

[54] **METHOD FOR INCREASING THE MOBILITY OF WAXY CRUDE OILS**

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[58] Field of Search **137/13; 252/8.3, 252/8.55 B**

[56] **References Cited**

UNITED STATES PATENTS

3,669,189 6/1972 Fischer 252/8.3

Primary Examiner—Alan Cohan

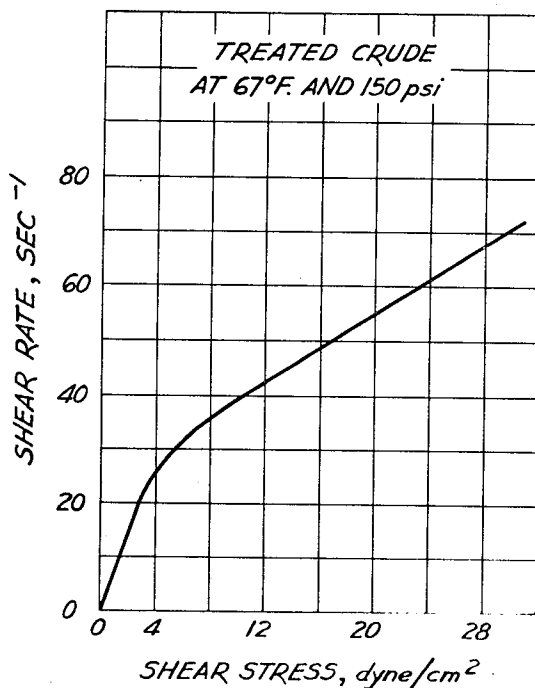
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[57]

ABSTRACT

The mobility of waxy crude oils is increased by cooling a mixture of the crude oil and an amphipathic additive from a temperature higher than the nucleation temperature of the crude oil at a rate less than 10° F. per hour to a temperature at which nucleation of wax particles causing high pour point is virtually complete. Preferred amphipathic additives are alkylated phenols and copolymers of ethylene with polar organic compounds such as acetate or acrylate esters. The increased mobility is characterized by reduced pressures required to start flow through a pipeline and reduced pressure drop in a pipeline after flow has commenced.

