United States Patent

McDougall et al.

[15] **3,693,720**

[45] **Sept. 26, 1972**

[54] **CRUDE OIL RECOVERY METHOD USING A POLYMERIC WAX INHIBITOR**

[72] Inventors: **Lee A. McDougall**, Houston, Tex.; **Albert Rossi**, Warren, N.J.; **Max J. Wisotsky**, Highland Park, N.J.

[73] Assignee: **Esso Research and Engineering Co.**

[22] Filed: **Jan. 29, 1971**

[21] Appl. No.: **111,151**

[52] **U.S. Cl.** ....**166/304,** 252/8.55 B

[51] **Int. Cl.** **E21b 43/00,** C09k 3/00

[58] **Field of Search** .....166/304; 252/8.55 B, 8.3, 56; 260/87.3, 85.5 ES, 28.5 AV

[56] **References Cited**

UNITED STATES PATENTS

2,800,453	7/1957	Bondi et al.	260/87.3 UX
2,927,078	3/1960	Nathan	252/8.55 B X
3,093,623	6/1963	Ilnyckyj	260/87.3
3,131,168	4/1964	Ilnyckyj et al.	260/87.3
3,162,601	12/1964	Jones	252/8.55 B X
3,193,499	7/1965	Carr	252/8.55 B
3,395,757	8/1968	Crossland	166/304
3,481,870	12/1969	Cheng et al.	252/8.55 B X
3,640,824	2/1972	Bucaram et al.	166/304 X

Primary Examiner—Stephen J. Novosad
Attorney—Pearlman & Schlager and Carl G. Seutter

[57] **ABSTRACT**

The recovery of crude oil may be improved by inhibiting deposition of wax from the oil. Wax deposition may be inhibited by adding to the oil a polymer having pendant polar and non-polar moieties, such as a partially hydrolyzed ethylene-vinyl acetate copolymer.

8 Claims, No Drawings

CRUDE OIL RECOVERY METHOD USING A POLYMERIC WAX INHIBITOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of recovering a petroleum crude oil by the addition to said oil a polymeric material. More specifically, this invention relates to inhibiting deposition of wax on a surface with which the oil may come into contact.

2. Description of the Prior Art

As is well known to those skilled in the art, petroleum crude oils, as found in nature, may contain a wide variety of components. Among these components may be waxy components including paraffins, e.g. straight chain, higher molecular weight hydrocarbons. These waxy components may be soluble in the petroleum crude oil particularly at elevated temperatures of e.g. 20°–200°C. and elevated pressures of e.g. 70–700 atmospheres at which the oil may be found in petroleum-bearing formations. It is also well known that these waxy components may deposit on surfaces; and that these deposits may form constrictions or plugs which may interfere with the recovery of crude oil. The flow of oil in oil wells may, for example, be found after extended periods of time to drop typically to 50–60% of the initial flow, typically because of such deposits in the casing.

Although a major cause of deposition of waxy components from petroleum crude oils during their recovery appears to be the decrease of temperature and pressure and the liberation of light ends which help to retain the waxy components in solution, other factors which may also increase or facilitate wax deposition may include:

1. Intermittent coating and draining of oil;
2. Contacting of oil with a cold surface;
3. Spraying of oil as a mist;
4. Flowing of oil at a low rate;
5. Agitating oil thus hastening wax particle growth;
6. The presence of sand, silt and water;
7. The presence of rough tubing surfaces;
8. The presence of oil of viscosity insufficient to prevent wax particles from settling out.

As a result of these factors, deposits of waxy components may occur at the bottom of the well, in pipes, and in surface equipment.

Deposition of these waxy components, in addition to interfering with flow and possibly shutting it off, causes other problems. Typical of these may be decreased equipment life and increased operating costs.

Prior art attempts to remove these waxy compositions have included mechanical, thermal, and chemical methods, and combinations thereof.

