United States Patent [19]

Cole et al.

[11] **3,792,984**

[45] **Feb. 19, 1974**

[54] **FUEL OIL BLENDING TO IMPROVE POUR REDUCTION**

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[22] Filed: **June 25, 1970**

[21] Appl. No.: **49,991**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 878,919, Nov. 21, 1969, abandoned.

[52] **U.S. Cl.** **44/62,** 44/70

[51] **Int. Cl.** **C10l 1/18**

[58] **Field of Search** 44/62, 70; 252/56

[56] **References Cited**

UNITED STATES PATENTS

2,664,388	12/1953	Winterhalter	208/15 X
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[57] **ABSTRACT**

A low pour point fuel oil blend is prepared from a major amount of a high pour point, low sulfur, waxy, residual fuel and a minor amount of low-waxy, low pour, residual fuel oil by adding thereto from 0.01 to 0.5 percent by weight of an oil soluble ethylene-vinyl fatty acid ester copolymer in which the fatty acid component of the ester has a carbon content of from about 2 to about 6; the copolymer having a molecular weight between about 20,000 and 31,000, a melt index of about 5 to about 28 and a vinyl fatty acid ester content of from about 24 to about 34 percent. The copolymer may be added either in a water-glycol emulsion or in a hydrocarbon to one of the blend components which has been heated to between about 200° to 400°F.

6 Claims, No Drawings

FUEL OIL BLENDING TO IMPROVE POUR REDUCTION

CROSS-REFERENCE TO CO-PENDING APPLICATION

This application is a continuation-in-part application of commonly assigned application Ser. No. 878,919 filed Nov. 21, 1969 now abandoned.

This invention is concerned with means for providing a low sulfur, low pour fuel oil blend. More particularly, the invention is concerned with a fuel oil blend containing a major amount of a high pour, low sulfur, waxy residual fuel and a minor amount of a low-waxy, low pour residual fuel oil, this blend having a reduced pour point relative to its components owing to the incorporation therein of certain high molecular weight ethylene-vinyl fatty acid ester copolymers.

As is well known, residual fuel oils contain quantities of wax and asphaltic compounds which render them viscous and which sometimes interfere with practical use thereof. Particularly serious problems can be encountered in pumping residual fuel oils to a burner and in making them flow at low temperatures. Other factors to be reckoned with in regard to these oils are the facts that they behave as non-Newtonian liquids at low temperatures; exhibit variable solidifying temperatures and manifest peculiar hysteresis phenomena — all of which result in difficulties in equipment design.

One approach used in making these oils easier to handle has been to subject them to fairly lengthy and costly dewaxing procedures.

Another approach which has been suggested and tried in order to bring the viscosity of residual fuel oils to suitable levels has been to dilute or "cut" them with a major amount of lighter distillate oils. This procedure is expensive because of the considerably higher cost of the distillate oils relative to that of residual oils.

In recent years it has been recommended to incorporate additives in lubricating oils and in so-called middle distillates in order to tie in the wax present therein and to improve flow characteristics at reduced temperatures. The additives in question consist either of compounds formed by alkylating benzene or naphthalene derivatives; or, of copolymers of ethylene-vinyl fatty acid ester of a molecular weight up to 3,000 containing from 15 to 25 percent by weight of the vinyl fatty acid ester.

In commonly assigned, co-pending application, U. S. Ser. No. 832,856, filed June 12, 1969, now abandoned, there has been disclosed and claimed a residual fuel oil composition containing an additive comprising a middle distillate heating oil boiling from about 350° to 650°F and an effective pour point depressant amount of an oil soluble ethylene-vinyl fatty acid ester copolymer or resin in which the fatty acid component of the ester has a carbon content of from about two to about six, the copolymers having a molecular weight of about 20,000 to about 31,000, a melt index of about 5 to about 28 and a vinyl fatty acid ester content of from about 24 to 34 percent.

In the present invention use is made of the same above-described copolymer with high pour residual fuels of low sulfur content so as to comply with current air pollution restrictions in respect to sulfur.

The main object of the present invention, accordingly, is to provide for critical blending of high pour waxy residual fuel oils with low-waxy, low pour residual fuel oils to give large increases in pour reduction without employing elaborate dewaxing procedures.

An equally important object of the claimed invention is to provide a novel fuel oil blend characterized by a low sulfur content and a reduced pour point resulting from the incorporation therein of a small amount of certain ethylene-vinyl fatty acid ester copolymers.

A further object of the claimed invention is to provide a fuel oil blend which will be stable at different blend temperatures over storage times of up to about 3 months.

Other objects of this invention will in part be obvious and in part hereinafter pointed out.