11 Claims, 3 Drawing Figures



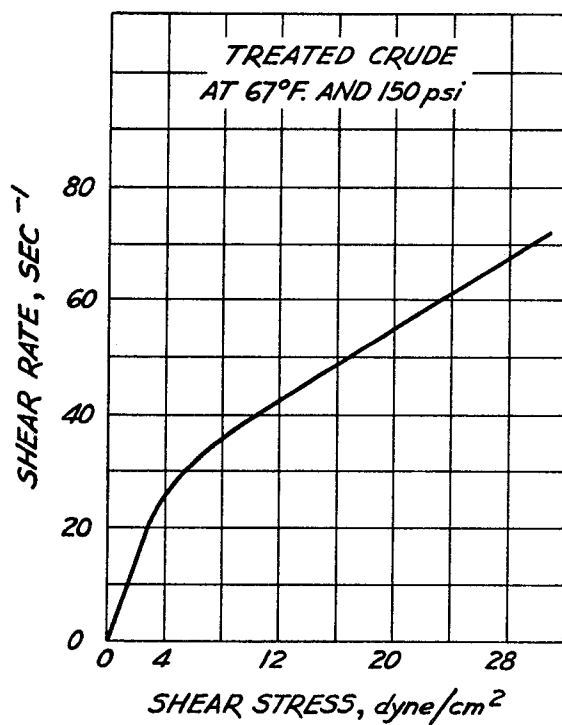


Fig. 3

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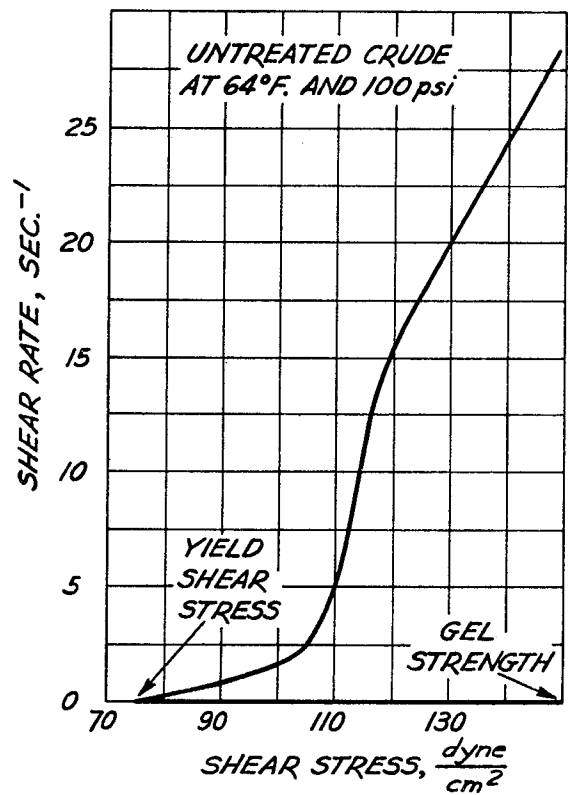


Fig. 1

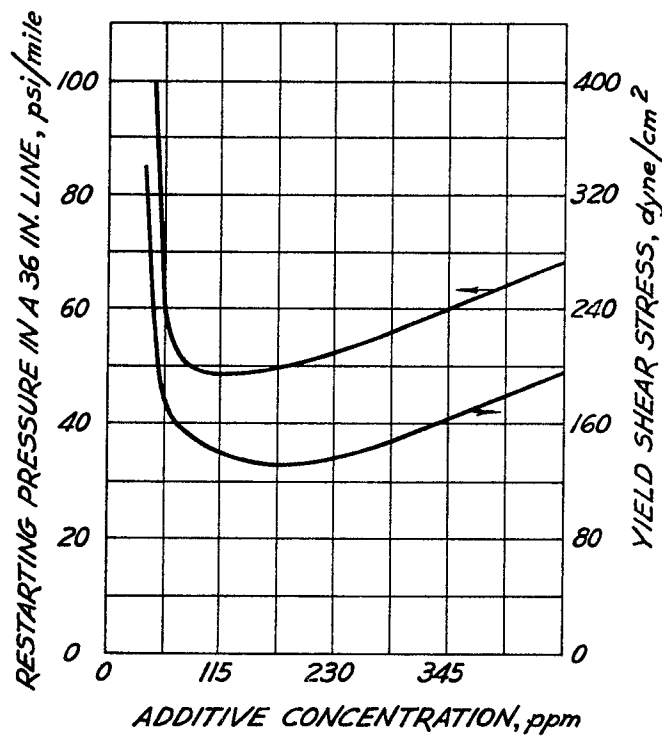


Fig. 2

METHOD FOR INCREASING THE MOBILITY OF WAXY CRUDE OILS

This invention relates to the treatment of waxy crude oils and more particularly to a method of increasing the mobility of such crude oils to facilitate pumping them through pipelines.

Two problems related to waxes in crude oils are frequently encountered in the production and transportation of crude oils. Upon cooling a waxy crude oil from the formation temperature along its production path either a wall deposit is formed, usually in the temperature range between 160°-95°F., or the waxy crude oil congeals at or above ambient temperatures forming while at rest a highly viscous and thixotropic material of substantially zero mobility. The wall deposits, commonly referred to as "paraffin" deposits, reduce the effective diameter of tubing or pipe and thereby impede the well production. Congealing waxy crude oils are referred to as high pour point crude oils because their pour point, i.e., the temperature at which they cease to flow under a head of 1 inch, is considerably higher than the pour point, below 32° F., of conventional crude oils. Consequently, the pipelining of high pour point crude oils at ambient conditions can become uneconomical owing to an excessive pressure drop, and restarting of flow after a shut down can become impossible owing to a high strength of crude gel. This invention is concerned with a method of treating those crude oils that congeal to an oil of low mobility, hereinafter referred to as waxy crude oils.

