

WAX CRYSTAL MODIFIERS FORMED FROM DIALKYL PHENYL FUMARATE

FIELD OF THE INVENTION

The invention relates to wax crystal modifier compounds and their use in improving the flow characteristics of oleagenous fluids especially oils such as crude oil, lubricating oil, fuel oil and distillate oil.

BACKGROUND OF THE INVENTION

Many oils, especially lubricating oils, fuel oils, distillate oils, and crude oils, contain straight chain and branched alkanes that crystallize as their temperature is lowered. Alkane (wax) crystallization in oleagenous fluids can affect the fluid's ability to flow. This may result in problems such as pipelininig difficulties in crudes. The temperature at which wax begins to crystallize in an oil is called the wax appearance temperature (WAT) of the oil. Polymeric and copolymeric additive compounds can be combined with an oil in order to improve an oil's flow properties. Such additives, known as wax crystal modifiers, are capable of altering the crystallization properties of waxes present in oil. It is believed that wax crystal modifiers improve an oil's flow properties by suppressing the WAT or by modifying the growth of wax crystals in the oil so that the resulting crystals are small enough so as not to affect the oil's flow properties or both. Among these compounds, dialkyl fumarate vinyl acetate copolymer with C₆ to C₁₈ alkyls is particularly popular.

There remains a need, though, for wax crystal modifiers that are capable of improving the flow properties of oleagenous fluids, especially oils such as lubricating oils, crude oils, fuel oils, and distillate oils.

SUMMARY OF THE INVENTION

In one embodiment, the invention is a copolymer of dialkyl phenyl fumarate and at least one compound selected from the group consisting of vinyl acetate, styrene, C_3 to C_{30} α olefin, ethylene, and carbon monoxide.

In another embodiment, the invention is a flow improver for use in an oleagenous fluid comprising one or more copolymers from dialkyl phenyl fumarate wherein the alkyl is straight chain or branched and ranges in size from C_6 to C_{150} and at least one compound selected from the group consisting of vinyl acetate, styrene, C_3 to C_{30} α olefin, ethylene, and carbon monoxide.

In another embodiment, the invention is a method for improving the flow properties in an oleagenous fluid comprising: adding to a major amount of the oleagenous fluid a minor amount of at least one copolymer of dialkyl phenyl fumarate having C_6 to C_{150} straight chain or branched alkyl and at least one compound selected from the group consisting of C_3 to C_{30} alpha olefin, ethylene, styrene, and carbon monoxide.

In another embodiment, the invention is a method for forming a copolymer comprising combining under free radical polymerization conditions a C_6 to C_{150} dialkyl phenyl fumarate in a solvent selected from the group consisting of hexane, benzene, cyclohexane, and heptane; at least one compound selected from the group consisting of ethylene and carbon monoxide; and an initiator selected from the group consisting of t-butyl peroxyvalate, benzoyl peroxide, t-butylper benzoate, and t-butyl peroxide, for a time, temperature, and pressure sufficient to form the copolymer.

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In another embodiment, the invention is a method for forming a copolymer comprising:

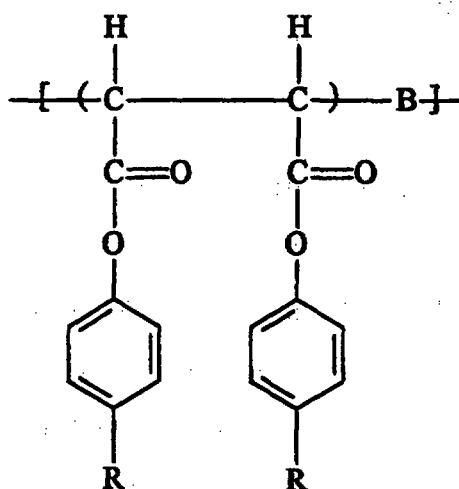
combining C_6 to C_{150} dialkyl phenyl fumarate; a compound selected from the group consisting of vinyl acetate, styrene, and C_3 to C_{30} alpha olefin; and an initiator selected from the group consisting of ditertiary-butyl peroxide, 2,5-dimethyl-2,5-di-tertiary-butylperoxyhexane, di-cumyl peroxide, benzoyl peroxide, tertiary-butyl peroxyvalate, tertiary-butyl perbenzoate, azobisisobutyronitrile, and 1,1'-azobis(cyanocyclohexane) under free radical polymerization conditions for a time and at a temperature sufficient to form the copolymer.

