rate of 300 s.c.f. per barrel of liquid feed for operating control. The treat gas should preferably contain at least 70 vol. percent of hydrogen.

The following examples are illustrative of the present invention.

EXAMPLE 1

A non-phenol treated distillate oil produced by distilling a 40 SSU/100° F. stream from North Louisiana crude was treated with hydrogen in contact with 1/8" catalyst pills containing 2.43 wt. percent CoO and 9.86 wt. percent MoO₃ dispersed on alumina. The catalyst was sulfided for 6 hours with a 1.4 wt. percent sulfur content sour gas oil at 700° F., 600 p.s.i.g. and 1.0 v./v./hr. The treatment was effected at a pressure of 600 p.s.i.g. at a feed rate of 2 v./v./hr. while charging hydrogen treat gas at the rate of 720 s.c.f./b. of liquid feed. The catalyst in the form of 8 to 20 mesh particles (mean particle size=12 mesh) was arranged in two separate vessels each having an L/D ratio of 90.

The reaction conditions and the results of these runs are summarized in Table I.

Table I

Run No.	Spec.	Feed	263	264	275	266	(1)	A ₂	B ₂
Hydrofining conditions:									
Pressure, p.s.i.g.	600	600	600	600	600	600	600	600	600
Temperature, °F., #1 reactor			375	425	475	500	500	525	575
Temperature, °F., #2 reactor			275	275	225	200	250	175	175
Feed rate, v.v./hr.	2	2	2	2	2	2	2	2	2
H ₂ rate, s.c.f./b.	720	720	720	720	720	720	720	720	720
L/D ratio	90	90	90	90	90	90	90	90	90
Inspections:									
Gravity, ° API	³ 39.5	38.5	38.6	38.5	39.3	38.6	38.6	38.5	38.6
Flash, ° F.	³ 250	290	280	280	280	280	280	280	280
Fire, ° F.	³ 300		320	310	310	310		315	305
V. 100, SSU	³ 40	41	41	41	41	41	41	41	41
Color, Saybolt	³ +15	+14	+4	+9	+17	+18	29	+22	+22
Colorhold, Saybolt		+14	-10	-5	+15	+16		+19	+19
Bromine number		3.5	1.5	1.8	1.2	0.4		1.5	2.2
Aniline point, ° F.		182.0	181.7	182.4	182.4	182.8	197	182.4	182.8
Unsulphonated residue, percent	³ 90		90.0	90.0	89.5	91.0		90.0	91.0
Corrosion, 3 hrs. at 212° F.	⁴ J-5	J-3							
Sulfur, percent	⁴ 0.15	0.26	0.20	0.19	0.18	0.15	0.02	0.14	0.12
Cloud, ° F.	⁴ 36		26	28	30	26		28	26
Alcoa stain test		D				A		A	A
Rating		Fail				Perfect		Good	Good
Odor					(2)	(2)		(2)	(2)

¹ This run was made with a catalyst of the same composition from a different manufacturer.

² Runs designated A and B represent correlated values for higher temperature first stage operations to bring sulfur content below 0.15 max.

³ Minimum. ⁴ Maximum. ⁵ Borderline. ⁶ Satisfactory.

EXAMPLE 2

A light distillate oil (Menton 28) was hydrofined in a two-stage operation with cobalt molybdate-on-alumina catalyst. The reaction conditions, feed and product inspections are summarized in Table II below.

Table II

	Feed	Product		Prod. spec.
		1st stage	2nd stage	
Process conditions:				
Temperature, ° F.....		500	250	
Pressure, p.s.i.....		600	600	
V./v./hr.....		3	3	
Product inspections:				
Color, Saybolt.....	—5	—8	+18	+15 min.
Sulfur, weight percent....	2.65	0.19	0.08	.15 max.

The foregoing specification contains a limited number of embodiments of the present invention. It will be understood however, that numerous variations are possible without departing from the scope of this invention.

What is claimed is:

1. The method for upgrading light distillate petroleum oils which comprises treating said oils in admixture with a hydrogen rich gas in a first reaction zone in contact with a hydrofining catalyst at temperatures between 450 and 650° F. and pressures of between 400 and 1000 p.s.i.g. at feed rates of 1/2 to 4 v./v./hr. and treating the reaction mixture discharged from the first reaction zone in contact with a hydrofining catalyst at temperatures be-

tween 150 and 250° F. and at essentially the same pressure as in the first reaction zone.

2. The method for upgrading light distillate petroleum oils which comprises treating said oils in admixture with a hydrogen rich gas in a first reaction zone in contact with a cobalt oxide-molybdenum oxide-alumina hydrofining catalyst at temperatures between 450 and 650° F. and pressures of between 400 and 1000 p.s.i.g. at feed rates of 1/2 to 4 v./v./hr. and treating the reaction mixture discharged from the first reaction zone in contact with a cobalt oxide-molybdenum oxide-alumina hydrofining catalyst at temperatures between 150 and 250° F. and at essentially the same pressure as in the first reaction zone.

3. The method as defined in claim 2 in which the temperature in the first reaction zone is about 500-550° F. and the temperature in the second reaction zone is about 175-225° F.

4. The method for upgrading petroleum oils having an initial boiling point of at least 425° F. and an end point of about 700° F. which comprises treating said oils in admixture with a hydrogen rich gas in a first reaction zone in contact with a hydrofining catalyst at temperatures between 450 and 650° F. and pressures of between 400 and 1000 p.s.i.g. at feed rates of 1/2 to 4 v./v./hr. and treating the reaction mixture discharged from the first reaction zone in contact with a hydrofining catalyst at temperatures between 150 and 250° F. and at essentially the same pressure as in the first reaction zone.

5. The method for upgrading petroleum oils having an initial boiling point of at least 425° F. and an end point of about 700° F. which comprises treating said oils in admixture with a hydrogen rich gas in a first reaction zone in contact with a cobalt oxide-molybdenum oxide-alumina hydrofining catalyst at temperatures between 450 and 650° F. and pressures of between 400 and 1000 p.s.i.g. at feed rates of 1/2 to 4 v./v./hr. and treating the reaction mixture discharged from the first reaction zone in contact with a cobalt oxide-molybdenum oxide-alumina hydrofining catalyst at temperatures between 150 and 250° F. and at essentially the same pressure as in the first reaction zone.

6. The method for upgrading light distillate petroleum oils boiling in the range of about 425° F. to about 700° F., which comprises treating said oils in admixture with a hydrogen-rich gas in a first reaction zone in contact with a cobalt oxide-molybdenum oxide hydrofining catalyst at temperatures between 500° and 550° F. and

pressures of between about 200 to 600 p.s.i.g. at feed rates of $\frac{1}{2}$ to 4 v./v./hr. and treating the reaction mixture discharged from the first reaction zone in a second reaction zone by contacting said reaction mixture with a sulfided cobalt oxide-molybdenum oxide hydrofining catalyst at temperatures between about 175° and 225° F. and at essentially the same pressure as in the first reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,116,061	Dorrer	May 3, 1938
2,497,176	Mason	Feb. 14, 1950
2,706,167	Harper et al.	Apr. 12, 1955
2,769,754	Sweetser et al.	Nov. 6, 1956