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PROCESS FOR DECOLORIZING PETROLEUM RESINS AND PRODUCTS OBTAINED BY ADDING THE DECOLORIZED RESINS TO FUEL OIL

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This invention relates to the decolorization of hydrocarbon oil additives and more particularly to the hydrodecolorization of resinous petroleum fractions useful, for instance, in hydrocarbon fuel oils as a pour point depressant.

Many petroleum stocks which could be considered suitable for diesel and heating fuels are limited in utility by the inability to meet certain specifications, for example, as to pour point. That is, these stocks do not pour readily at the low temperatures frequently encountered due to place or time of use. The high pour points that characterize these fuels may be substantially reduced to meet pour point specifications by incorporating into the heating fuels a small amount of a propane-insoluble heavy petroleum resin. However, use of the resinous additive as a pour depressor in the production of fuel oil distillates has been found to present undesirable off-color finished fuels. Attempts have been made to eliminate the objectionable color of the resin-containing finished fuels by subjecting the raw petroleum resin to hydrodecolorization operations prior to its incorporation into the fuel oil distillate. These attempts have proved unsuccessful in that during the hydrodecolorization operation the pour depressor properties of the petroleum resin are invariably destroyed.

I have now found that the oil-soluble propane-insoluble petroleum resins prepared for use as fuel pour depressors can be successfully hydrodecolorized without loss of depressor properties by sufficiently diluting the resinous depressor with fuel oil stock prior to hydrogen treatment.

The petroleum resin additive hydrodecolorized in my invention is obtained as a propane-insoluble fraction from the propane treatment of reduced crude or bottoms fraction from a Pennsylvania or paraffin base crude oil. The resins have viscosities of about 3000 to 10,000 SSU at 210° F. As the viscosity increases, their tendency to precipitate from the propane solution increases and advantage is taken of this fact to effect a fractionation of the wide range resin and obtain any desired resin fraction, the preferred fraction having a viscosity of about 5000 to 8000 SSU at 210° F. Similar fractions having the desired properties can be obtained by distillation of Pennsylvania reduced crudes.

In carrying out my invention about 0.05 percent to 2 percent, preferably about .30 to 1.0 percent of the petroleum resin additive is incorporated into petroleum fuel oil stocks characterized by boiling in a range of about 300 to 900° F., preferably about 350 to 700° F., and the blend subjected to hydrodesulfurization processing. The hydrodesulfurized products can then be used as such, for instance as fuel, or incorporated into an additional amount of a petroleum hydrocarbon fuel oil boiling in

the range of about 300 to 900° F., preferably about 300 to 750° F. to provide a pour depressed fuel oil of acceptable color containing from about 0.01 to 1.5 percent, preferably about 0.01 to 0.15 percent, of the pour depressor resin.

The petroleum fuel stocks with which the defined resinous depressor may be diluted prior to hydrodesulfurization are mineral oil fractions of the indicated boiling range and known in the art, for instance, as heavy and light catalytically cracked distallates, thermally cracked distillates, such as coker gas oils, other cycle oils from the coking of residuums or heavy stock, straight run stocks, or mixtures of the straight run stocks with any of the above cracked components. Frequently, the distillate fuel materials employed comprise about 15 to 100 percent cracked distillate with substantially the balance being straight run stock and are characterized by pour points of at least about 5° F.

Base fuel materials which can be modified by the addition of the hydrodecolorized products of my invention to effect pour point lowering are characterized by boiling ranges of about 300 to 900° F. Typical materials are any of the cracked distillate fuel materials or blends thereof described above as possible diluent stocks for the defined resinous pour depressor. These stocks can be blended with straight run distillate fuels boiling within about 300 to 675° F. to improve the sulfur content, volatility and percentage carbon residue. This blending may result in slightly improved pour point also, but usually the improvement obtained is insufficient to meet specifications. Substantial amounts, i.e. up to about 10 percent of high boiling, high pour point marginal stocks, such as paraffin tower overhead, may also be included. Base compositions thus comprise about 15 to 100 percent of cracked distillate and substantially the balance straight run stock and usually are characterized by pour points of at least about 5° F., cetane numbers of about 25 to 50, boiling ranges within about 300 to 900° F., and have 90 percent points of at least about 600° F. and preferably at least about 700° F. The preferred diesel fuel base material is about a 50/50 blend of heavy and light catalytically cracked distillates.

