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2,917,375

FUEL OILS

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The present invention relates to new compositions of matter. More particularly the present invention relates to mineral oil compositions containing pour depressors and pour depressor aids which in addition prevent or avoid the formation of suspended or settled solids in the compositions.

In order to meet pour point specifications for mineral oil compositions such as heating oils and diesel fuels, it is frequently necessary to employ an additive known as a pour depressor. Many materials are known pour depressors and among these a highly effective class is represented by a group of synthetic resins derived by the polymerization of esters of acrylic and methacrylic acids. One disadvantage of polymers of esters of acrylic acids as pour depressors is their high expense. Such disadvantage is generally not shared by other known pour depressors; however, the effectiveness of the acrylic resins has, in the past, outweighed their expense.

It is also known in the prior art that the effect of pour depressors can be aided by incorporating in the mineral oil-pour depressor composition a material known in the art as a pour depressor aid. Examples of known pour depressor aids include hydrocarbon waxes, for example amorphous waxes and crystalline waxes such as paraffin waxes, both those derived from petroleum and native paraffin waxes, e.g. ozocerite (see U.S. patent to Martin 2,615,799). While the use of pour depressor aids of the type mentioned is effective in reducing concentration of pour depressor needed, generally the mineral oil-pour depressor-pour depressor aid composition experiences the formation of solids, i.e. suspended (haze) or settled wax precipitates, when stored for short periods of time, e.g. in excess of about 24 hours.

Among the undesirable effects resulting from solids formation in mineral oils of the type described above, the deleterious effects to the free flow of the mineral oils through oil screens and lines, due to the obstructive nature of the solids formed therein, are particularly undesirable. Further, the expense of acrylic type pour depressors limits the quantity which may be incorporated in marginal fuels. At very low concentrations of pour depressor in marginal fuels, known pour depressor aids have not been especially satisfactory in facilitating a lowering of the pour points.

I have now discovered that paraffin base microcrystalline wax when used in conjunction with acrylic type pour depressor resins in mineral oil compositions, containing marginal oils as well as cracked oils, permits the use of exceedingly low concentrations of pour depressor. I have also discovered that paraffin base microcrystalline wax can be used as a pour depressor aid for acrylic type pour depressors in distillate fuels containing marginal as well as cracked components. The use of such an aid in this manner results in a composition characterized by great stability in storage and superior resistance to solids formation, i.e. suspended (haze) or settled wax precipitates. In accordance with my invention small amounts of microcrystalline waxes derived from paraffin base oils are used as pour depressor aids to obtain the advantages described.

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The microcrystalline waxes which are used as pour depressor aids in the present invention are commercially available and are derived from paraffin base oils. More particularly a Pennsylvania vacuum still bottoms or reduced crude is treated with propane to precipitate the resins contained therein; after separating the resins, microcrystalline waxes are obtained by employing the conventional methylethyl ketone dewaxing process.

When employing the paraffin base microcrystalline wax pour depressor aids of the present invention in conjunction with acrylic type pour depressors in distillate fuels containing marginal and cracked components, I have found that concentrations of depressor aid of about 0.2 to 0.4 weight percent are effective with acrylic type pour depressor concentrations of about 0.01 to 0.03 weight percent of commercial concentrates, or concentrations of about 0.003 or 0.004 to 0.02 on a 100 percent basis, to lower the pour point. Use of these concentrations advantageously results in distillate fuel compositions with superior resistance to solids formation than known distillate fuel-acrylic type depressor-depressor aid compositions. Concentrations of depressor aid of about 0.2 to 0.4 weight percent permit the use of as low as 0.01 to 0.03 weight percent of commercial concentrates of acrylic resin to effectively lower the pour point of marginal stock-containing compositions.

Marginal stock as used in this specification is intended to indicate petroleum hydrocarbons which may or may not include cracked components, such as straight run gas oils and catalytic or thermal cycle or gas oils for example, generally at least about 10 weight percent and usually not more than about 70 percent and preferably from about 10 to 50 percent gas oil that normally cannot be employed in fuel oils because of their high pour point. Such stocks generally have distillation end points of 600° F. to 675° F. or even to 700° F. Cracked oils as used in this specification is intended to indicate, for instance, cracked light gas oil, and will generally comprise at least about 10 percent but usually about 10 to 50 percent of the composition.

