

- [54] **HYDROCARBON OIL CONTAINING ETHYLENE COPOLYMER POUR DEPRESSANT**
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- [63] Continuation of Ser. No. 779,592, Nov. 27, 1968, abandoned.

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- [58] Field of Search 44/62, 66, 70; 252/56 R

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[57] **ABSTRACT**

Hydrocarbon oils such as residua fuels, residua-containing fuels, flash distillate fuels and crude oils are improved in their pour points by the incorporation of a pour point depressing copolymer of 82 to 90 mole percent ethylene with certain substituted ethylenes of 3 to 40 carbon atoms which have less than 18 carbon atoms in any linear side chains.

9 Claims, No Drawings

HYDROCARBON OIL CONTAINING ETHYLENE COPOLYMER POUR DEPRESSANT

This application is a continuation of Ser. 779,592, filed Nov. 27, 1968, now abandoned.

This invention relates to fuel compositions based on residua-containing fuels, crude oils and other base oils.

Although various pour point depressants are known and have been used, they have been reasonably successful only with middle distillate fuels. It has been found difficult to obtain a potent pour point depressant for shale oils, crude oils, residua-containing fuels, and flash distillate fuels. We have now discovered certain polymers which are potent as pour point depressants in certain hydrocarbons, e.g. residua-containing fuels or crude oils.

Fuel or crude oil pour point has great practical significance. It should be beneath a minimum temperature at which the fuel or crude oil is stored, transported and used, in order to obviate difficulties when the fuels are used in practice.

According to this invention hydrocarbon-containing compositions comprise a major proportion by weight of a residua-containing fuel, flash distillate fuel, shale oil or a crude oil, and a minor proportion by weight of an oil-soluble copolymer of ethylene and one or more substituted ethylenes, wherein if there is any saturated linear side chains present in the substituted ethylene each of said linear side chains must contain less than 18 carbon atoms, provided said copolymer has a number average molecular weight of above 800, and provided said copolymer is not a dipolymer having a number average molecular weight of above 3,000, of ethylene and a vinyl or hydrocarbyl substituted vinyl ester of a carboxylic acid.

The residua-containing fuel is defined as a fuel comprising residua from the distillation of crude oil or shale oil or mixtures thereof. Generally the residua-containing fuel (hereinafter referred to simply as the "fuel") will contain from about 10 to 100 percent, e.g. from about 35 to 100 percent, by weight of residua, preferably boiling above 600°F at atmospheric pressure, and will usually have kinematic viscosities ranging from 10 to 3,500 cS at 100°F. However, the viscosity of some particularly waxy fuels may be difficult to measure accurately at 100°F, and it is well known in the art that the viscosity of such fuel is measured by the viscosity at a higher temperature. The viscosity at 100°F is then obtained by extrapolation using a R.E.F.U.T.A.S. viscosity temperature chart. The extrapolated kinematic viscosity will then fall in the desired range at 100°F. The R.E.F.U.T.A.S. temperature viscosity chart was designed by C. I. Kelly, M.S.C. TECH., F.I.C., M. Inst., P.T., A.M.I.A.E. Copyright reserved in Great Britain and U.S.A. by Baird & Tatlock (London) Ltd., 14-17, Cross Street, Hatton Garden, London, E.C.1. Fuels having kinematic viscosities of between 15 and 1500 cS at 100°F are preferred, and also fuels wherein at least 30 percent, preferably at least 60 percent by weight of the fuel boils above 500°F at atmospheric pressure are particularly suitable.

The fuels to which this invention applies include therefore, light, medium, heavy and bunker or furnace fuels, the viscosities ranging from about 15-2,000 cS at 100°F, but usually, however, the maximum viscosity will be about 1,500 cS at 100°F. Examples of suitable

fuels are described in Pt 3 Industrial and Marine Fuels of BS2689:1957.