The hydrodesulfurization operation of my invention should be conducted under conditions that are unlikely to produce substantial cracking of the fuel oil diluent-pour depressor composition. Employment of hydrodesulfurization conditions effecting substantial cracking has been found to destroy the pour depressor properties of the resin and should for that reason be avoided. Suitable processing conditions affording a product of acceptable color level are in the following approximate ranges:

WHSV [1]	0.5–4.0.
Pressure	300–1000 p.s.i.
H_2/HC molar ratio	3–20 to 1, preferably 5–10 to 1.
Temperature	600–780° F., preferably 650–700° F.

[1] Weight of hydrocarbon per weight of catalyst per hour.

Any suitable desulfurization or decolorization catalyst can be employed, for instance, a calcined or activated catalyst containing minor amounts of cobalt and molybdena or cobalt molybdate supported on alumina.

The following examples are presented in order to further illustrate my invention. The physical properties of the heavy petroleum resin and cracked fuel oil distillates employed in the examples are indicated in Table I.

TABLE I

Tests on stocks

	Fluid Catalytic Cycle Oil	Pennsylvania Heavy Resin
Gravity, ° API	23.6	13.5.
Flash, ° F	215 (PM)	680 (COC).
Fire, ° F		740.
Viscosity at 100° F., cs	3.595	
Viscosity at 210° F., SSU		7745.
Cloud Point, ° F	16	
Pour Point, ° F	15	
Color	2½ (NPA)	61,580 (OD).
Carbon Residue, Percent		12.76.
Sulfur, Percent	1.82	0.31.
Ash, Percent	Nil	0.258.
Distillation (200 ml.) IBP, ° F	440	

EXAMPLE I

To a fluid light cycle fuel oil having the physical properties shown in Table I were added various amounts of a Pennsylvania heavy resin whose physical properties are also shown in Table I.

A 50 gram portion of a calcined cobalt-molybdena on alumina desulfurization catalyst typically analyzing 25% Co, 9.0% MoO_3, was charged to a one inch reactor as a solid bed, with ¼" Alundum balls filling the entire space above the catalyst. The reactor was pressure tested and placed in a furnace. The catalyst was purged with hydrogen for 2 hours at 680° F., and 1 atmosphere, after which the reactor was pressured and the entire system pressure tested. Hydrogen gas recycle flow was started and the light cycle oil-resinous additive feed cut in. Process conditions and test results on the charge to the hydrodesulfurization unit and the tests on the hydrodesulfurized products are shown in Table II.

TABLE II

Process Conditions	Test No. 1	2	3	4
Feed Percent Penn. Heavy Resin	0.33	.66	.66	1.0
Fluid Light Cycle Oil	99.67	99.34	99.34	99.0
Temperature, ° F	680	680	720	680
Pressure, P.s.i.g.	500	500	500	500
WHSV	2	2	2	2
Recycle H_2, Ft.³/bbl	3,500	3,500	3,500	3,500
Tests on Charge to Hydrodesulfurization Unit:				
Color, NPA	Dark	Dark	Dark	Dark
Color, O.D	264	456	456	691
Sulfur, Percent	1.87	1.84	1.84	1.82
Tests on Products of Hydrodesulfurization Unit:				
Color, NPA	6—	3½	3—	8—
Color, O.D	161	30	20	229
Sulfur, Percent	0.14	0.14	0.05	.12

Comparison of tests 1 through 4 on the hydrodesulfurized products to those on the feeds to the unit shows that a substantial reduction of both sulfur and color was effected by the various process conditions. The sulfur removal indicates no apparent loss of desulfurization activity during the course of the tests. Although all percentages of Pennsylvania heavy resin to light cycle oil afforded a product of lighter color, the most favorable results are produced when about 0.5 to 0.75, e.g. 0.66, percent by weight of the resin is incorporated in the cycle oil. The adding of this amount of heavy resin effects a more desirable NPA color of below 4 to 5 when operating within the process conditions of this invention. If any dark colored hydrodesulfurized products should result under a particular set of operating conditions wherein the resin is employed, it may be remedied by simply adjusting the conditions of space velocity and/or temperature to increase the severity while avoiding cracking.

The hydrodesulfurized products of tests 1 to 4 were added to heating oil to produce a fuel blend composed of 70 percent heating oil and 30 percent hydrodesulfurized products. Tests on these fuel oil blends are reported in Table III.