DETAILED DESCRIPTION OF THE INVENTION

The invention is based on the discovery that copolymers can be formed having the formula AB wherein A is formed from dialkyl phenyl fumarate and B is formed from at least one compound selected from the group consisting of vinyl acetate, styrene, C_3 to C_{30} α -olefin, ethylene, and carbon monoxide. The invention is also based on the discovery that such copolymers are capable, when used in an effective amount, of improving flow properties like viscosity in oleagenous fluids, especially lubricating oils, fuel oils, distillate oils, and crude oils. While not wishing to be bound by any theory, it is believed that the copolymers of the invention improve the flow properties in oleagenous materials because they function as wax crystal modifiers.

The copolymers of the present invention are represented by the formula AB wherein A is formed from dialkyl phenyl fumarate (DAPhF). As such, these copolymers have the structure:

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Comonomer B is formed from at least one compound selected from the group consisting of vinyl acetate, styrene, C₃ to C₃₀ α-olefin, ethylene, and carbon monoxide. The term copolymer is thus used in accordance with its more general meaning where the polymer comprises two or more different monomers.

R represents independently selected straight chain or branched alkyl groups of from about C₈ to about C₁₅₀ carbon atoms. Preferred alkyls range from about C₈ to about C₄₀.

Copolymers of the present invention are prepared from dialkyl phenyl fumarate esters. Such esters may be prepared by reacting fumaric chloride with an alkyl phenol in the presence of triethylamine.

The copolymers of this invention can be synthesized using free-radical polymerization. In case of copolymers of dialkyl phenyl fumarate with monomers like vinyl acetate, styrene or α-olefins, polymerization can be carried out in a standard glass reactor. Typically, inhibitors from the monomers such as vinyl acetate or styrene are removed via an inhibitor remover column. The purified monomers are then placed in tubes with the DAPhF ester monomers.

The tubes are capped with septa and flushed with nitrogen for one to four hours before polymerization. The relative amounts of monomer A: monomer B in the copolymer can be varied from 5:95 to 95:5 mole percent.

The reactions can be carried out in solvent or neat. Whenever a solvent is used, solvent should be nonreactive or noninterfering in free radical polymerization can be used. Such solvents include benzene, cyclohexane, hexane, heptane, etc. Solvents like xylene or oil can also be used. The solvent may be flushed with argon or nitrogen and then added to the monomers.

The polymerization reactions can be carried out from 40 to 100°C depending on reactivity of monomers, half-life of the initiator used, or the boiling point of the solvent. The reactions are carried out under inert atmosphere. The solvents are brought to the reaction temperatures, and the initiator (dissolved in the appropriate solvents) is added to the solution. Typical free radical initiators includes dialkyl peroxides such as ditertiary-butyl peroxide, 2,5-dimethyl-2,5-di-tertiary-butylperoxyhexane, di-cumyl peroxide; alkyl peroxides such as benzoyl peroxide; peroxy esters such as tertiary-butyl peroxyvalerate, tertiary-butyl perbenzoate; and also compounds such as azo-bis-isobutyronitrile. A free radical initiator with an appropriate half life at reaction temperature of from about 60°C to about 140°C can be used. For the reactions done neat (without solvent), both monomers and initiator are loaded together, flushed with nitrogen, and then brought to reaction temperature. The mixture is stirred for a time sufficient to ensure that a substantially homogeneous mixture is obtained. The time and temperature of the reactions can be varied. Reactions can be stopped after 1 hour to 48 hours. The resulting copolymer can be isolated by precipitating the polymer in non-solvent (solvent in which polymer is not soluble). The product is then dried in vacuum oven.

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When using monomers that are gases at room temperature, such as ethylene or carbon monoxide, the reactions are generally carried out in high pressure reactors such as autoclave reactors. In such copolymerizations, the reactor is initially charged with monomers like dialkyl phenyl fumarate dissolved in solvent like hexane, and initiator is added. Typical initiators include t-butyl peroxyvalate, benzoyl peroxide, t-butylper benzoate, t-butyl peroxide. The reactor is sealed and purged with purified nitrogen. The reactor is then pressurized with carbon monoxide and/or ethylene monomer to appropriate pressure. The pressure can range from about 100 to about 3000 psig. The preferred polymerization pressure ranges from about 500 to about 1200 psig. Reaction temperature can range from about 40 to about 200°C, depending on solvent and the initiator half-life. The pressure of the reaction can be maintained for few hours to 48 hours depending on monomer reactivity, solvent, and the initiator half-life. The reactor is allowed to cool to room temperature and is then depressurized. The solvent is removed on rotary evaporator to obtain the product.