Suitable fuels also include "flash-distillate fuels" which are defined as those distillate fuels obtained by the flash distillation at reduced pressure of the residue obtained from the distillation of crude oil at atmospheric pressure. Such fuels are prepared by distilling under atmospheric pressure a crude oil to a bottom temperature of approximately 350°C thereby obtained an atmospheric residue which is then divided by "flashing" under greatly reduced pressure, into a "flashed" distillate and a vacuum residue. In "flash" distillation, preheated feed is continuously introduced into a "flash" chamber, where evaporation occurs under constant equilibrium conditions. Gaseous and liquid products are continuously removed. Fractionation plays no significant part in "flashing". Temperature at which "flashing" is conducted is limited by potential cracking and carbonization. These side reactions begin to set in if temperatures exceed 400°C. "Flashing" is conducted at greatly reduced pressure, in order to secure high distillate yield from a given atmospheric residue.

Crude oils from which the fuels are derived, or shale oil or mixtures may also be used. The crude oil may be a waxy crude oil, and usually the pour point of such crude oils is greater than -10°F.

The substituted ethylene is preferably an ethylenically unsaturated acid, or a salt thereof, an anhydride, an ester of an unsaturated carboxylic acid, amine, hydroxy compound, nitrile, amide or imide, all of which must be compounds wherein if there is any saturated linear side chains therein each linear side chain has less than 18 carbon atoms. These substituted ethylenes preferably contain from 3 to 40 carbon atoms per molecule.

Thus, suitable ethylenically unsaturated monocarboxylic acids include acrylic acid, methacrylic acid, vinyl acetic acid, angelic acid, tiglic acid, undecylenic acid, oleic acid, elaidic acid. Suitable ethylenically unsaturated dicarboxylic acids include maleic acid, fumaric acid, mesaconic acid, citraconic acid, itaconic acid, trans- and cis-glutaconic acids. Other ethylenically unsaturated polybasic acids, e.g. cis- and trans-acetic acids may be used.

Examples of suitable esters of unsaturated acids, e.g. those mentioned above are the C₁ to C₁₇ alkyl esters (preferably straight chain alkyl esters and lower alkyl esters) of the above acids; either mono or di-esters of unsaturated dicarboxylic acids may be used. Branched chain esters, e.g. Oxo esters of ethylenically unsaturated esters may also be used provided that they do not contain any linear side chains containing more than 17 carbon atoms. Thus the methyl, ethyl, butyl, isopropyl, n-butyl, n-octyl 2-ethyl hexyl, decyl, dodecyl, heptadecyl esters of acrylic or methacrylic acids or the mono or di- methyl, ethyl, n-butyl, hexyl or dodecyl esters of fumaric, maleic or citraconic acids may be used.

Suitable ethylenically unsaturated amides include those corresponding to the acids mentioned above, i.e. both mono- and poly-amides; whereas suitable anhydrides and imides are those (where they exist) corresponding to the above-mentioned acids. Suitable salts may be the ammonium or metal, e.g. sodium or potassium, salts of the above acids. Thus, for example, one may use maleic anhydride, maleimide, acrylamide, methacrylamide, citraconamides, itaconamide, n-alkyl

maleimides containing up to 17 carbon atoms in any linear side chain.

Examples of suitable ethylenically unsaturated hydroxy compounds include monohydric alcohols, polyols, and phenolic compounds. Thus, examples of suitable monohydric alcohols are allyl alcohol, but 1-ene-1-ol, hex-2-ene-1-ol, hydroxyethyl methacrylate, eicos-4-ene-1-ol, 1-methyl-hex-2-ene-1-ol, 7-methyleicos-2-ene-1-ol, or 1-1 dimethyl-hex-2-ene-1-ol; diols include but-2-ene-1, 4-diol. Examples of suitable phenols include phenols having an unsaturated side chain, e.g. para allyl phenol (chavicol).

Suitable ethylenically unsaturated amines and nitriles include allyl amine, allyl cyanide, 1-amino-but-2-ene, 1-amino-hex-5-ene, 1-amino-nonadecen-18-ene, 1-amino-but-3-ene, dimethylaminoethyl methacrylate, dimethylaminomethylacrylates, diethylaminomethylmethacrylate, acrylonitrile, methacrylonitrile.

Other suitable examples of the substituted ethylene include an alpha-olefin, an alkenyl alkyl ether, styrene or a hydrocarbyl substituted styrene, alkenyl halides (e.g. a vinyl or allyl halide), an unsaturated aldehyde, or an unsaturated ketone. Examples of alpha-olefins are prop-1-ene, but-1-ene, hex-1-ene, dec-1-ene, and dodec-1-ene, nonadec-1-ene, whereas examples of suitable alkenyl alkyl ethers are vinyl methyl ether, vinyl ethyl ether, vinyl n-octyl ether, vinyl-n-heptadecyl ether, allyl methyl ether, allyl n-hexyl ether, allyl n-heptadecyl ether.

