

[54] **PETROLEUM CRUDE OILS CONTAINING
POLYMERS COMPRISED OF C₁₈-C₄₀
ALPHA-OLEFINS HAVE REDUCED
TENDENCY TO DEPOSIT WAX**

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[58] Field of Search **44/62, 80**

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[57]

ABSTRACT

Paraffin deposition in flow systems handling petroleum crude oil is substantially reduced or inhibited by blending the crude oil with a polymer comprised of 20 to 100 wt. % of a C₁₈—C₄₀ alpha-olefin and 0 to 80 wt. % of a C₃—C₁₆ alpha-olefin. The polymers have a number average molecular weight within the range between about 500 and 125,000 and are preferably copolymers containing 4 to 50 wt. % of a C₃—C₈ alpha-olefin and 50 to 96 wt. % of a C₂₀—C₂₈ alpha-olefin.

4 Claims, No Drawings

**PETROLEUM CRUDE OILS CONTAINING
POLYMERS COMPRISED OF C₁₈-C₄₀
ALPHA-OLEFINS HAVE REDUCED TENDENCY TO
DEPOSIT WAX**

This is a continuation of application Ser. No. 762,368, filed Sept. 16, 1968, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to petroleum crude oils having a reduced tendency to deposit paraffin, i.e., wax, on the surfaces of handling systems. More particularly, the invention is concerned with petroleum crude oils containing hydrocarbon polymers comprised of alpha-olefins, which polymers reduce or inhibit the deposition of paraffin from the crude oil.

2. Description of the Prior Art

Paraffin deposition on metal surfaces of oil-well pumps, rods, and other downhole equipment, as well as surface valves and flow lines, is a serious problem in petroleum crude oil production. Considerable expense is involved for periodic deposit removal, production losses resulting from restricted flow capacity, and unproductive down time.

The paraffin problem is found in virtually all the major oil-producing areas of the world. It is generally accepted that the major causes of paraffin deposition are the cooling of the crude oil during production, and the escape of light ends or gases which previously helped retain the paraffin in solution in the oil. Other contributing factors are:

1. Alternate coating and draining of oil.
2. Contact of oil with a cold surface.
3. Spraying of oil as a mist.
4. Flow of oil at a low rate.
5. Agitation hastening paraffin particle growth.
6. Sand, silt, water.
7. Rough tubing surfaces.
8. Viscosity of oil not so high as to prevent wax particles from settling out.

As a result of these influences, paraffin deposits occur at the bottom of the well, in tubing, and in surface equipment. Paraffin deposition in surface flow lines has been alleviated by the installation of large-diameter lines, or the use of pumpable plugs. When such paraffin deposition occurs below the surface, however, its removal is more laborious and costly.

Remedial expense varies widely in different cases, depending on well conditions and severity of the problem. An average of from 2 to 10 cents per barrel of crude is involved. In addition to the obvious costs of paraffin removal, decreased equipment life and increased lifting costs are also involved. Numerous methods have been developed for removing the paraffin plugging deposits. In general, these involve mechanical, thermal, and chemical methods, and combinations thereof.

The mechanical method involves the physical scraping of paraffin deposits from the tubing. Thermal methods include circulating hot oil or hot water down the well bore, or the use of bottomhole heaters. The chemical treatment method involves the use of special solvents that dissolve the paraffin so that it can be brought to the surface in liquid form.

In accordance with this invention, a new approach to the paraffin deposition problem is the development of a new class of polymeric wax crystal modifiers which

when blended with the crude oil reduce or inhibit the deposition of paraffin on the surface of flow lines. These additives also improve the (viscosity) flow properties of the crude, thereby facilitating production and handling of crude in pipelines, pumps, etc.