Mechanical methods may include the physical scraping of paraffin deposits from the metal surface, e.g. the tubing. Thermal methods include circulating hot oil or hot water in contact with the surface, typically down the well bore, or the use of bottom hole heaters. Typical chemical treatments may include the use of special solvents that dissolve the waxy deposit so that it can be brought to the surface in liquid form, etc. An example of this technique is disclosed in U.S. Pat. No. 3,437,146.

Certain attempts to add polymeric materials to an oil well for various purposes, including that of inhibiting wax deposition, have been made in the prior art. Among these are those described U.S. Pat. Nos. 3,244,188; 2,836,559; 2,927,078; 3,162,601; 3,215,154; 3,244,188; 3,249,535; 3,271,307; 3,395,757; 3,416,605; 3,431,976; 3,434,485; and journal articles published in World Oil, November, 1966, pages 95 through 99 and in Journal of Petroleum Technology, September, 1969, pages 1151 through 1156.

It has also been known in the prior art that polymers can be produced containing pendant polar and non-polar moieties. Among these are those disclosed in U.S. Pat. Nos. 2,386,347; 2,399,653; 2,490,550; 2,660,563; 2,703,794; 2,800,453 and 3,093,623; and in British Pat. Nos. 777,773 and 1,140,080.

It is an object of this invention to provide a method of recovering crude petroleum oil. Other objects will be apparent to those skilled in the art from the following description.

SUMMARY OF THE INVENTION

In accordance with certain of its aspects, the method of this invention for recovering a crude petroleum oil containing waxy components from a reservoir wherein the oil is at a temperature above its wax deposition temperature may comprise:

a. passing a portion of said crude petroleum oil from said reservoir to a first central collection point;

b. passing said oil from said first central collection point to a second collection point whereby the temperature of said oil decreases and passes through a wax-deposition temperature at which waxy components begin to precipitate and deposit on surfaces with which said oil comes in contact as it passes to said second collection point;

c. collecting said crude petroleum oil at said second collection point; and

d. adding to said crude petroleum oil before the temperature of said oil decreases to said wax deposition temperature, a wax-deposit-inhibiting amount of a polymer

$$[(CH_2CHR)_m(CH_2CHX)_n(CH_2CHY)_p]_q \qquad (I)$$

wherein X is a non-polar moiety, Y is a polar moiety, R is H, an alkyl, aryl, aralkyl, or alkaryl moiety, m is 1.5–3, n is 0.1–0.8, p is 0.01–0.5, $m/(m+n+p)$ is 0.65–0.97, $p/(n+p)$ is 0.1–0.85, q is 2 to 500, and the molecular weight $\bar{M}_n$ of said polymer is 500–100,000.

DESCRIPTION OF THE INVENTION

The crude petroleum oils which may be treated by the process of this invention include crude petroleum oils in the underground or subsurface reservoirs including those in which they may be found in nature. Commonly, naturally occurring crude petroleum oils may contain a wide variety of waxy components, typically 3 - 40%, commonly 5 - 20% of waxy components which may deposit from the oil as the temperature is lowered. The waxy component content of oils may be determined by standard technique such as extraction with secondary butyl alcohol.

Crude petroleum oils, particularly those commonly designated as paraffinic crudes, which are typical oils which may be treated by the process of this invention, may be found in domestic and foreign oil production areas on land, in inland waters, and offshore. Illustrative of such paraffinic crude petroleum oils may be:

a. A Grand Isle T-1 crude characterized by a 46° C. cloud point and a −1° C. pour point;

b. A crude from offshore Louisiana (Eugene Island 126) characterized by a 21° C. cloud point and a −12° C. pour point.

c. A crude from West Texas (Powell 15) characterized by a 27° C. cloud point and a −7° C. pour point, etc.

Commonly, such oils as found in their reservoirs may be at a temperature of 20° - 200° C., typically 50° - 70° C., say 60° C. and a pressure of 70–700 atmospheres, typically 70 - 350 atmospheres, say 175 atmospheres. If the temperature and pressure of these oils is lowered, it may be found that the light ends (e.g. methane, ethane, etc.) boil off and the temperature of the oil passes through a wax deposition point at which waxy components of the oil may begin to deposit on surfaces in contact with the oil. The wax deposition point may be the cloud point as determined by ASTM Test D 97–57.