Suitable hydrocarbyl substituted styrenes include alkyl (e.g. methyl or ethyl) substituted styrenes wherein the substituents are in the benzene ring or attached to the alpha carbon atom of the vinyl group adjacent to the benzene ring, e.g. α -methyl styrene, α -ethyl styrene, p-methyl styrene, p-ethyl styrene, p-n-heptadecyl styrene.

Examples of vinyl or allyl halides are vinyl chloride, vinyl bromide, allyl chloride.

Suitable unsaturated aldehydes and ketones include acrolein, methyl vinyl ketone, mesityl oxide, ethyl vinyl ketone, n-heptadecyl vinyl ketone, cinnamaldehyde.

Further examples of substituted ethylenes are unsaturated esters of saturated carboxylic acids (provided that if there are any linear side chains present therein each linear side chain must contain less than 18 carbon atoms). These include the vinyl or allyl esters of C_1 to C_{18} monocarboxylic acids, e.g. vinyl acetate, allyl acetate, allyl propionate, vinyl butyrate, allyl stearate, isopropenyl acetate. With regard to these unsaturated esters of saturated carboxylic acids if the number average molecular weight of the copolymer is above 3,000, such esters must be co-polymerised not only with ethylene but also with another monomer which is not a vinyl or hydrocarbyl substituted vinyl ester of a carboxylic acid e.g. any of the previously mentioned monomers, i.e. the ester is a third co-monomer.

Other examples of substituted ethylenes which may be used are: vinyl substituted heterocyclics, e.g. N-vinyl pyrrolidone, vinyl pyridine, N-vinyl carbazole; vinyl derivatives of silicones and phosphorus compounds, e.g. di-ethoxy vinyl silane, di-ethyl vinyl phosphonate; vinyl isothiocyanate; hydrocarbyl vinyl sulphides, sulphoxides and sulphones or vinylene carbonate.

Ethylene may of course be copolymerised with two or more of any of the above mentioned monomers; e.g. vinyl acetate with acrylic acid, methacrylic acid, their

metal salts amides or nitriles; a vinyl halide with vinyl methyl ether or acrylic acid; or N-vinyl pyrrolidone with methyl vinyl ketone or vinyl methyl ether.

The resulting polymer should contain from 99 to 82 mole percent, preferably 97 to 86 mole percent of ethylene.

One method of preparing the copolymers involves feeding the monomers into a tubular reactor which has been previously purged with nitrogen. A small amount of oxygen, usually 0.005 to 0.05 wt. percent based on the weight of ethylene is also introduced into the reactor. Alternatively a peroxide initiator, e.g. di-t-butyl peroxide, or a mixture of peroxide initiator and oxygen may be introduced into the reactor in place of oxygen alone. A solvent (e.g. benzene, water, heptane, cyclohexane, acetone, methanol, t-butyl alcohol) may also be employed in the reaction. The pressure is maintained between 60 and 2,700 atmospheres (900 and 40,000 p.s.i.g.), preferably between 135 and 2,000 atmospheres (2,000 and 30,000 p.s.i.g.). The temperature should be maintained between 40°C and 300°C, preferably between 70°C and 250°C.

Another method of preparing the copolymers is via a batch process. Such a process requires a solvent for the reactants, the solvent being for example toluene, hexane, benzene, acetone, cyclohexane, t-butyl alcohol, water. The reaction initiator may be any peroxy compound, e.g. di-t-butyl peroxide, lauroyl peroxide, or azo compounds e.g. azobisisobutyronitrile. The temperature of the polymerisation reaction is dependent upon the particular peroxide initiator employed and should be high enough for sufficient decomposition of the initiator to occur. This temperature will usually be between 40°C and 300°C. For di-tert-butyl peroxide, the most suitable temperature is between 130°C and 160°C, whilst for lauroyl peroxide the most suitable temperature is between 60° and 120°C. The pressure should be between 60 and 1,000 atmospheres (900 and 15,000 p.s.i.g.), and preferably being between 75 and 667 atmospheres (1,100 and 10,000 p.s.i.g.). The autoclave or similar equipment containing the solvent, initiator and substituted ethylene is purged with nitrogen and then with ethylene before charging with a sufficient amount of ethylene to yield the desired pressure when heated to a reaction temperature. During the polymerization additional ethylene is added to maintain the pressure at the desired level. Further amounts of initiator and/or solvent, and/or substituted ethylene may also be added during the reaction. On completion of the reaction free solvent and unreacted monomers are removed by stripping or some other suitable process yielding the desired polymer.