The fuel blend of the invention comprises a major amount (i.e., over 50 percent by volume) of a high pour, waxy, residual fuel oil having an API gravity of about 20.0 to about 25.0; a sulfur content of between about 0.40 wt. percent and about 0.96 wt. percent; a Furol viscosity at 122°F of about 60 to about 230; a flash point of between about 300° and 450°F, with a wax content of between about 10 and 20 percent; and a minor amount (i.e., less than 50 percent by volume) of a low-waxy, low pour residual fuel oil having an API gravity of about 10.0 to about 15.0; a Furol viscosity at 122°F of about 150 to about 250; a flash point of about 220° to about 350°F; a pour point of between about 25°F and about 45°F; a wax content of between about 2 and 5 weight per cent with a sulfur content of between about 0.50 and about 0.90 weight percent. A waxy, low pour residual fuel oil which has given particularly good results as the minor constituent of the claimed blend is that known as No. 6 Fuel Oil which has an API gravity of about 12.3, a Furol viscosity of 207.0 at 122°F, a pour point of about 40°F and a wax content of about 3 percent.

The pour point depressant additives suitable in the practice of the invention comprise oil soluble ethylene-vinyl fatty acid ester copolymers in which the fatty component of the ester has a carbon content of from about 2 to about 6, the copolymers having an average molecular weight of about 20,000 to about 31,000 determined as the Number Average Molecular Weight by the Membrane Osmometry Analytical Method, a vinyl fatty acid ester content of from about 24 to about 34 percent and a melt index of about 5 to about 28. The preferred copolymers are sold under the trade name of "Elvax" by the E. I. Du Pont de Nemours Company, the most suitable being Elvax 250 which contains 27 to 29 percent of vinyl acetate, has an inherent viscosity at 100°F. of 0.78 dcl./gm. in toluene; a softening point as determined by A.S.T.M. E 28 of 280°F; a cloud point in paraffin wax of 150°F, a Melt Index of 12–18 and a molecular weight of 23,000 to 27,000. The material is supplied by its manufacturer for use in blends containing wax to provide toughness, flexibility, adhesion and barrier properties — properties having nothing common with pour point reduction in fuel oil blends.

The subject copolymers can be prepared by any convenient process such as taht of U. S. Pat. No. 3,215,678 by a free radical-initiated polymerization reaction of ethylene and a vinyl ester of a lower saturated monobasic aliphatic carboxylic acid. The characterization of the various "Elvax" additives is given in Table A below:

TABLE A

"ELVAX"	% Vinyl Acetate in Copolymer	Melt Index*
40	39–42	45–70
150	32–34	22–28
210	27–29	335–465
220	27–29	125–175
240	27–29	22–28
250	27–29	12–18
260	27–29	5–7
310	24–26	335–465
350	24–26	16–22
360	24–26	1.6–2.4
410	17–19	430–580
460	17–19	2.1–2.9

*in g/10 min. as determined by ASTM 1328 modified.

The specific properties of the oils used in examples of the practice of the invention appear in Table I below:

TABLE I

BASE STOCKS INSPECTION TESTS

Base Stock	F/18 Fuel Oil (1)	F/18 Fuel Oil (2)	F/18 Fuel Oil (3)	NO.6 Fuel Oil
TESTS				
Gravity, API	22.3	23.5	22.6	12.3
Flash Point (COC), °F	425	395	330	270
Viscosity, SUS				
at 122°F	1043	1971	701	1968
at 150°F	435	404	315	748
ASTM Pour Point, °F	100	100	90	40
Carbon Residue, WT.%	6.8	6.99	6.78	13.61
Wax Content, WT.%	16.80	15.99	12.36	3.05
Sulfur, WT.%	0.96	0.54	0.84	0.74

It was observed in experimental work leading to the present invention that the copolymer additives did not significantly lower the pour points of either of the components of the blends themselves. Thus addition of 0.125 percent by weight of Elvax 250 to 100 percent of the F/18 (1 oil) lowers the average pour point thereof by only 1°F. Similarly 0.125 percent by weight of the same additive lowers the pour point of the No. 6 oil only by about 6° F. Unexpectedly this last mentioned amount of Elvax 250 lowers the pour point of a 60/40 percent by volume mixture of these two oils by 27°. This will be seen in Tables 2 and 3 below.

TABLE II

Averages of Duplicate Samples at 0, 3 weeks, 6 weeks, 3 months

100% Stocks Blended at 200°F	Elvax 250, % 0	.125	.094	.062	.031
F/18 (1)	92	91	—	92	94
F/18 (2)	98	96	—	91	91
F/18 (3)	96	88	—	89	91
Louisiana No. 6	32	26	—	29	28

TABLE III

100% Stocks Blended at 350° F	Elvax 250, % 0	.125	.094	.062	.031
F/18 (1)	93	—	94	94	97
F/18 (2)	94	—	94	98	99
F/18 (3)	97	—	90	94	94
Louisiana No. 6	37	—	38	36	40

In practice the claimed fuel blends suitably are prepared in the following manner. Either of the fuel oil components is brought up to a temperature of between 200° and 400°F. The pour depressant is then uniformly dispersed in the fuel oil by injecting it into the residuum run downstream in the refinery process area. The component to which the pour depressant has been added is then thoroughly mixed with the other component of the blend. Tables IV and V below show the average pour points of dupliate samples at 0, 3 weeks, 6 weeks and 3 months. These data show that the blends produced by the invention desirably remain stable over storage times of a least up to three months. The data show also that lesser quantities of the additives lower the pour points to a lesser degree. The data moreover show that blending the fuel and additives at 350°F. gives a slightly smaller reduction than those blending at 200°F.