In British Pat. Nos. 1,056,710 and 930,843, a thermal treatment method for reducing the pour point of crude oils is described in which the crude oil is heated to a temperature at which all of the wax in the crude oil is in solution and thereafter cooled rapidly at a rate ranging from as low as 30° F. per hour in British Pat. No. 930,843 to as high as 600° F. per hour in British Pat. No. 1,056,710. Both patents describe the cooling as occurring under static or substantially static conditions to a temperature close to the minimum temperature at which it is subsequently to be pumped. While the processes described in British Pat. Nos. 930,843 and 1,056,710 are effective in reducing the pour point of crude oil, the improved properties of the crude oil are transitory and are lost on aging of the crude oil such as occurs during normal storage at temperatures above the minimum temperature of the treatment. Thus, the processes described in British Pat. Nos. 930,843 and 1,056,710 are advantageous if the treated oil can be delivered directly after the treatment into a pipeline which is maintained at substantially the minimum temperature used in the thermal treatment of the crude oil.

This invention resides in a method of improving the mobility of waxy crude oils, in which an amphipathic additive is mixed with the crude oil at a temperature above the nucleation temperature, and the resulting mixture is cooled at a slow rate, less than 10° per hour, to a temperature at which nucleation is substantially complete. If the temperature of the crude oil at the well head exceeds the nucleation temperature, the crude oil can be treated immediately with the amphipathic compound, but if the temperature at the well head is below the nucleation temperature, or the oil is allowed to cool below the nucleation temperature, the oil must be heated to a temperature above the nucleation temperature either during or after mixing with the amphipathic

additive. The crude oil is sheared during the cooling operation. The term amphipathic additive is used to designate an organic compound containing both polar and nonpolar effective constituents.

In the drawings:

FIG. 1 is a curve showing the relationship between the shear stress and the shear rate of an untreated waxy crude oil at a temperature of 64° F.

FIG. 2 is a curve showing the relationship between additive concentration and the restarting pressure for pumping the crude oil through a pipeline and the relationship between the additive concentration and the yield shear stress of the treated crude oil.

FIG. 3 is a curve showing the relationship between the shear stress and shear rate of a waxy crude oil at 67° F. after treatment in accordance with this invention.

It is believed that the congealing or gelation and consequent loss of mobility of the crude oil is the result of solvation of nucleated wax solids by relatively low molecular weight liquids in the crude oil. The term solvation is used to designate the formation of an envelope of low molecular weight hydrocarbon liquids around the nucleated solid particles. The solvation has the effect of increasing hydrodynamic volume of solids and removing the more fluid solvent hydrocarbons from the crude oil. Continued solvation results in a continued reduction in the mobility of the crude oil until it gels. Without being bound by any theory concerning the mechanism of this invention, it is believed that the limited solubility in solvent fractions of the crude oil of the amphipathic additive owing to the polar constituents drastically limits the solvation of the nucleated solids and that the slow cooling used in this invention results in the growth of relatively large nucleated solid particles of wax that are solvated only to a minor extent. Such large particles have been shown not to interfere with pumping of liquids that do not contain the several components necessary to build up the surface envelopes.

The characteristics of a waxy crude oil most pertinent to its mobility and, therefore, to the problem of pumping the crude oil are the gel strength and the yield value and plastic viscosity. The gel strength will determine the pressure required to start flow through a pipeline and is calculated in terms of pressure per unit length of pipe of specified diameter. The yield value and plastic viscosity of the crude oil will determine the frictional losses that are encountered in pumping the crude oil through a pipeline. The restarting pressure and the frictional losses can be computed from a curve of the type shown in FIG. 1 which is obtained by runs in a rotational viscometer. For example, using a Fann viscometer, from a position of rest the shear stress is gradually increased until the spindle of the viscometer begins to deflect. The maximum deflection indicates the gel strength of the oil and is shown as 150 dynes/cm² in FIG. 1. Once the gel strength has been exceeded, the shear stress manifested by deflection of the spindle decreases until deflection of the spindle virtually stabilizes at a finite speed of the rotor (shear rate). The shear rate is stepwise increased and the shear stress measured at a number of different values of the shear rate to give points on the non-Newtonian viscosity curve. That shear stress at which the non-Newtonian curve indicates flow recommences is the yield value of the liquid. In practice, the curve is extrapolated to zero shear strength to indicate the yield shear stress. The re-

starting pressure can be correlated with and computed from the gel strength of the crude oil. The pressure drop through a pipeline can be correlated with and computed from the plastic viscosity, which is determined from the slope of the viscosity curve, and the yield value of the crude oil.