The products are generally characterized by standard techniques like FTIR, NMR, and GPC.

According to the present invention, wax crystal modifiers are added to the oleagenous fluid in a concentration ranging from about 10 to about 50,000 ppm based on the weight of the oleagenous fluid. The preferred concentration is about 500 ppm. Non-limiting examples of oleagenous fluids containing paraffinic (alkane) species that benefit from the addition of the compounds of the invention include crude oils, i.e., oils as obtained from drilling and before refining or separating, fuel oils such as middle distillate fuel oil, and oils of lubricating viscosity ("lubricating oils").

The oleagenous compositions and additive compounds of the present invention may be used in combination with other co-additives such as ethylene-vinyl acetate copolymers, fumarate-vinyl acetate copolymers, and mixtures thereof.

It is believed that copolymer flow improvers of this invention when present in an effective amount are capable of inhibiting the nucleation and growth of wax crystals in oleagenous fluids such as oils. While not wishing to be bound by any theory, it is believed that the presence of an effective amount of copolymer results in a lowering the oil's wax appearance temperature because the copolymer molecules are sufficiently similar to the paraffinic crude species to incorporate themselves into growing wax crystals. Once incorporated, it is believed that the polymeric nature of the flow improver, i.e., its "branchiness" and high molecular weight, prevent the further addition of the crude's paraffinic species to the crystal. The presence of the copolymer in the growing wax crystal is also believed to alter the crystals' morphology by inhibiting growth that naturally tends towards undesirable large flat platelets. Such platelets are believed to result from the interlocking, intergrowth, and agglomeration of nucleated wax crystallites. Such changes in crystal shape resulting from copolymer incorporation greatly diminish the wax crystals' ability to interlock, intergrow, and agglomerate.

In the practice of the invention, it is desirable to first determine the molecular weight distribution of the paraffinic species present in the oleagenous fluid. It is believed that the compounds of the present invention are most effective when the molecular weight distribution of the alkyls present in the fumaric species of the copolymer is approximately the same as the molecular weight distribution of the oil's paraffinic species.

While the compounds of the present invention are useful in all oleogenous fluids containing paraffinic species, the preferred compound will depend on the type of fluid used.

For lubricating oils, for example, flow improvement is needed at temperatures much lower than are ordinarily required for crude oil transportation. Consequently, copolymers with alkyls in the fumarate species ranging from about C₁₂ to about C₁₄ and molecular weights ranging from about 2000 to about 100,000 are preferred. In crude oils, compounds of reduced solubility are required, and the preferred compounds contain alkyls ranging from about C₁₅ to about C₄₀ and molecular weights ranging from about 2,000 to about 50,000. For distillate oils, preferred copolymers contain alkyls ranging from about C₁₀ to about C₂₂ and have molecular weights ranging from about 2,000 to about 20,000.