The copolymers useful in the invention may have a number average molecular weight from 1,000 to 60,000 e.g. above 3,000 or above 3,500 as measured by Vapour Phase Osmometry (using a Mechrolab* Vapour Phase Osmometer model 301A) and/or Membrane Osmometry (using a Mechrolab* Membrane Osmometer model 501). The number average molecular weight of the copolymer used in this invention should preferably be between 1,500 and 30,000, particularly 4,000 to 20,000. It is understood that the average molecular weight of these copolymers will vary depending on the pressure, temperature and initiator concentration used during polymerization.

*Mechrolab Inc., 1062 Linda Vista Avenue, Mountain View, California.

The proportion of copolymer used in this invention should preferably be between 0.0001 and 10 percent, e.g. between 0.0005 and 0.5 percent by weight based on the weight of residual fuel, shale oil, crude oil or flash distillate.

The copolymer can also be applied down oil wells to crude oil to inhibit the formation of paraffin deposits, or to dissolve existing deposits on the sides of the well casing. The copolymer in this application can be applied either continuously or discontinuously to the oil well. The copolymer can also be added to crude oils or residua above ground to facilitate their movement through pipe lines. Thus, for example, the copolymer can be added to any North African crude, to lower the pour points so that they can be more readily pumped.

These copolymers also find application in certain fuels such as light oils where their presence reduces the size of wax particles which separate out. Thus certain grades of fuel such as light fuel oils develop problems due to "waxing." The wax which is present as the solid phase in such fuels at normal storage temperatures slowly agglomerates, and particles of such a size that they block filters prior to the burner are formed, thus resulting in loss of fuel flow to the burner and flame-out. The copolymers described in this invention when applied to the fuels and crude oils as herein described reduce the size of wax particles thus allowing them to pass more readily through filters.

The blending of the above-mentioned copolymers in fuels, crude oils, etc., can be facilitated by first forming copolymer concentrates in suitable hydrocarbon blend stocks, or water emulsions. Examples of suitable solvents are those containing a high proportion of aromatic hydrocarbons, e.g. toluene, xylene, kerosene extract, this extract being the highly aromatic fraction separated from a crude kerosene by a liquid sulphur dioxide extraction process. Further suitable solvents are slack waxes, which are the waxes obtained without purification or refining from lubricating oil dewaxing processes. Such suitable slack waxes will usually have melting points between 20°C and 62°C and oil contents of 5 to 50 wt. percent.

The copolymers may also be used in the fuels, crude oils, etc., in conjunction with other additives commonly used in fuels, e.g. rust-inhibitors, demulsifying agents, corrosion inhibitors, anti-oxidants or dispersants, or other flow improvers or pour depressants.

EXAMPLE 1

Copolymers of ethylene and substituted ethylenes were prepared by the following procedure:

A 1 litre stainless steel magnetically stirred autoclave was charged with benzene and then purged with nitrogen and thereafter with ethylene. The autoclave was then heated and pressurised with ethylene. A small quantity of the substituted ethylene was then introduced into the autoclave via a metering pump. A solution of 12.5 wt. percent of lauroyl peroxide in benzene was introduced to the autoclave over a period of time. Concurrently a further quantity of the substituted ethylene was introduced over a period of time into the autoclave. The temperature and pressure of the autoclave was kept substantially constant during the reaction. After addition of the peroxide was completed the reaction mixture was then cooled and the pressure released. Free solvent and unreacted monomers were removed by stripping to give the desired copolymers.

Precise reaction conditions for each copolymer are given in Table I.