In the treatment of the waxy crude oil in accordance with this invention, an amphipathic additive is mixed in the crude oil at a temperature at which all of the waxy constituents of the crude oil are in solution and the mixture slowly cooled to a temperature at which nucleation is substantially completed. That temperature at which the cooling begins is just above the highest temperature at which nuclei of solid particles of wax begin to form on cooling the crude oil and is hereinafter referred to as the nucleation temperature. The amphipathic additive can be mixed with the crude oil at temperatures below the nucleation temperature but it will then be necessary to heat the mixture above the nucleation temperature to destroy solvated wax particles caused by the past thermal history of the crude oil before commencing the slow cooling. If at the time of mixing the crude oil is at a temperature above the nucleation temperature, the slow cooling can begin immediately after the mixing. Ordinarily, a temperature of 150° F. is high enough to dissolve the waxy constituents in the crude oil; however, it is preferred to heat the crude oil to a temperature above 170° F. to insure solution of all the waxes in the crude oil. Some crude oils may require a temperature in excess of 200° F. to make sure that all solvated waxy nuclei have been eliminated from the crude oil.

While the mechanism of this invention is not known with certainty, and it is not intended to be bound to any particular theory of operation, it is believed that the limited solubility of the nonpolar constituents of the additive in the low molecular weight hydrocarbon liquids, designated by the term "solvent fractions," in the crude oil causes the amphipathic additive to swell but not completely dissolve in the solvent fractions even at the high temperature at which the amphipathic additive is added to the crude oil or to which the mixture is heated. On subsequent slow cooling of the crude oil, low molecular weight solvent fractions of the crude oil are believed to be squeezed from the polar groups to make those solvent fractions available in the crude oil to increase its mobility, whereas if the crude oil is cooled rapidly, the solvent fractions are trapped in the additive. The amphipathic additive is believed thereby to tie-up the solvent fractions in the crude oil during the period of nucleation and to promote the growth of non-solvated waxy particles and return the solvent fractions to increase the mobility of the crude oil after growth of wax particles is substantially completed.

Preferred amphipathic additives are copolymers of olefinic hydrocarbons with organic compounds containing polar groups. Examples of highly effective amphipathic compounds are copolymers of ethylene and vinyl acetate and copolymers of ethylene and methyl acrylate having a molecular weight in the range of 1,000-30,000 and containing 5-33 percent acrylate ester. Copolymers of ethylene and vinyl acetate containing 5-33 percent acetate ester and having a molecular weight in the range of 1,000-30,000 also can be used. A method for preparing a copolymer of ethylene and methyl acrylate suitable for use in this invention is described in U. S. Pat. No. 3,350,372.

It is essential to increasing the mobility of waxy crude oils by this invention that the amphipathic additive be partially, but not completely, soluble in the crude oil. The solubility of copolymers in the crude oil fraction decreases with increasing molecular weight of the copolymer. Moreover, solubility of the copolymers decreases with increasing polarity of the copolymer. By selection of an amphipathic additive of carefully selected molecular weight and polarity, effective treatment of certain waxy crude oils by this invention is possible. Because of the complexity of crude oils, selection of an amphipathic additive for most effective treatment can be made by mixing samples of the crude oil with amphipathic additive at a temperature above the nucleation temperature in proportions that would be used in the treatment. An increase in viscosity of the crude oil resulting from the incorporation indicates that the crude oil can be effectively treated by this invention with that additive. For example, mixing about 320 parts per million of ethylene methyl acrylate copolymer with Cabinda crude at 150° F. increased the viscosity from about 3.2 centipoises to about 4.7 centipoises. In addition to the copolymer type of amphipathic additive, alkylated phenols in which the alkyl group contains 20-60 carbon atoms have been found to be effective.