SUMMARY OF THE INVENTION

Petroleum crude oils having a reduced tendency to deposit wax are prepared by incorporating into the crude oil from about 0.0001 to 2.00 wt. % based on crude oil to be treated, preferably 0.0005 to 0.45 wt. % of an oil-soluble polymer comprising at least 20 wt. % of a C₁₈-C₄₀ alpha-olefin, said polymer having a number average molecular weight in the range of about 500 to 125,000, preferably about 1000 to about 40,000 as measured by Vapor Phase Osmometry (VPO).

The C₁₈-C₄₀ alpha-olefin monomer which is used to prepare the polymer of the invention may be represented by the following general formula: H₂C = CHR wherein R is a substantially linear aliphatic hydrocarbon radical containing from 16 to 38 carbon atoms. It is preferred, however, that R have the formula: CH₃-(CH₂)_n-CH₂- wherein n is a whole number ranging from about 14 to 36, more preferably from about 16 to 24. The term "substantially linear" is used herein to denote those aliphatic side chains, i.e., R, which contain no more than one lower alkyl side chain such as methyl, ethyl, etc., in the radical and wherein said lower alkyl side chain, when present in the radical, is located at a position such that R has a linear portion containing at least 16 carbon atoms. Examples of such monomers include, among others, n-eicosene-1, 3-methyl eicosene-1, n-docosene-1, n-tetracosene-1, 3-methyl tetracosene-1, n-hexacosene-1, n-triacontene-1 and the like.

Polymers prepared from the aforescribed C₁₈-C₄₀ alpha-olefins when blended in petroleum crude oils are effective for reducing or inhibiting the deposition of wax from the crude oil and for improving the flow properties of these oils. It has unexpectedly been found, however, that the polymers having the greatest ability to inhibit wax deposition in crude oils are prepared from the aforescribed C₁₈-C₄₀ alpha-olefins and certain lower alpha-olefins. While not known with certainty, this unexpected improvement in the inhibition of wax deposition may be due to the fact that copolymerization with lower alpha-olefins results in a polymer of lower order thereby improving oil solubility and ability to co-crystallize with the wax to result in smaller wax crystals. Accordingly, the preferred polymer of this invention comprises 0 to 80 wt. % of a C₃-C₁₆ alpha-olefin and 20 to 100 wt. % of the aforescribed C₁₈-C₄₀ alpha-olefin. Of these, copolymers containing 4 to 50 wt. % of a C₃-C₈ alpha-olefin and 50 to 96 wt. % of a linear C₂₀-C₂₈ alpha-olefin are particularly effective. An especially preferred polymer comprises 20 to 40 wt. % of a C₄-C₆ alpha-olefin and 60 to 80 wt. % of a C₂₀-C₂₈ alpha-olefin.

The C₃-C₁₆ alpha-olefins which are polymerized with the aforescribed C₁₈-C₄₀ alpha-olefins may be represented by the following general formula: H₂C = CHR' wherein R' is a hydrocarbon radical containing from 1 to 14 carbon atoms. Since the lower alpha-olefin apparently serves only to disrupt the order of the polymer, there appears to be no criticality as to the configuration of R'. Accordingly, R' may be an alkyl, aralkyl, aryl, alkylaryl, or cycloaliphatic group. Examples of such monomers include propylene, butene-1,

hexene-1, octene-1, decene-1, 3-methyl decene-1, tetradecene-1, styrene and styrene derivatives such as p-methyl styrene, p-isopropyl styrene, alpha-methyl styrene, etc.

The aforescribed C_{18} — C_{40} alpha-olefins may be polymerized with various other monomers. For example, effective copolymers comprise 20–100 wt. % of a C_{18} — C_{40} alpha-olefin of the invention and 0–80 wt. % of a polymerizable C_6 — C_{28} diolefin. Similarly, the polymers of the invention may comprise 20 to 100 wt. % of the aforescribed C_{18} — C_{40} alpha-olefin, 0 to 80 wt. % of the aforescribed C_3 — C_{16} alpha-olefin and 0 to 80 wt. % of a polymerizable C_6 — C_{28} diolefin. These diolefins which are useful for polymerization with the aforescribed alpha-olefins include the bicyclic, alicyclic or aliphatic diolefins containing from about 6 to about 28 carbon atoms, preferably from about 6 to 12 carbon atoms. Non-limiting examples of suitable monomers include 1,5-cyclooctadiene, methylene norbornene, dimethylene norbornene, 1,5-hexadiene dicyclopentadiene, 5-vinyl-2-norbornene, 1,5-cyclodecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl) cyclopentene, 1,5-octadecadiene, and the like.