TABLE I.—COPOLYMERISATION REACTION CONDITIONS

Ethylene comonomer	Wt. percent of comonomer in copolymer	M.W. of copolymer	Benzene solvent (ml.)	Temp., ° C.	Ethylene pressure, kg./cm. ²	Monomer addition		Catalyst addition		Yield copolymer, g.	Pour point, ° F.	
						G. originally	G. added	Hours	Ml. added ²		Hours	Upper light fuel
Ethylvinyl ether	9.4	3,400	100	82	316	20	100	4	85	4¼	+25	
		4,100	100	82	316	10	120	4	85	4¼	+30	
		3,000	100	82	316	20	200	4	85	4¼	+30	
N-vinyl pyrrolidone	49	2,700	100	79	316	15	180	6	100	6¼	+25	
	53	2,500	100	79	316	20	115	5¾	100	6	+25	
Methylvinyl ketone		7,940	150	110	316	40	160	4	85	4¼	+30	
Ethyl acrylate		7,500	150	79	316	10	180	4	85	4¼	+35	
Di-n-butyl fumarate	36	3,100	150	66	211	20	100	4	85	4¼	+35	
		3,300	100	71	316	30	180	3	65	3¼	+65	
N-vinyl carbazole	51	860	100	82	316	30	300	4	85	4¼	+95	+5
		1,000	100	82	316	10	80	4	85	4¼	+95	+5

¹ Number average molecular weight determined at 130° C. using o-dichlorobenzene as solvent.

² Of 12.5 wt. percent solution of lauroyl peroxide in benzene.

³ 20 wt. percent solution of N-vinyl carbazole in benzene.

Some of the copolymers were added at 0.1 wt. percent concentration to a light fuel oil containing residua having an upper pour point of 50°F (determined by Institute of Petroleum Method 15/67), a viscosity of 26.7 cS at 122°F and 43.7 cS at 100°F, a carbon content of 86.3 wt. percent and a hydrogen content of 12.4 wt. percent and a specific gravity at 15°C of 0.921.

The upper pour point as determined by the Institute of Petroleum Method 15/67 was measured for each

EXAMPLE II

Some commercially available ethylene/ethyl acrylate and ethylene/isobutyl acrylate copolymers available from Dow Chemical Company were added at 0.02 wt. percent concentration to the light fuel oil described in Example 1. The results given in Table II below show that the upper pour points of the blends of fuel oil and copolymer are lower than that of the fuel oil alone (50°F).

TABLE II

Copolymer Trade Name	Copolymer	Melt Index	Wt% of acrylate copolymer	Upper Pour Point °F (1)
Zetafax 1170	ethylene/ethyl acrylate	2.5	30	+ 15
Zetafax 1270	ethylene/isobutyl acrylate	2.5	20	+ 15
Zetafax 1275	ethylene/isobutyl acrylate	2.0	20	+ 20

(1) By Institute of Petroleum Method 15/67.

blend of copolymer and light fuel oil.

The results are given in Table I, and it is seen that the upper pour point of the light fuel oil/copolymer blend is reduced in each case from the upper point of 50°F for the fuel oil alone.

Some of the copolymers were added at 0.15 wt. percent concentration to a residual fuel prepared from a North African crude oil by distillation to a final vapour temperature at 710°F. This fuel had an upper pour point of +110°F as determined by Institute of Petroleum Method 15/67, a viscosity of 325.5 cS at 122°F, a carbon content of 86.6 wt. percent and a hydrogen content of 12.8 wt. percent. The kinematic viscosity of this fuel could not be determined at 100°F. It consisted of 100 percent of residua.

Some of the copolymers were added at 0.05 wt. percent concentration to a North African crude oil with an upper pour point of 35°F, a gravity (° API) of 40.2 and a kinematic viscosity at 100°F at 3.6 cS.

The results of these residual fuel or crude oil blends are also given in Table I, and it is seen that the upper pour point of the residual fuel/copolymer and crude oil/copolymer blends are reduced in each case from the upper pour points of 110°F and 35°F (as determined by the Institute of Petroleum Method 15/67).

EXAMPLE III

Various ethylene/substituted ethylene copolymers were prepared in a stirred autoclave essentially by the method described in Example I and added to the light fuel oil and residual fuel described in Example I and to a crude oil having an upper pour point of +75°F, a viscosity of 5.73 cS at 122°F and an extrapolated viscosity at 100°F of 7.56 cS, and containing 86.5 wt. percent carbon and 13.1 wt. percent hydrocarbon.