The amphipathic additive is incorporated in the crude oil in a concentration, in the range of 50-600 parts per million, and preferably in the range of 60-400 parts per million. The relationship between concentration of vinyl acetate-ethylene copolymer additive and mobility of the treated crude oil is illustrated in FIG. 2. The amphipathic additives may be added to the crude oil in the form of solid particles, in a dispersion or solution, or as an aqueous emulsion. The concentration is of the amphipathic additive, not to the emulsion or solution. Concentrated solutions or gels of the amphipathic additives have a high viscosity and, consequently, are difficult to disperse in the crude oil. Aqueous emulsions of the amphipathic additives stabilized by emulsifiers can be used in place of solutions of the additive. Suitable emulsions which can be readily dispersed in the crude oil may contain as much as 40-50 percent water. The concentrations of 50-600 parts per million refer to concentrations of the amphipathic additive, not the emulsion.

The mixture of crude oil and amphipathic additive is cooled at a slow rate, less than 10° per hour and preferably less than 6° per hour to a temperature slightly above the pour point of the untreated crude oil. For example, in the treatment of a crude oil having a pour point of 85° F., continuing the slow cooling of the crude oil, to which an amphipathic additive had been added at a temperature above the nucleation temperature, to a temperature of 90° F. is effective in increasing the mobility of the oil. The cooling can be continued below the pour point of the untreated crude oil if desired. In most instances continuing the cooling to a temperature of 90° F. will be adequate. The crude oil preferably is sheared during the cooling. Adequate shearing can be accomplished by pumping crude oil through a pipeline at normal pumping rates while the oil is cooled at the required low rate. Another method of conducting the treatment is to agitate the crude oil continuously with a mixer while cooling at the desired low rate in a vessel equipped with cooling coils or a jacket through which cooling water is circulated. It has been found that the combination of the amphipathic additive and the low

rate of cooling while flowing improves the pumpability of the waxy crude oil, and the improved pumping characteristics are maintained by the crude oil during normal storage periods.

The following examples illustrate the treatment of a waxy crude according to this invention.

EXAMPLE 1

A sample of a waxy crude oil from a Cabinda filed having a pour point of 85° F. was mixed at 175° F. in a pressure vessel with 110 parts per million of a vinyl acetate-ethylene copolymer, having a molecular weight of approximately 20,000 and containing approximately 25 percent of vinyl acetate. The treated crude oil was cooled to approximately 70° F. at a rate not exceeding 6° per hour. Cooling was accomplished in a pressure vessel which allowed the treated crude oil to be agitated continuously during the cooling. The treated sample was then aged for 10–15 days at a temperature of 90°–95° and the gel strength, yield shear stress, and plastic viscosity were measured. For comparison, measurements were also made on a sample of the untreated waxy crude. From those parameters, the following behavior in a 36 inch pipeline was calculated:

TABLE I

Waxy Crude	Restarting pressure 50°F. psi/mile	Pressure losses 50°F. at flow rate of 30,000 bbl/hr: psi/mile
Untreated	458	
Treated	66	60

*Beyond the scope of measurement.

It is important that the improved pumping characteristics resulting from the combination of the amphiphathic additive and the cooling is not merely another method of presenting the effect of the treatment on the pour point of the oil. Samples of the same waxy crude oil having a pour point of 85° F. were heated to a temperature of 175° F. and 150 parts per million of a vinyl acetate-ethylene copolymer having a molecular weight of approximately 20,000 were mixed with two samples at the elevated temperature. One of those samples was cooled at a rate less than 10° per hour and the other at a rate of 60° per hour. Similarly, samples of the crude oil to which the additive had not been added were heated to 175° F. and cooled at the same rates. The results are presented in Table II.