Heating oils and fuel oils encompassed by the present invention include those distillate fuels having boiling ranges intermediate the boiling range of kerosene and lubricating oils, i.e. about 340° to 700° F., and normally have pour points of about 5° to 15° F. These include virgin light distillates and catalytically cracked cycle oils and blends of the foregoing. Also, blends of more than two distillate fuels having boiling points within the defined range can be employed.

The acrylic resin pour depressors to be used in the instant invention are known articles of commerce available commercially as Acryloid 150 (a methacrylate ester polymer prepared from cetyl, lauryl and octyl alcohols with a molecular weight of about 10,000 to 15,000), Acryloid 710 (a methacrylate ester polymer prepared from lauryl and octyl alcohols with a molecular weight of about 10,000 to 20,000), and Acryloid 763 (from Rohm and Haas). These resins are oil-soluble and are partially polymerized esters of alpha-methacrylic acid or acrylic acid and monohydric aliphatic saturated alcohols. The alcohols employed are those having at least 12 carbon atoms on the average and preferably 12 to 24 or more carbon atoms per molecule. Typical pour depressors are polymers of dodecyl methacrylate, tetradecyl methacrylate, hexadecyl methacrylate, and octadecyl methacrylate. The polymers have molecular weights of about 500 to 20,000. In commercial form, the pour depressors are available as a 40 weight percent concentrate in a high grade solvent. These concentrates normally have API gravities of about 23 to 28, and a viscosity at 210° F. of about 2500 to 4000 SUS.

Compositions of the present invention can be produced by incorporating the microcrystalline wax in the mineral

oil fraction either before or after the pour depressor is added, or the depressor aid can be added to the pour depressor separately from the oil and then incorporated in the oil as a mixture with the pour depressor. Microcrystalline waxes generally are highly soluble in acrylic type pour depressors and, of course, both the waxes and the pour depressor are highly soluble in mineral oils generally. Special conditions of temperature and pressure need not be observed in effecting solution of pour depressor and pour depressor aid in the oil; to form a solution of pour depressor and pour depressor aid in the absence of the distillate fuel, it is desirable to heat to an elevated temperature, e.g. to about 125° F. to effect the solution.

The invention will be further described by the following specific examples.

EXAMPLE I

A mineral oil heating fuel was made by blending 6.3 percent of a naphtha having a boiling range of about 300° to 400° F., 19 percent of water white distillate, 34.7 percent of a 675° F. cut point light gas oil and 40 percent of a 675° F. cut point light cycle oil (all quantities are volume percent). The characteristics of the blend are as follows:

Tests:

Gravity, ° API	33.7
Flash, ° F.	160
Viscosity, centistokes, at 100° F.	3.297
Cloud, ° F.	12
Pour, ° F.	10
Color, NPA	2—
Distillation—	
IBP	340
5%	408
10%	434
20%	473
30%	504
40%	528
50%	546
60%	566
70%	582
80%	608
90%	618
95%	632
EP	652
Res.	1.0
Cetane No.	45

To samples of this blend, commercial "Acryloid 763" was added in varied amounts. "Acryloid 763," a 40 weight percent concentrate of acrylate in solution, has an API gravity of about 24.0 and a viscosity at 210° F. of about 3577 SUS. To several of the samples containing the pour depressor, varying concentrations of microcrystalline waxes derived from paraffin base oils were added. Samples of microcrystalline wax derived from a Mid-Continent base oil were added to other samples of the fuel blend containing "Acryloid 763." The properties of the waxes employed are as follows:

Test	Paraffin Base-Microcrystalline Wax	Mid-Continent Base Microcrystalline Wax
Gravity, ° API	32.8	32.8
Flash, ° F.	545	545
Fire, ° F.	620	645
Viscosity, SUS at 210° F.	89.4	92.8
Petroleum Melting Point, ° F.	123	158
Color, NPA	4—	6—
Penetration at 77° F., 100 gm. Needle	96	96
Percent Oil, ASTM D721-51T	1.78	4.66