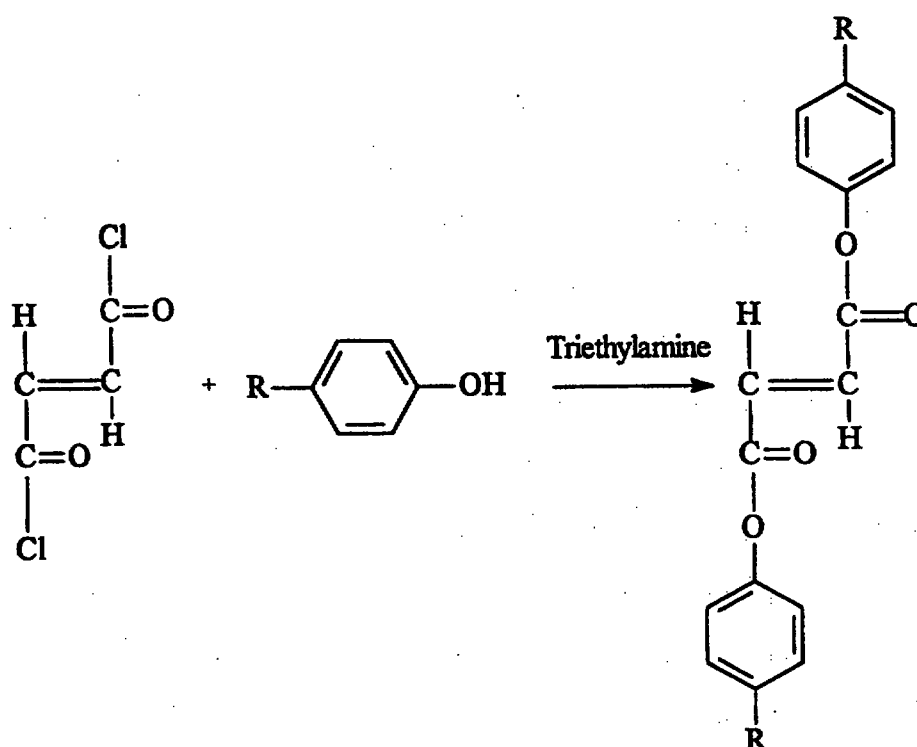
The invention is further described in the following non-limiting examples. In these examples, alkyl chain lengths are sometimes represented by a range of carbon and hydrogen atoms, such as C₂₄₋₂₈H₄₉₋₅₇. In such cases, the alkyl groups present in the fumaric species of the inventions monomers, polymers, and copolymers are random mixtures of alkyl groups ranging in size, approximately, over the entire range.

EXAMPLES

Example 1: Reaction of fumaric chloride and dodecyl phenol.

Into a round bottom flask, 16.95g (0.065 mole) of dodecyl phenol was placed with 325 mL toluene. Into this solution was added 30 mL of triethylamine. 5.2g (0.034 mole) of fumaryl chloride diluted with 25 mL of toluene was then slowly added over a period of 1 hour at room temperature. The mixture

was heated to 80°C for 4 h, cooled to room temperature, and poured into 200 mL 5% HCl. The solution was extracted with ether and dried with NaHCO₃. The solvents, ether and toluene, were removed on a rotary evaporator to obtain 18.4 of the product. An IR spectrum of the product showed the absorption peak due to ester carbonyl at 1741 cm⁻¹ and the double bond peak at 1647 cm⁻¹. The product also showed peaks at 1604 and 1593 cm⁻¹ due to aromatic rings. ¹³C NMR of the product showed the double bond absorption peak at 134.0 ppm (-HC=CH-, carbon) and the carbonyl ester peak at 163 ppm.



Example 2: The synthesis of dialkyl phenyl fumarate monomer (C₃₀PhF)

C₃₀+ olefin alkylated phenol was synthesized by reaction of phenol with C₃₀+ alpha olefin using a strongly acidic resin (obtained from Aldrich, Inc., Milwaukee, WI under the tradename AMBERLYST 15™) comprising divinyl benzene-crosslinked polystyrene, to which sulfonic groups are attached, as a catalyst. C₃₀+ phenol fumarate ester was synthesized using a procedure similar

to that used to synthesize dodecyl phenol fumarate. An IR spectrum of the product showed absorption peaks due to ester carbonyl at 1757 and 1710 cm^{-1} and the double bond peak at 1641 cm^{-1} . The product also showed a peak at 1606 cm^{-1} due to an aromatic ring. The ^{13}C NMR spectrum of product showed the double bond absorption peak at 134.0 ppm ($-\text{HC}=\text{CH}-$, carbon) and the carbonyl ester peak at 163 ppm. The aliphatic region of the spectrum suggests that alkyl chains are substantially linear.

Example 3: The synthesis of dialkyl phenyl fumarate monomer $\text{C}_{24-28}\text{PhF}$

C_{24-28}^+ olefin alkylated phenol was synthesized by reaction of phenol with C_{24-28}^+ alpha olefin using a strongly acidic resin (obtained from Aldrich, Inc., Milwaukee, WI under the tradename AMBERLYST 15TM) comprising divinyl benzene-crosslinked polystyrene, to which sulfonic groups are attached, as a catalyst. C_{24-30}^+ phenol fumarate ester synthesized using a procedure similar to that used to synthesize dodecyl phenol fumarate. An IR spectrum of the product showed absorption peaks due to ester carbonyl at 1746 and 1710 cm^{-1} and the double bond peak at 1645 cm^{-1} . The product also showed a peak at 1605 cm^{-1} due to an aromatic ring. The ^{13}C NMR spectrum of product showed the double bond absorption peak at 134.0 ppm ($-\text{HC}=\text{CH}-$, carbon) and the carbonyl ester peak at 163 ppm. The aliphatic region of the spectrum suggests that alkyl chains are substantially linear.