TABLE II

Temp. of Reheating °F.	Pour point temperatures, °F. of a waxy crude attained:			
	without additive		with 150 ppm additive	
	at cooling rates lower than 10°F/hr.	controlled 60°F/hr.	at cooling rates lower than 10°F/hr.	controlled 60°F/hr.
170	80	50	50	70

The pour points of the samples were determined by cooling to the pour point of the sample or 50° F., whichever is higher. It will be noted that the sample to which an additive had been added and was cooled at 60° per hour had a higher pour point than the sample to which no additive was added and was cooled at the same rate. In contrast, the pumpability of the treated oil was much higher than of the untreated oil.

EXAMPLE 2

Treatment of the waxy crude similar to the treatment described for Example 1 was performed using an emul-

sion of a vinyl acetate-ethylene copolymer in one instance and a dispersion gel of the copolymer in petroleum distillate in another. The dispersion is a gel at ambient temperature but at the temperature at which it is added to the crude oil is a viscous liquid. The non-copolymer phase of the emulsion contained water and glycol in the ratio of 6:4. The treated samples were aged for 10–15 days at 70° F. and the gel strength was determined at 70° F. The computed restarting pressures for the untreated and treated oil are presented in Table III. The concentrations are of the additive, not the emulsion or solution.

TABLE III

Amph. Add.	Conc. Add. ppm	Restarting pressure at 70°F psi/mile 60
Untreated Emulsion of copolymer	90	19
Gel of copolymer	75	14

The effect of the rate of cooling on the improvement of the mobility of the waxy crude oil is shown in Example 3.

EXAMPLE 3

Two samples of waxy crude oil were treated with 110 parts per million of a vinyl acetate-ethylene copolymer having a molecular weight of approximately 20,000 in a pressure viscometer at a temperature of 175° F. and a pressure of 800 psi. One sample was cooled to 67° F. at a rate of 60° F. per hour and the other at a rate of 8.5° F. per hour. The viscosity of each sample was measured at 67° F. The two samples were sheared at the same rate during the cooling. The effect of cooling at different rates while shearing on the viscosity are presented in Table IV. The data show the slowly cooled sample to have a much lower viscosity. Addition of the amphiphathic additive will not give the desired improvement in viscosity unless combined with slow cooling. An untreated crude oil sample cooled from a temperature above the nucleation temperature at a low rate to erase the effects of the past thermal history had a viscosity of 320 cps at 67° F. Thus, slow cooling alone or the additive alone fail to give the desired reduction in viscosity.

TABLE IV

Cooling Rate °F/hr.	Shear rate while cooling, sec ⁻¹	Viscosity at 67°F. cp
50	60	54
8.5	54	258
8.5 (Untreated)	54	13
		320

EXAMPLE 4

Data obtained by heating a waxy crude oil to a temperature at which all waxy solid particles are dissolved and then cooling the oil at a very low rate indicated that about one-third of the waxes present in the crude oil are nucleated by the time the crude oil is cooled to a temperature of 125° F. To determine the effect of preventing solvation of only a part of the waxy solids, a waxy crude was heated to a temperature of 150° F. and cooled at a rate of 6° per hour to 125° F. 155 parts per million of methyl acrylate-ethylene copolymer having a molecular weight of approximately 5,000 were added to the crude oil and the temperature maintained at 125° F. for about 2 ½ hours. Thereafter, the cooling was continued at a rate of 6° per hour until a temperature

of 70° F. had been reached. The gel strength of the treated sample was determined at 70° F. and the computed restarting pressure in a 36 inch pipeline was 28 psi per mile. A comparison with the data in Table III shows that although there was a substantial improvement in the restarting characteristics of the crude oil, the improvement was not as great as when the additive was mixed with the crude oil at 175° F.

Although the above examples treat the waxy crude oil with polymeric amphipathic additives, this invention is not limited to those compounds. Alkylated phenols are also effective, as shown by the following example.