The oil-pour depressor-pour depressor aid compositions

were tested for cloud and pour points according to the ASTM standard tests. The results are as follows:

MICROCRYSTALLINE WAX, WEIGHT PERCENT

Sample	Acryloid 763, Wt. Percent	Paraffin Base	Mid-Continent Base	Pour, ° F.	Cloud, ° F.
1	0	—	—	+10	12
2	0.05	—	—	+10	12
3	0.1	—	—	+10	14
4	0.01	0.3	—	0	18
5	0.01	0.4	—	-10	18
6	0.01	—	0.3	+15	18
7	0.01	—	0.4	+15	18
8	0.03	0.3	—	-20	18
9	0.03	0.4	—	-20	18
10	0.03	—	0.3	+15	18
11	0.03	—	0.4	+10	18

From the above data it is apparent that use of the defined microcrystalline waxes as depressor aids facilitates the lowering of the pour points of distillate fuels containing marginal stocks at low concentrations of acrylic-type pour depressors, while waxes derived from Mid-Continent oils had substantially no effect at the same concentrations of pour depressor. The compositions were permitted to stand for about four days and were then inspected for haze formation. Each of the samples containing the paraffin base microcrystalline wax was clear while a haze had developed in each of the samples containing the microcrystalline wax derived from Mid-Continent crude oil.

EXAMPLE II

The following tests demonstrate the superior resistance to solids formation, i.e. suspended (haze) or settled wax precipitates, exhibited by the compositions of the present invention using paraffin base microcrystalline wax in comparison with similar compositions containing microcrystalline wax derived from Mid-Continent crude oil. All oils were essentially clear of suspended precipitate except the oil containing depressor aid A, which was hazy in appearance following storage at a temperature of 40° F.

The tests which formed the basis for the above conclusions were obtained by storing samples of the depressed fuel in gallon bottles under conditions of room temperature as well as cold room temperatures of 40° F. and 10° F. These samples were periodically inspected for solids formation. The distillate fuel used is a fuel (Fuel I) predominantly derived from Mid-Continent crude oil having characteristics shown below in Table III. This fuel was depressed with 0.01 percent Acryloid 763¹ in combination with the following depressor aids:

- Microcrystalline wax with a melting point² of 165° F. and derived from Mid-Continent, i.e. Colorado-Kansas, crude oil.
- Microcrystalline wax with a melting point² of 160° F. and derived from Mid-Continent, i.e. East Texas, crude oil.
- Microcrystalline wax with a melting point² of 123° F. and derived from paraffin base, i.e. Pennsylvania, crude oil.
- Microcrystalline wax with a melting point² of 105° F. and derived from paraffin base, i.e. Pennsylvania, crude oil.

Additional samples of neat fuel were set up for comparison purposes. The results of the visual inspections are tabulated below in Table I. Since the visual information on the 10° F. samples were indistinguishable a more accurate means of developing information on solids formation was developed and include a quantita-

¹ A commercial Acryloid, containing 40 weight percent of acrylate in a hydrocarbon solvent, with an API gravity of about 24.0 and a viscosity at 210° F. of about 3577 SUS.

² Melting point determined by test method ASTM D-127-49.

tive relationship established by separating and weighing the wax precipitates. This was done by filtering, with filter aid, a liter of the fuel at the test temperature (+10° F.) and washing the cake free of oil with pentane. The cake was extracted with boiling hexane and the solution filtered. The hexane was evaporated from the filtrate and the wax residue determined by weighing. The results of these determinations are listed in Table II. The amount of wax recovered ranged from nil for the neat fuel to over 1000 mg./liter for the sample containing aid B.

At 10° F. the amount of insolubles formation, as shown with data presented in Table II, was considerably less in the samples containing aids C and D than that from samples containing aids A and B. The 40° F. and room temperature storage samples show, with data presented in Table I, that samples containing aids A and B exhibited the heaviest precipitates while samples containing aids C and D exhibited the lightest precipitates. In addition the latter samples took longer to form their respective precipitates.