The upper point of the residual fuel and crude oil before and after addition of the copolymer was measured by Institute of Petroleum Method 15/67. The pour point of the light fuel oil before and after addition of the copolymer was determined by a modified method. In this modified pour point method a sample of fuel was heated to 200°F, removed from the bath and allowed to cool to 120°F. This sample was then placed in a cooling bath at a temperature of -30°F and cooled to 0°F. The sample was then removed from this bath, reheated to 200°F using a 205°F bath, and after remaining at this temperature for ½ hour it was removed and allowed to air cool to 90°F. This sample was then placed in a bath held at 30°F, and the pour point was then determined according to Institute of Petroleum Method 15/67. The pour point of the light fuel oil using this modified pour point procedure was +35°F.

The reaction conditions and pour point readings are given in Table III.

TABLE III.—COPOLYMERISATION REACTION CONDITIONS

Ethylene comonomer	Wt. percent of comonomer in copolymer	MW of copolymer ¹	Temp. °C.	Ethylene pressure, (kg/cm. ²)	Monomer addition		Catalyst addition		Hours	Yield copolymer, g.	Wt. percent copolymer in oil or fuel	Pour point, °		
					G. originally	G. Added	Type ²	G. added ³				Hours	LF	RF
Ethyl acrylate	4.6	10,000	135	420	9	18	1	25 TBP	4.5	583	0.05	+31
Do	8.9	10,160	135	490	23	21	2 1/4	23 TBP	5	140	0.10	+45
Do	13.2	3,760	150	140	23	21	2 1/4	23 TBP	5	383	0.10	+10
Do	17.0	4,630	110	430	23	12	2 1/4	23 TBP	3	157	0.20	+20
Do	19.9	4,560	110	280	23	21	2 1/4	23 LP	3	201	0.20	+20	+90
Do	22.4	3,720	150	280	23	9	1 1/4	23 TBP	2 1/2	254	0.10	+20
Do	20.8	3,230	110	210	23	18	1	23 TBP	9	192	0.10	+20
Do	23.1	4,150	110	420	23	21	2 1/4	23 LP	5	175	0.10	+20	+75
Do	23.2	4,150	110	420	23	21	2 1/4	23 LP	5	175	0.10	+15
Do	20.3	4,590	110	280	23	21	2 1/4	23 LP	5	192	0.10	+15
Do	18.6	3,940	135	140	23	21	2 1/4	23 TBP	6	274	0.10	+15
Isobutyl acrylate	27.9	1,340	150	140	23	137	2 1/4	23 TBP	10	505	0.05	+15	+45
Methyl methacrylate	14.9	3,870	150	140	40	0	23 TBP	5	231	0.10
C ₈ aca fumarate	14.9	3,870	150	140	40	0	23 TBP	5	231	0.20	+85
C ₈ aca fumarate	17.7	3,120	150	140	50	0	23 TBP	3	220	0.20	+95
C ₈ aca fumarate	10.6	3,190	150	140	50	0	23 TBP	3	202	0.10	+15
C ₈ aca fumarate	10.6	3,190	150	140	40	0	23 TBP	3	202	0.20	+10	+90
n-Butyl maleate	9.1	3,510	150	140	40	0	23 TBP	8	368	0.10
n-Butyl maleate	9.1	3,510	150	140	40	0	23 TBP	8	368	0.10	+10
2-ethyl hexyl itaconate	14.2	3,210	150	140	50	0	23 TBP	2	258	0.10
2-ethyl hexyl itaconate	15.3	3,180	150	140	50	0	23 TBP	2	359	0.20	+5
Oleic acid	23.2	3,990	150	280	50	44	23 TBP	2	486	0.20	+15	+85
Do	23.2	3,990	150	140	50	45	23 TBP	10	486	0.10	+95
Do	23.2	2,700	150	140	50	0	23 TBP	2	76	0.20	+90
Acrylonitrile	22.7	2,700	150	140	50	0	23 TBP	2	76	0.10	+35
Do	12.5	3,000	110	260	0	22	1 LP	1	21	0.10	+6
Do	12.5	3,000	110	260	0	22	1 LP	1	21	0.10	+6
Diacetone acrylamide	36.7	2,750	135	70	50	20	2 10 TBP	19	195	0.20	+95