EXAMPLE 5

An alkylated phenol having a C₂₅ alkyl group was added to one sample of a waxy West African crude oil and an alkylated phenol having a C₄₀ alkyl group was added to a second sample of the same crude oil. Both additives were mixed with the crude oil at a temperature of 155° F., which was above the nucleation temperature. The treated crude oil was then cooled at a rate that did not exceed 6° per hour to a temperature of approximately 70° F. The samples were aged at 90°–95° F. for a period of 14 days, and the restarting pressures computed from the gel strength data on the aged samples. Restarting pressures were also computed on the crude oil subjected to the same thermal conditions but not treated with the alkylated phenol. The data are presented in the following Table V.

TABLE V

Alkylated phenol	Conc. ppm	°F.	Restarting pressure in 36-inch line, psi/mile	
			Treated Crude	Untreated Crude
C ₂₅ chain	210	68	21	65
C ₄₀ chain	225	69	22	60

This invention provides a method of increasing the mobility of waxy crude oils having an API gravity in the range of 30°–40° that tend to gel on aging. Unlike thermal treating methods heretofore available the improved mobility of the crude oil persists even though the crude oil is stored for extended periods in hot climates. The improved mobility of the oil which facilitates pumping it through pipelines is the result of the reduction in gel strength and viscosity by the combination of slow cooling from a temperature above the nucleation temperature while shearing or agitating with the incorporation of an amphipathic additive in the oil.

We claim:

1. A method for increasing the mobility of waxy crude oils comprising treating the waxy crude oil with an amphipathic additive at a temperature above the nucleation temperature of the crude oil and thereafter cooling the treated crude oil at a rate less than 10° per hour to approximately the pour point of the untreated crude oil.

2. A method as set forth in claim 1 in which the waxy crude oil is treated with 50–600 parts of the amphipathic additive per million parts of waxy crude oil.

3. A method of improving the mobility of the waxy crude oil having an API gravity in the range of about 30°–40° to increase its mobility comprising mixing an amphipathic additive with the oil in a ratio of 50–600 parts of amphipathic additive per million parts of waxy crude oil at a temperature above the nucleation temperature, and thereafter cooling the mixture at a rate less than 10° F. per hour to approximately the pour point of the untreated crude oil.

4. A method of treating a waxy crude oil having an API gravity in the range of about 30°–40° to increase its mobility comprising mixing with the crude oil an amphipathic additive in an amount in the range of 50–600 parts per million of crude oil, heating the mixture above the nucleation temperature of the crude oil and thereafter cooling the mixture at a rate of less than 10° F. per hour to approximately the pour point of the untreated crude oil.

5. A method as set forth in claim 1 in which the treating of the waxy crude oil with an amphipathic additive is at a temperature above 150° F., the waxy crude oil is treated with 50–600 parts of amphipathic additive per million parts of crude oil, and the treated crude oil is cooled at a rate less than 10° F. per hour to a temperature below 90° F.

6. A method as set forth in claim 5 in which the amphipathic additive is selected from the group consisting of alkylated phenols having 20–60 carbon atoms in the alkyl group, copolymers having a molecular weight in the range of 1,000–30,000 of ethylene and acetate esters, and copolymers having a molecular weight in the range of 1,000–30,000 of ethylene and acrylate esters.

7. A method as set forth in claim 5 in which the amphipathic additive is a copolymer having a molecular weight in the range of 1,000–30,000 of ethylene and an organic polar compound.

8. A method as set forth in claim 7 in which the amphipathic additive is a copolymer having a molecular weight in the range of 1,000–30,000 of ethylene and an organic polar compound selected from the group consisting of the acetate esters and acrylic esters.

9. A method as set forth in claim 5 in which the amphipathic additive is an alkylated phenol having 20–60 carbon atoms in the alkyl group.

10. A method as set forth in claim 4 in which the amphipathic additive is a copolymer having a molecular weight of 1,000–30,000 of ethylene and vinyl acetate.

11. A method as set forth in claim 4 in which the amphipathic additive is a copolymer having a molecular weight of 1,000–30,000 of ethylene and methyl acrylate.

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