TABLE IV

Averages of Duplicate Samples at 0, 3 Weeks, 6 Weeks, 3 Months

Fuel Mixture 60 % (V) F/18–40% (V) No. 6 Blended at 200° F.	Elvax 250, % 0	.125	.094	.062	.031
F/18 (1) – No.6	80	53	53	61	76
F/18 (2) – No. 6	82	52	57	67	81
F/18 (3) – No. 6	79	44	47	49	69

TABLE V

Fuel Mixture 60 % (V) F/18-40% (V) No. 6 Blended at 350°F.	Elvax 250, % 0	.125	.094	.062	.031
F/18 (1) – No. 6	83	—	60	74	81
F/18 (2) – No. 6	84	—	71	73	76
F/18 (3) – No. 6	77	—	62	70	70

The sulfur levels in the blends of the invention range from 0.62 to 0.97 wt. per cent.

Where it is desired to incorporate the copolymers at low temperatures in one of the oils comprising the blend, it will be preferred to dissolve them in a hydrocarbon such as toluene, kerosene, and the like and to emulsify with a mixture of ethylene glycol, water and detergent to form an oil in water emulsion. The pour point of the resultant emulsion will be essentially that of the water-glycol phase. A practical example of this approach is the use of a water-glycol emulsion which contain 22.3 percent of the polymer.

On the contrary, where it is desired to use a temperature of around 250°C. for incorporating the copolymers, it will be preferred to add the copolymers to the oil at the said temperature in the form of a hydrocarbon solution in, for example, toluene. This can be done by making a 12½ percent Udex extract hydrocarbon blend incorporating the polymer.

The unexpected and unobvious nature of the present invention can best be appreciated from the comparison tabulated below in Table VI of the pour points obtained with various additives differing in vinyl acetate content and melt index. It will be apparent from Table VI that only certain additives reduce the pour point while certain others have little effect or even increase it. Thus the copolymer Elvax 40 having a percent of vinyl acetate in excess of 34 gave a pour point of 80°F, a reduction of only 5°F from the control and Elvax 460 appeared to increase it by 5°F.

TABLE VI

Elvax No. (0.1% in Blend)	Pour Point (°F) F18/No. 6 Fuel Blend
None	85
EFFECTIVE	—
150	50
240	50
250	40
260	55
300	60
350	45
NOT EFFECTIVE	—
40	80
210	75
220	75
360	70
410	80
460	90

We claim:

1. Process for producing a low pour point, low sulfur fuel oil blend comprising blending a major amount of a high pour, waxy residual fuel oil having a pour point of between about 80° and 120°F.; and a minor amount of a low waxy, low pour, residual fuel oil, bringing one of said oils to a temperature of between about 200° and 400°F.; adding to the said oil a pour depressant consisting of an oil soluble, ethylene-vinyl fatty acid ester copolymer in which the fatty acid component of the ester has a carbon content of from about two to about six, said copolymer having a molecular weight of about 20,000 to about 31,000, a vinyl fatty acid ester content of from about 24 to about 34 percent and a melt index of about 5 to about 28; uniformly dispersing said copolymer in said oil at said temperature; and mixing said oils to produce a blend having a pour point substantially lower than either of said oils.

2. A fuel oil blend characterized by a lowered pour point and a low sulfur content comprising a major amount of a high pour, waxy, residual fuel oil having a pour point of between about 80° and 120°F. and a minor amount of a low waxy, low pour, residual fuel oil and an effective pour depressant amount of an oil soluble, ethylene-vinyl fatty acid ester copolymer in which the fatty acid component of the ester has a carbon content of from about two to about six, said copolymer having a molecular weight of between about 20,000 to about 31,000; a vinyl fatty acid ester content of from about 24 to 34 percent, and a melt index of about 5 to about 28.

3. The composition according to claim **2** wherein the said vinyl ester is vinyl acetate and wherein the said composition contains over 50 percent by volume of the said high-pour fuel oil.

4. The composition according to claim **2** wherein said copolymer is present in a concentration ranging from about 0.01 to about 0.5 percent by weight.

5. The composition of claim **2** containing 60 percent by volume of said high pour fuel oil and 40 percent by volume of said low pour fuel oil.

6. The composition of claim **2,** wherein said high pour, residual fuel oil has an API gravity ranging between about 20.0 and about 25.0; a sulfur content between about 0.40 weight percent and about 0.96 weight percent; a Furol viscosity at 122°F. of about 60 to about 230; a flash point of between 300° and 450°F. and a wax content of between about 10 and 20 percent; said low waxy, low pour residual fuel oil having an API gravity of about 10.0 to about 15.0; a Furol viscosity at 122°F. of about 150 to about 250; a flash point of about 220 to about 350°F.; a pour point of about 25°F. and 45°F.; a wax content of about 2 to about 5 weight percent and a sulfur content of between about 0.50 and about 0.90 weight percent.

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