¹ Number average molecular weight determined by vapour phase chromatography.
² TBP represents di-tertiary butyl peroxide and LP represents lauroyl peroxide; 2.5 TBP means a solution of 2.5 wt. percent of tertiary butyl peroxide in benzene, whereas 23 LP means a 23 wt. percent solution of lauroyl peroxide in benzene.
³ Quantity of neat peroxide added over the given time.
⁴ LF represents the light fuel oil having a pour point of +38° F. as determined by the modified pour point procedure, RF represents the residual fuel having a pour point of +110° F. as determined by Institute of Petroleum Method 15/67; C represents the crude oil having a pour point of +75° F. as determined by Institute of Petroleum Method 15/67.

Note.—After completion of the addition of the peroxide initiator the reaction mass was held for a further 15 minutes at the pressure and temperature herein denoted.

EXAMPLE IV

Preparation of Copolymers

Five different ethylene/vinyl acetate/methacrylic acid copolymers were prepared, each by a batch process, using differing amounts of vinyl acetate and methacrylic acid.

A 1 litre stainless steel magnetically stirred autoclave was charged with 150 ml. of benzene and 15 ml. of a mixture of 99.5 volume percent of vinyl acetate and 0.5 volume percent of methacrylic acid. The autoclave was

then purged with nitrogen, and then with ethylene, after which the autoclave was heated to 175°F and pressurised with ethylene to 200 atmospheres. 150 ml. of a mixture of 99.5 volume percent of vinyl acetate and 0.5 volume percent of methacrylic acid was introduced via a metering pump over a period of 6 hours. Concurrently a solution of 8g. of lauroyl peroxide in 92 ml. of benzene was introduced into the reactor over a period of 6¼ hours. The temperature was maintained at 175°F and the pressure at 200 atmospheres during the reaction. On completion of the addition of the lauroyl peroxide the reaction mass was cooled and the pressure released. Free solvent and unreacted monomers were removed by stripping to give copolymer 1. Copolymers 2, 3, 4 and 5 were prepared following the same procedure using the charges and reaction conditions given in Table IV.

TABLE IV

Polymer Preparation	1	2	3	4	5
Reaction Pressure (Atmospheres)	← 200 →				
Reaction Temperature (°F)	← 175 →				
Initial Charges					
Benzene (ml)	← 150 →				
Vinyl Acetate/Methacrylic Acid (vol. %)	99.05/0.5	99/1	98/2	97/4	90/10
Vinyl Acetate/Methacrylic Acid (ml)	← 15 →				
Feed Rates					
Vinyl Acetate/Methacrylic Acid (ml/hr)	← 25 →				
Over total time (hrs)	← 6 →				
Initiator	← lauroyl peroxide →				
Initiator (ml/hr)*	← 16 →				
Over total time (hrs)	← 6¼ →				
Yield (g.)	80	132	125	97	78
Polymers	1	2	3	4	5

* ml/hr of 12%wt.% solution of lauroyl peroxide in benzene. Copolymers 1, 2, 3, 4 and 5 had the following properties.

Polymer Properties

Copolymer	1	2	3	4	5
% Vinyl Acetate	25	24	26	29	38
% Methacrylic Acid	0.5	1.2	2.4	3.8	10

25 wt. percent copolymer concentrates in toluene were prepared using the above described copolymers 1 to 5, and these concentrates were used to prepare fuel oil blends in the light fuel oil and residual fuel described in Example 1.

With different concentrations of polymers 1, 2, 3, 4 and 5 in the fuel oils depressions of the upper pour point (as determined by Institute of Petroleum Method 15/67) compared with the fuel oils containing no pour point depressant were measured in each case (Table V).

TABLE V

Additive	Light Fuel Oil		Residual Fuel	
	Additive Concentration (Weight %)	Upper Pour Point (°F)	Additive Concentration (Weight %)	Upper Pour Point (°F)
None	—	50	—	100
Copolymer 1	0.02	-25	0.15	90
Copolymer 2	0.02	5	0.15	85
Copolymer 3	0.02	15	0.15	75
Copolymer 4	0.02	25	0.15	80
Copolymer 5	0.02	50	0.15	85

EXAMPLE V

In this example, four copolymers were used, and added in different concentrations to two different fuels and one crude oil.