The polymers of this invention may be conventionally prepared by polymerizing the monomers under relatively mild conditions of temperatures and pressure in the presence of a Ziegler-type catalyst, i.e., a mixture of a compound derived from a Group IV, V or VI metal of the Periodic Table in combination with an organo metallic compound of a Group I, II, or III metal of the Periodic Table wherein the amount of the compound derived from a Group IV – VI metal may range from 0.01 to 2.0 moles per mole of the organo metallic compound.

Effective catalysts for polymerizing the monomers of the invention include the following combinations: aluminum triisobutyl and vanadium trichloride; aluminum triisobutyl, aluminum chloride, and vanadium trichloride; vanadium tetrachloride and aluminum trihexyl; vanadium trichloride and aluminum trihexyl; vanadium triacetylacetonate and aluminum diethyl chloride; titanium tetrachloride and aluminum trihexyl; vanadium trichloride and aluminum trihexyl; titanium trichloride and aluminum trihexyl; titanium dichloride and aluminum trihexyl; etc.

The polymerization is usually carried out by mixing the catalyst components in an inert diluent such as a hydrocarbon solvent, e.g., hexane, benzene, toluene, xylene, heptane, etc., and then adding the monomers into the catalyst at atmospheric or superatmospheric pressure and temperatures within the range between about 50° and 180°F. Usually atmospheric pressure is employed when polymerizing the monomers containing more than 4 carbon atoms in the molecule and higher pressures are used for the more volatile C_3 — C_4 alpha-olefins. The time of reaction will depend upon, and is interrelated to, the temperature of the reaction, the choice of catalyst, and the pressure employed. In general, however, ½ to 5 hours will complete the reaction.

Usually, based upon 100 parts by weight of polymer to be produced, about 120 to 100,000 parts by weight of solvent, and about 0.05 to 5 parts by weight of catalyst will be used in the polymerization.

Petroleum crude oils are often classified into asphalt-base, paraffin-base, and mixed-base, depending on whether they contain asphalt, wax, or a mixture of both in the distillation residue. The present invention is concerned with all petroleum crude oils containing wax

fractions which deposit from the crude oil when subjected to temperatures below the ASTM cloud point of the crude oil.

In accordance with the invention, reduction or inhibition of wax deposition can be effected by blending the oil with the polymeric wax crystal modifier of the invention at a point downhole, at the well head or a surface point downstream from the well site.

For ease in handling, the polymeric additive of the invention may be utilized in a concentrate form. For example, to facilitate storage and transportation, the polymer may be blended with a hydrocarbon solvent such as mineral oil to form a concentrate comprising from about 20 to about 80 wt. % hydrocarbon solvent and from about 20 to about 80 wt. % of the polymer of the invention.

The polymers of the invention may be used alone as the sole additive, or in combination with other additives such as corrosion inhibitors, demulsifying agents, scale inhibitors, etc.