Example 4: The synthesis of dialkyl phenyl fumarate/carbon monoxide copolymer

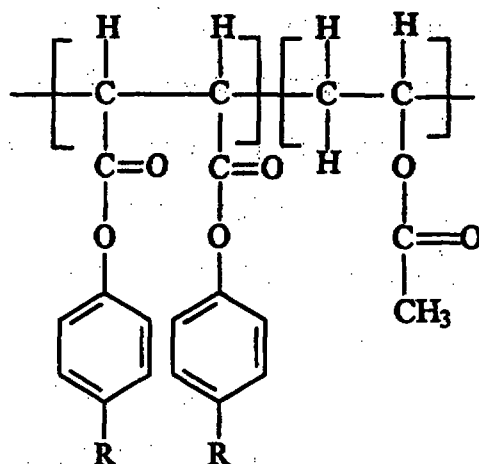
A 300 mL autoclave engineer's reactor was charged with 2.5 g of dialkyl phenyl fumarate (C_{30}PhF) dissolved in 150 mL *n*-hexane and 0.606 g of a 75% solution of *t*-butyl peroxy-pivalate in mineral spirits. [*t*-Butyl peroxy-pivalate has a 10-hour half life 55°C in a 0.2 M benzene solution (Swern,

Organic Peroxides, John Wiley and Sons, 1970, Vol. 1 pp 82, 87)]. The reactor was sealed and purged with purified nitrogen. The reactor was then pressurized with carbon monoxide to 700 psig. The temperature was raised to 66°C while stirring, and the pressure was maintained for 24 hours. The reactor was allowed to cool to room temperature and was then depressurized. Then hexane was removed on a rotary evaporator leaving 3.65g of product. An IR spectrum of the product showed the ester carbonyl peak at 1757 cm⁻¹. ¹³C NMR of the product was recorded in CDCl₃ using chromium (III) acetylacetonate ("Cr(acac)₃") as a relaxation agent, following quantification of the spectrum. ¹³C NMR of this product showed the disappearance of the double bond peak at 134 ppm and the monomer carbonyl peak at 163 ppm. The product contained two types of carbonyls (multiple peaks around 210 ppm and 172 ppm). The relative integration of the carbonyls in the product suggested that there was 3.4 mole % CO incorporation from carbon monoxide in the copolymer. GPC of the product was recorded in THF using polystyrene standards. GPC of the product showed that the polymer had a peak molecular weight of 4300.

Examples 5 through 9: Synthesis of Dialkyl Fumarate with Vinyl Acetate

Copolymers of dialkyl phenyl fumarate with vinyl acetate were synthesized with R groups of C₁₂H₂₅, C₂₄₋₂₈, H₄₉₋₅₇, C₃₀H₆₁. Such copolymers have the structure

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Copolymers were formed using free-radical polymerization techniques as follows:

Hydroquinone inhibitor was removed from the vinyl acetate by passing it through an inhibitor remover column. The purified vinyl acetate was placed in tubes with the dialkyl phenyl fumarate ester monomers. The tubes were capped with septa and flushed with nitrogen for one hour. The solvent was flushed with nitrogen and added to the tubes containing the monomers. The solutions were brought to their reaction temperatures, and the initiator (dissolved in the appropriate solvents) was added to each monomer solution. For the runs done neat (without solvent), both monomers and initiator were loaded together, flushed with nitrogen, and then brought to reaction temperature. The mixtures were stirred overnight. The next day, the polymer solutions were precipitated in methanol and vacuum dried.

Table 1 sets forth copolymerization reaction details. 3% azobisisobutyronitrile is available from Aldrich, Inc., Milwaukee, WI under the

tradename AIBN™, and 3% [1,1'-azobis(cyanocyclohexane)] is an available from DuPont Chemicals, Wilmington, DE under the tradename V-88™.