Table I

PRECIPITATE FORMATION IN POUR DEPRESSED FUEL I

Depressor Aid ¹	Conc., Percent	Room Temperature Storage		40° F. Storage		
		Appearance of 1st Insolubles, Days	Condition of Oil After 18 Days	Appearance of 1st Insolubles, Days	Condition of Oil After 20 Days	Condition of Oil After 5 Days Back At Room Temperature
Neat		10	Trace Ppt.	20	Trace Ppt.	Trace Ppt.
A	0.3	3	Medium Ppt.	4	Heavy Ppt.	Medium Ppt.
B	0.3	3	Heavy Ppt.	4	do	Do.
C	0.3	18+	No Ppt.	6	Trace Ppt.	Trace Ppt.
D	0.3	18+	do	20	do	Do.

¹ All fuels except neat contain 0.01% Acryloid 763.

Explanation of precipitate observations:

Trace Ppt: Upon hard shaking of bottle small wisp of deposit rises from bottom.

Light Ppt: Upon light shaking of bottle small cloud of deposit rises up from bottom.

Medium Ppt: Upon light shaking of bottle cloud of deposit rises filling about half of bottle.

Heavy Ppt: Precipitate covers whole bottom of bottle but to insignificant depth. Upon light shaking of bottle large cloud of deposit rolls up filling most of bottle.

Table II

LOW TEMPERATURE (10° F.) INSOLUBLE DEVELOPMENT IN POUR DEPRESSED FUEL I

Depressor Aid ¹	Conc., Percent	Original Pour Point, ° F.	Pour Point of 10° F. Filtrate, ° F.	Wax Filtered Off at 10° F. mg./1,000 ml.
Neat		-5		2 CK ² 21
A	0.3	-30	-25	714
B	0.3	-20		1007 CK ² 813
C	0.3	B-30	-30	277 CK ² 853
D	0.3	B-30	-30	94 CK ² 100

¹ All fuels except neat contain 0.01% Acryloid 763.

² The numbers before "CK" represent the initial values obtained and the numbers following "CK" represent values obtained upon checking the initial values.

Table III

PHYSICAL CHARACTERISTICS OF A FUEL OIL (REFERRED TO AS FUEL I)¹ FOR POUR DEPRESSOR AID EVALUATION

Gravity, ° API	34.8
Flash, ° F.	154
Cloud point, ° F.	0
Pour point, ° F.	0
Color, NPA	1½+
Distillation (200 ml.):	
Initial boiling point, ° F.	351
5%	397
10%	412
20%	436
30%	457
40%	476
50%	494
60%	513

70%	535
80%	559
90%	588
95%	607
End point	630
Recovery, percent	99.5
Residue	0.5

¹ Fuel I is a mineral heating fuel made by blending 10 percent of a naphtha having a boiling range of about 300° to 400° F., 25 percent of water white distillate, 35 percent of a 641° F. end point light gas² oil, and 30 percent of a 557° F. end point light cycle oil or cracked light gas oil (all quantities are volume percent).

² Distillation characteristics of the light gas oil:

Initial boiling point, ° F.	452
10%	553
20%	565
30%	573
40%	580
50%	585
60%	590
70%	595
80%	602
90%	612
End point	641
Pour point	+30

This application is a continuation-in-part of application Serial No. 457,998, filed September 23, 1954, and now abandoned.

I claim:

1. A distillate fuel composition consisting essentially of a base distillate fuel oil having an end point above about 600° F., about 0.003 to 0.02 weight percent of a viscous oil-soluble polymerization product of an ester of acrylic acid and a saturated aliphatic alcohol having at least 12 carbon atoms per molecule and about 0.2 to 0.4 weight percent of a paraffin base microcrystalline wax; said composition containing at least about 10 weight percent of cracked fuel components.

2. The composition of claim 1 wherein the base fuel oil contains from about 10 to 50 percent of cracked gas oil.

References Cited in the file of this patent

UNITED STATES PATENTS

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