The invention will be further understood by reference to the following examples which include preferred embodiments of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

A homopolymer of n-eicosene-1 was prepared as follows:

Into a 500 ml. four-neck flask fitted with a mechanical stirrer, heating mantle, thermometer, condenser and gas inlet were charged under anhydrous conditions, 0.21 gram of $TiCl_3 \cdot 1/3 AlCl_3$, 200 ml. of toluene as solvent and 0.4 gram of $Al(n-C_8H_{17})_3$. After stirring the catalyst-solvent mixture at room temperature for about 30 minutes, the mixture was heated to about 75°C. under a nitrogen blanket and 20 grams of a C_{20} alpha-olefin (n-eicosene-1) dissolved in 10 grams of normal hexane was added thereto. After addition of the alpha-olefin solution was completed, the reaction mixture was heated to 70° to 80°C. for about 2 hours, whereupon 1 ml. of isopropyl alcohol was added to stop the reaction. The product mixture was then cooled to room temperature and thereafter mixed with about 5 volumes of methanol to precipitate the solid C_{20} alpha-olefin homopolymer which was then filtered off and dried for about 12 hours in an oven maintained at about 60°C. and 120 mm. pressure. The resulting polymer weighed 6.7 grams and had a number average molecular weight of 2100 as determined by Vapor Phase Osmometry (VPO).

EXAMPLE 2

A polymer of propylene and C_{22} — C_{28} alpha-olefins was prepared in the following manner:

A 150 cc. stirred autoclave was charged under anhydrous conditions with 0.400 gram of triethyl aluminum, i.e., $Al(C_2H_5)_3$, 22 grams of xylene solvent and 0.424 gram of aluminum activated titanium trichloride, i.e., $TiCl_3 \cdot 1/3 AlCl_3$, with a dry nitrogen blanket. The catalyst-solvent mixture was then stirred at 70° to 80°C. for 2 hours. To the reactor contents were then added 82.2 grams of a normal hexane solution containing 8 wt. % of a C_{22} — C_{28} alpha-olefin mixture containing 32 wt. % n— C_{22} alpha-olefin, 35 wt. % n— C_{24} alpha-olefin, 22 wt. % n— C_{26} alpha-olefin, 7.8 wt. % n— C_{28} alpha-olefin and 3.2 wt. % C_{30+} alpha-olefins (wt. % based on

polymerizable material; 42 wt. % inert material present). After addition of the C_{22} — C_{28} alpha-olefin solution was completed, propylene was pressured into the autoclave until the pressure was raised from atmospheric to 6 psig. Propylene pressure was maintained in the reactor for 2 hours at a temperature of 70° to 80°C. Then, after adding 0.9 gram of isopropanol to kill the reaction, the reactor was opened and the contents were diluted with n-heptane and added to 4000 ml. of methanol to precipitate the polymer product. The empty reactor was rinsed with 30 ml. of n-hexane which was also added to the methanol. The precipitated product was then dried for about 12 hours in an oven maintained at 60°C. and 120 mm. pressure. The propylene/ C_{22} — C_{28} alpha-olefin polymer product weighed 5.2 grams and had a number average molecular weight of 1890 as measured by Vapor Phase Osmometry (VPO).

EXAMPLE 3

A copolymer of butene-1 and n- C_{22} alpha-olefin was prepared by reacting 4.1 grams of liquefied butene-1 in a stirred glass closed reactor containing 10.0 grams of C_{22} alpha-olefin dissolved in a catalyst-solvent mixture consisting of 122.5 ml. of toluene, 0.40 gram of $Al(n-C_3H_8)_3$ and 0.21 gram of $TiCl_3 \cdot 1/3AlCl_3$, which catalyst-solvent mixture was prepared in accordance with the method of Example 1. The polymerization was then carried out by reacting the reactants at 70°–80°C. for about 4 hours. Termination of the reaction and recovery of the product was then carried out in accordance with the steps given in the above examples. The butene-1/docosene-1 copolymer product weighed 7.8 grams and had a number average molecular weight of about 4300 as measured by Vapor Phase Osmometry.