TABLE 1

Example Number	Monomers	Monomer Ratio	Reaction Solvent	Wt% Initiator	Reaction Temp. (°C)
5	C ₁₂ PhF/VA	50/50 wt%	Neat	3% AIBN	65
6	C ₁₂ PhF/VA	50/50 wt%	Chloroform	3% AIBN	65
7	C ₃₀ PhF/VA	7/93 wt%	Neat	3% V-88	76
8	C ₂₄₋₂₈ PhF/VA	50/50 wt%	Chloroform	5% AIBN	62
9	C ₂₄₋₂₈ PhF/VA	50/50 wt%	Neat	5% AIBN	76

C₁₂PhF = Didodecylphenol fumarate

C₃₀PhF = Di[p-alkyl (C₃₀) phenyl] fumarate

C₂₄₋₂₈PhF = Di[p-alkyl (C₂₄₋₂₈)phenyl] fumarate

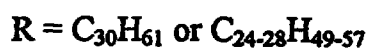
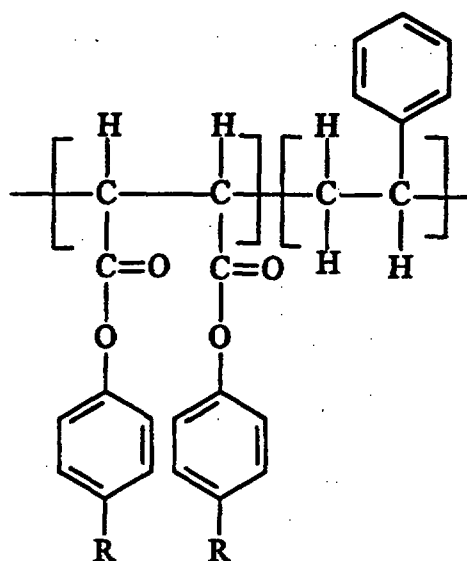
Table 2 sets forth characterization results for these copolymers.

TABLE 2

Example Number	Mole Ratio by NMR	GPC			
		Peak MW	Mn	Mw	Mw/Mn
5		4,660	4,500	7,370	1.6
6		1,790	1,570	2,020	1.3
7	31/69	22,634	19,387	57,222	2.95
8	40/60	4,976	4,346	6,185	1.42
9		14,390	10,100	23,700	2.35

Examples 10 through 12: Synthesis of Di(p-alkylphenyl) Fumarate with Styrene

Dialkyl phenyl fumarate - styrene copolymer having the structure:



Copolymers were synthesized according to the polymerization conditions set forth in Examples 5 through 9. Tables 3 and 4 show the polymerization conditions and characterization results, respectively.

TABLE 3

Example Number	Monomers	Mole Ratio	Reaction Solvent	Wt % Initiator	Reaction Temp. (°C)
10	C ₃₀ PhF/Styrene	9/91 wt%	Neat	3% V-88	76
11	C ₂₄₋₂₈ PhF-Styrene	50/50 wt%	Chloroform	5% AIBN	62
12	C ₂₄₋₂₈ PhF-Styrene	50/50 wt%	Neat	5% AIBN	76

C₃₀PhF: Di[p-alkyl(C₃₀)phenyl] fumarate

C₂₄₋₂₈PhF: Di[p-alkyl(C₂₄₋₂₈)phenyl] fumarate

TABLE 4

Example Number	Mole Ratio By NMR	GPC			
		Peak MW	Mn	Mw	Mw/Mn
10	10/90	86,455	50,308	23,3020	4.63
11	14/86	14,700	5,498	14,653	2.67
12		28,040	14,700	44,650	3.00

Example 13: Wax Crystallization Studies

Seven samples of Alaska North Slope crude oil were prepared. The samples were studied using differential scanning calorimetry at a cooling rate of 10°C per minute. The results are set forth in Table 5.

TABLE 5

Additive	Additive Treat Level, ppm	WAT	ΔWAT
Alaskan North Slope Crude	-	14.5	-
Example 4	500	13.3	1.2
	2,500	12.4	2.1
Example 8	5,000	13.8	0.7
Example 9	5,000	11.0	3.5
Example 11	500	13.6	0.9
Example 12	500	13.5	1.0

These differential scanning calorimetry ("DSC") studies are used to study the thermodynamics and kinetics of oleagenous fluids containing some of the additives of the present invention. DSC is used herein to reveal phase transition in oleagenous fluids containing the additives of the present invention in order to study interactions between the fluid and the additives.