TABLE III

Tests on Fuel Oil Blend No. 1 [1]	Test No. 1	2	3	4
70/30 Blend No. 1/Hydrodesulfurization Product:				
Color, NPA	4	2½	2	4½
Cloud Point, ° F	6	8	8	2
Pour Point, ° F	B—30	B—30	B—5	B—30
70/30 Blend No. 1/Feed to Hydrodesulfurization Unit:				
Color, NPA	4½	6	6	8
Cloud Point, ° F	8	4	4	Too Dark
Pour Point, ° F	B—30	B—30	B—30	B—30

[1] Fuel Oil Blend No. 1 Composition: 60% heating oil, 415 to 640° F. boiling range; 10% light run naphtha, 317 to 437° F. boiling range; and 30% fluid catalytic cycle oil, 440 to 660° F. boiling range.

Tests:
Color NPA 1½
Cloud Point, ° F 6
Pour Point, ° F 5
B=below.

As shown, addition of the undesulfurized heavy resin-light cycle oil blend reduced the pour point of fuel blend No. 1 from 5° F. to below —30° F. but resulted in products in tests 2, 3 and 4 that are too dark (NPA 6 and 8) for ready acceptance. On the other hand, incorporation of the hydrodesulfurized products obtained under the process conditions of the tests in Table II into fuel blend No. 1 gave a fuel of reduced pour point and of lighter color. The color reductions (NPA color of 2½ and 2) were obtained with the hydrodesulfurization product afforded under the conditions of tests 2 and 3 in Table II, wherein .66 percent of the resin was present in the oil desulfurized; however, the more severe conditions in test 3 gave some loss of pour point depressor properties. Preferably, the decolorizing conditions should not be so severe that more than 10° F. of pour depressing properties are lost.

I claim:

1. A process for the decolorization of an oil-soluble, propane-insoluble, paraffin base-derived resinous petroleum fraction having a viscosity of about 3,000 to 10,000 SSU at 210° F. for use as a pour depressor in petroleum hydrocarbon stocks, which comprises contacting a blend consisting essentially of about 0.05 to 2.0 percent by weight of said resinous petroleum fraction and a petroleum fuel oil stock boiling in the range of about 300 to 900° F. with a desulfurization catalyst under non-cracking conditions of approximately 600 to 780° F., 0.5 to 4.0 WHSV, 300 to 1000 p.s.i. and 3 to 20 to 1 hydrogen to fuel oil stock ratio.

2. A process for the decolorization of an oil-soluble, propane-insoluble, paraffin base-derived resinous petroleum fraction having a viscosity of about 5000 to 8000 SSU at 210° F. for use as a pour depressor in petroleum hydrocarbon stocks, which comprises contacting a blend consisting essentially of about 0.3 to 1.0 percent by weight of said resinous petroleum fraction and a petrolem fuel oil stock boiling in the range of about 350 to 700° F. containing cracked components with a desulfurization catalyst under non-cracking conditions of approximately 650–700° F., 0.5–4.0 WHSV, 300 to 1000 p.s.i. and 5 to 10 hydrogen to fuel oil stock ratio.

3. A decolorized, pour depressed composition prepared by a process which comprises contacting a blend consisting essentially of about .05 to 2 percent by weight of an oil-soluble, propane-insoluble, paraffin base-derived resinous petroleum fraction having a viscosity of about 3,000 to 10,000 SSU at 210° F. and a petroleum fuel oil stock boiling in the range of about 300–900° F. with a desulfurization catalyst under non-cracking conditions of approximately 600–780° F., 0.5 to 4.0 WHSV, 300 to 1000 p.s.i. and 3 to 20 to 1 hydrogen to petroleum fuel oil stock ratio.

4. A pour depressed fuel oil composition consisting

essentially of a petroleum hydrocarbon fuel oil boiling in the range of about 300 to 900° F. and containing at least about 15 percent of cracked components and sufficient of the product of claim 1 to provide about 0.01 to 2.0 percent of the petroleum resin.

5. A pour depressed fuel oil composition consisting essentially of a petroleum hydrocarbon fuel oil boiling in the range of about 300 to 900° F. and containing at least about 15 percent of cracked components and sufficient of the product of claim 2 to provide about 0.01 to 2.0 percent of the petroleum resin.

6. A pour depressed fuel oil composition consisting essentially of a petroleum hydrocarbon fuel oil boiling in the range of about 300 to 750° F. and containing at least about 15 percent of cracked components and sufficient of the product of claim 2 to provide about 0.01 to 0.15 percent of the petroleum resin.

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