EXAMPLE 4

A number of polymers of lower alpha-olefins, higher alpha-olefins and cyclic olefins were prepared using the same general procedure as described in the above examples. In these runs, polymers prepared only from olefins containing 6 or more carbon atoms were made using the general process conditions set forth in Example 1, with the exception that different olefin-monomers and amounts were employed. Similarly, polymers prepared from propylene were made using the process described in Example 2. Polymers prepared from butene-1 were made using the process described in Example 3. The resulting polymers were then tested in a Texas Austin County petroleum crude oil known as Raccoon Bend crude and having an ASTM upper pour point of 75°F. and lower pour point of 35°F., a viscosity of 43 SUS at 100°F., and an API gravity of 31.8. The crude oil-polymer blends were tested for pour depression since this is a measure of the ability of the polymer additive to keep the wax in suspension and in a fluid state, thereby eliminating or reducing the amount of wax which will deposit upon flow surfaces exposed to the crude. The results are given in the following table.

TABLE

EVALUATION OF POLYMERIC ADDITIVES ⁽¹⁾ IN RACCOON BEND CRUDE OIL		
Additive	ASTM Pour Point, (°F.)	
	Upper	Lower
None	75	35
Hexene-1 homopolymer ⁽³⁾	70	35

TABLE-continued

EVALUATION OF POLYMERIC ADDITIVES ⁽¹⁾ IN RACCOON BEND CRUDE OIL		
Additive	ASTM Pour Point, (°F.)	
	Upper	Lower
Tetradecene-1 homopolymer ⁽⁴⁾	65	30
Hexadecene-1 homopolymer ⁽⁵⁾	65	45
Hexadecene-1/octadecene-1/ C_{20} — C_{30} polymer ⁽⁶⁾	—20	—15
Octadecene-1/propylene copolymer ⁽⁷⁾	65	10
Eicosene-1 homopolymer ⁽⁸⁾	—5	15
Eicosene-1/propylene copolymer ⁽⁹⁾	—5	—20
Docosene-1 homopolymer ⁽¹⁰⁾	40	30
Docosene-1/butene-1 copolymer ⁽¹¹⁾	0	—5
Docosene-1/hexene-1 copolymer ⁽¹²⁾	—5	—35
Docosene-1/hexene-1/DCPD terpolymer ⁽¹³⁾	20	10
Docosene-1/hexene-1/MNB terpolymer ⁽¹⁴⁾	70	—5
Docosene-1/styrene copolymer ⁽¹⁵⁾	5	—5
C_{22} — C_{28} alpha-olefin/propylene polymer ⁽¹⁶⁾	0	5
C_{22} — C_{28} alpha-olefin/styrene polymer ⁽¹⁷⁾	25	15
C_{22} — C_{28} alpha-olefin/4-methylpentene-1 polymer ⁽¹⁸⁾	20	20

⁽¹⁾ Amount of additive tested is 0.15 wt. % based on crude oil.

⁽²⁾ ASTM D-97, special procedure for black oils.

⁽³⁾ Number average molecular weight of about 17,000 (VPO).

⁽⁴⁾ Number average molecular weight <20,000.

⁽⁵⁾ Number average molecular weight of about 3600 (VPO).

⁽⁶⁾ Polymer prepared from 14 wt. % hexadecene-1, 11 wt. % octadecene-1, 7 wt. % eicosene-1, 35 wt. % of C_{22} — C_{28} alpha-olefin mixture described in Example 2 and 33 wt. % of alpha-olefin mixture containing 2 wt. % C_{24} alpha-olefin, 8 wt. % C_{26} alpha-olefin, 18 wt. % C_{28} alpha-olefin, 21 wt. % C_{30} alpha-olefin, 17 wt. % C_{32} alpha-olefin, 13 wt. % C_{34} alpha-olefin, 8 wt. % C_{36} alpha-olefin, 6 wt. % C_{38} alpha-olefin, and 7 wt. % of C_{40} alpha-olefins.

⁽⁷⁾ Copolymer prepared from 44.4 grams octadecene-1 and 4 psig. propylene using reactor system of Example 2 and having a number average molecular weight of about 6800 (VPO).

⁽⁸⁾ Polymer of Example 1.