DSC measurements were conducted over a temperature ranging from -140°C to 100°C, in both heating and cooling, at a rate of 10°C per minute. A nitrogen purge of 50 cm³ per minute was used, and all samples were warmed to about 60°C before sampling. In each sample, the additives were completely dissolved in the fluid, and care was taken to prevent loss of any low volatility species present.

WAT is a measure of the thermodynamic barrier for the formation of a stable nucleus for further crystal growth. It is the temperature at which stable wax crystals first begin to appear. For wax crystallization to take place, solutions have to be supercooled to cross this thermodynamic free energy barrier to nucleation. A lowering of the WAT is desirable, because it indicates a larger thermodynamic barrier for further wax crystal growth. Additives that interfere with the nucleation stage of wax formation increase the free energy barrier and, thereby, decrease the WAT. Larger decrease in WAT indicate better performance of the wax crystal modifier additive.

Table 5 shows that the additives of the present invention are effective wax crystal modifiers.

**WHAT IS CLAIMED IS:**

1. A copolymer of dialkyl phenyl fumarate and at least one compound selected from the group consisting of vinyl acetate, styrene, C_3 to C_{30} α olefin, ethylene, and carbon monoxide.
2. The composition of claim 1 wherein the alkyls range from C_6 to C_{150} .
3. The composition of claim 2 wherein the alkyls range from about C_8 to about C_{40} .
4. The composition of claim 3 wherein the alkyls are straight-chain.
5. A flow improver for use in an oleagenous fluid comprising one or more copolymers of dialkyl phenyl fumarate wherein the alkyl is straight chain or branched and ranges in size from C_6 to C_{150} and at least one compound selected from the group consisting of vinyl acetate, styrene, C_3 to C_{30} α olefin, ethylene, and carbon monoxide.
6. The composition of claim 5 wherein the alkyls range from C_6 to C_{150} .
7. The composition of claim 6 wherein the alkyls range from about C_8 to about C_{40} .
8. The composition of claim 7 wherein the alkyls are straight-chain.



9. A method for improving the flow properties in an oleagenous fluid comprising: adding to a major amount of the oleagenous fluid a minor amount of at least one copolymer of dialkyl phenyl fumarate having C_6 to C_{150} straight chain or branched alkyl and at least one compound selected from the group consisting of vinyl acetate, C_3 to C_{30} alpha olefin, ethylene, styrene, and carbon monoxide.

10. A method for forming a copolymer comprising combining under free radical polymerization conditions a C_6 to C_{150} dialkyl phenyl fumarate in a solvent selected from the group consisting of hexane, benzene, cyclohexane, and heptane; at least one compound selected from the group consisting of ethylene and carbon monoxide; and an initiator selected from the group consisting of t-butyl peroxyphthalate, benzoyl peroxide, t-butylper benzoate, and t-butyl peroxide, for a time, temperature, and pressure sufficient to form the copolymer.

11. The method of claim 10 wherein the pressure ranges from about 500 psig to about 1200 psig, the temperature ranges from about 50°C to about 100°C , the solvent is hexane, and the initiator is t-butyl peroxyphthalate.

12. The method of claim 11 including cooling and depressurizing the reactor and then recovering the copolymer from the solvent.

13. A method for forming a copolymer comprising:

combining a C_6 to C_{150} dialkyl phenyl fumarate;

a compound selected from the group consisting of vinyl acetate, styrene, and C_3 to C_{30} alpha olefin; and an initiator selected from the group consisting of ditertiary-butyl peroxide, 2,5-dimethyl-2,5-di-tertiary-butylperoxyhexane, di-cumyl peroxide, benzoyl peroxide, tertiary-butyl peroxy-pivalate, tertiary-butyl perbenzoate, azobisisobutyronitrile, and 1,1'-azobis(cyanocyclohexane) under free radical polymerization conditions for a time and at a temperature sufficient to form the copolymer.

14. The method of claim 13 including combining the dialkyl phenyl fumarate with a solvent selected from the group consisting of hexane, benzene, cyclohexane, chloroform, xylene, oil, and heptane.

15. The method of claim 14 wherein the temperature ranges from about 50°C to about 100°C, the solvent is chloroform, and the initiator is azobisisobutyronitrile or 1,1'-azobis(cyanocyclohexane).



16. The method of claim 15 including cooling and depressurizing the reactor and then recovering the copolymer from the solvent.