The four copolymers were random ethylene/vinyl acetate/methacrylic acid copolymers with the properties listed in Table VI.

TABLE VI

Properties of ethylene/vinyl acetate/methacrylic acid copolymers

Copolymer	M. Wt.	% Vinyl Acetate	% Methacrylic Acid
6	27,000 ⁽¹⁾	28	1
7	11,000 ⁽²⁾	25	1
8	18,000 ⁽²⁾	25	1.3
9	26,000 ⁽¹⁾	25	1

Notes to Table VI

⁽¹⁾ Molecular weight determined in toluene at 65°C using a Mechrolab membrane osmometer model 501.

⁽²⁾ Molecular weight determined in toluene at 37°C using a Mechrolab vapour phase osmometer model 301A.

25 wt. percent copolymer concentrates in kerosene extract were prepared, and these concentrates were used to prepare fuel oil blends in the light fuel oil and residual fuel described in Example 1 and in a crude oil (Table VII).

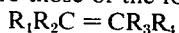
The crude oil was a North African crude with an upper pour point of 35°F (as determined by Institute of Petroleum Method 15/67), it had a gravity ° API of 40.2 and a kinematic viscosity at 100°F of 3.6 cS.

verage molecular weight in the range of about 4,000 to about 20,000 and having pour point depressing ability in said oil, said copolymer comprising a lower alkyl ester of an unsaturated mono- or dicarboxylic acid and

TABLE VII

Additive	Light Fuel		Residual Fuel		Crude Oil	
	Additive Concentration (Weight %)	Upper Pour Point (°F)	Additive Concentration (Weight %)	Upper Pour Point (°F)	Additive Concentration (Weight %)	Upper Pour Point (°F)
None	—	50	50	110	—	35
Copolymer 6	0.02	20	0.15	55	0.01	-10
Copolymer 7	—	—	0.15	55	0.01	0
Copolymer 8	0.02	5	0.15	55	0.01	-15
Copolymer 9	0.02	20	0.15	75	0.01	-5

Summarising, the preferred type of comonomer which may be used in the compositions of the invention are those of the formula



where R_1 and R_3 are hydrogen or C_1 to C_{10} hydrocarbyl, preferably alkyl

R_2 is $-\text{COOH}$, $-\text{COOR}_5$, $-\text{OR}_5$, $-\text{COR}_5$, $-\text{SR}_5$, $-\text{R}_4$ or $-\text{R}_5$.

R_5 is hydrocarbyl such as alkyl, or alkaryl, provided that any saturated linear side chain present therein contains less than 18 carbon atoms.

R_4 is R_1 , R_2 , $-\text{CONR}_1R_3$, $-\text{CH}_2\text{OH}$, $-\text{CN}$, $-\text{CH}_2\text{NR}_1R_3$, halogen, or $-\text{NCO}$.

What is claimed is:

1. A hydrocarbon-containing composition comprising a major proportion by weight of oil selected from the group consisting of crude oil and fuel oil of which at least 60 percent by weight boils above 500°F. at atmospheric pressure, said fuel oil being selected from the group consisting of a residua-containing fuel, and a flash distillate fuel, and 0.0005 to 0.5 percent by weight of an oil-soluble copolymer having a number av-

about 86 to about 97 mol percent ethylene.

2. A composition according to claim 1, wherein said lower alkyl group is selected from the group consisting of methyl, ethyl, isopropyl, butyl, n-octyl, and 2-ethyl hexyl groups and said acid is acrylic acid or methacrylic acid.

3. A composition as claimed in claim 1, wherein said oil is a residua-containing fuel of about 35 percent to 100 percent by weight residua.

4. A composition according to claim 1, wherein said oil is crude oil.

5. A composition according to claim 1, wherein said acid is a monocarboxylic acid.

6. A composition according to claim 1, wherein said acid is an acrylic acid.

7. A composition according to claim 1, wherein said acid is a dicarboxylic acid.

8. A composition according to claim 1, wherein said acid is fumaric acid.

9. A composition according to claim 1, wherein said copolymer consists only of said ethylene and ester.

* * * * *

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