⁽⁹⁾ Copolymer prepared from 12.1 grams of eicosene-1 and 6 psig. propylene using reactor system of Example 2 and having a number average molecular weight of about 1420 (VPO).

⁽¹⁰⁾ Number average molecular weight of about 7180 (VPO).

⁽¹¹⁾ Copolymer prepared from 67 wt. % docosene-1 and 33 wt. % butene-1 and having a number average molecular weight of about 3350 (VPO).

⁽¹²⁾ Copolymer prepared from 40 wt. % docosene-1 and 60 wt. % hexene-1 and having a number average molecular weight of about 5530 (VPO).

⁽¹³⁾ Terpolymer prepared from 60 wt. % docosene-1, 38 wt. % hexene-1 and 2 wt. % dicyclopentadiene (DCPD) and having a number average molecular weight of about 3640 (VPO).

⁽¹⁴⁾ Terpolymer prepared from 56 wt. % docosene-1, 36 wt. % hexene-1 and 8 wt. % methylene norbornene (MNB) and having a number average molecular weight of about 2540 (VPO).

⁽¹⁵⁾ Copolymer prepared from 72 wt. % docosene-1 and 28 wt. % styrene and having a number average molecular weight of about 8005 (VPO).

⁽¹⁶⁾ Polymer prepared from 6.6 grams of C_{22} — C_{28} alpha-olefin mixture described in Example 2 and 6 psig. propylene using reactor system of Example 2 and having a number average molecular weight of about 1890 (VPO).

⁽¹⁷⁾ Copolymer prepared from 72 wt. % of C_{22} — C_{28} alpha-olefin mixture of Example 2 and 28 wt. % styrene and having a number average molecular weight of about 8500 (VPO).

⁽¹⁸⁾ Copolymer prepared from 75 wt. % of C_{22} — C_{28} alpha-olefin mixture of Example 2 and 25 wt. % of 4-methylpentene-1 and having a number average molecular weight of about 677 (VPO).

It can be seen from the data in the above Table that polymers prepared from alpha-olefins containing at least 18 carbon atoms in the molecule are very effective for lowering the pour point and thus increasing the flowability of petroleum crude oil. Of particular interest, is the surprising discovery that the effectiveness of these C_{18} + alpha-olefin polymers is significantly improved by incorporating lower alpha-olefins, such as propylene, butene-1, hexene-1, etc., into the polymer molecule. For example, referring to the above Table, it is seen that homopolymers prepared from C_{20} or C_{22} alpha-olefin are substantially less effective than copolymers prepared from C_3 — C_6 alpha-olefins and C_{20} or C_{22} alpha-olefin. While not known with certainty, this unexpected improvement is believed to be due to the disrupting effect which the lower alpha-olefins have on

the order of the polymer. Also, as is illustrated in the above Table, non-linear olefins, e.g., styrene, 4-methylpentene-1, cyclooctadienes, etc., may be advantageously copolymerized with the higher olefins.

It is not intended that this invention be limited to the specific examples presented by way of illustration. The scope of the invention is limited by the appended claims.

What is claimed is:

1. An oil composition consisting essentially of a petroleum crude oil containing in the range of 0.0005 to 0.45 wt. % of a flow improving, oil-soluble copolymer prepared by using a Ziegler type polymerization catalyst and consisting essentially of 60 to 80 wt. % of a

sisting of eicosene, docosene, and mixtures of C_{22} to C_{28} olefin; and 40 to 20 wt. % of a lower alpha mono-olefin having 4 to 6 carbon atoms, said copolymer being substantially free of diene monomers, and having a number average molecular weight in the range of about 500 to 125,000.

2. An oil composition according to claim 1, wherein said molecular weight is in the range of 1000 to 40,000.

3. An oil composition according to claim 2, wherein said copolymer consists essentially of docosene and butene-1.

4. An oil composition according to claim 2, wherein said copolymer consists essentially of docosene and hexene-1.

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