In practice of this invention according to certain of its aspects, a portion of the crude petroleum oil may be passed from the reservoir, typically a subsurface reservoir, in which it is located to a first central collection point, typically at a subsurface location. Commonly, this point may be at the lower end of the conduit through which the oil is to be passed to a second collection point.

The oil collected at the first central collection point may be passed to a second collection point, commonly an above-surface collection point. The oil passing from the first collection point to the second collection point may commonly decrease in temperature by 0.5° - 1.5° C., say 1.0°C. per 30 meters of passage, e.g. upwardly, through the conduit or casing of an oil well until its temperature at the second collection point is typically 10° - 100° C., say 30° C.

As the oil passes upwardly, in a preferred embodiment, its waxy components may begin to precipitate (at the cloud point) as the temperature approaches the wax deposition temperature. The precipitating wax compounds may adhere to the surfaces of the e.g. conduit with which they come into contact; and as to the wax deposition temperature is passed, the waxy components may deposit on, rigidly adhere to, and form layers of increasing thickness on the surface.

In time, the deposit may become thicker and harder and the flow of the oil through the constricted passage in the conduit may decrease to 50–60% of the desired "clean flow". Commonly this deposit may be 0.25–2.5 cm., say 1.2 cm. thick and may occupy 3–1,500 meters, say 750 meters along the conduit. Similar deposits may also form and impede flow in above surface conduits, tanks, etc.

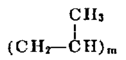
In practice this invention according to certain of its aspects, there may be added to the crude petroleum oil before the temperature of the oil decreases to said wax deposition temperature a wax-depositing inhibiting amount of an oil-soluble polymer

$$[\!-\!CH_2CHR\!-\!]_m\,[\!-\!CH_2CHX\!-\!]_n\,[\!-\!CH_2CHY\!-\!]_p]_q \quad (II)$$

wherein X is a non-polar moiety, Y is a polar moiety, R is hydrogen, an alkyl, aryl, aralkyl, or alkaryl moiety, m is 1.5–3, n is 0.1–0.8, p is 0.01–0.5, $m/(m+n+p)$ is 0.65–0.97, $p/(n+p)$ is 0.1–0.85, q is 2 to 500, and the molecular weight $\overline{M}_n$ of said polymer is 500–100,000.

The above polymer may typically be a polymer having a molecular weight $\overline{M}_n$ of 500–100,000, preferably 1,000–10,000, commonly 1,500–4,000, say 2,000, and characterized by a long straight backbone chain on which there may be pendant moieties X and Y.

In the above polymer, the moiety $-\!\!(CH_2CHR)_m$ may be derived from an alpha-olefin including ethylene, propylene, butene-1, styrene, 3-phenyl-1-propene, octene-1, etc. Preferred alpha-olefins may be the C_2–C_{30} alpha olefins and most preferred is ethylene. When the alpha olefin is propylene, the formula $-\!\!(CH_2—CHR)_m$ may be



$$(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H)_m$$

in which R is —CH_3. When the alpha olefin is ethylene, the formula may be $-\!\!(CH_2—CH_2\!-\!)_m$. The carbon atoms may bear inert substituents (i.e. in place of the hydrogen atoms) including alkyl, cycloalkyl, aryl, alkaryl, aralkyl, etc., moieties.

In the above polymer, the moiety $-\!\!(CH_2CHX)_n$ may be derived from an alpha-olefin which bears non-polar moiety X. The non-polar X moiety may be characterized by the fact that it does not contain a hydrogen atom active in the Zerewitinoff test for active hydrogen. Typically, the non-polar moiety will contain atoms of carbon, nitrogen, sulfur, phosphorous, boron, oxygen, etc. Typical nitrogenous non-polar moieties may include —CN, —NCl_2, —NRC(O)R, etc.

Typical sulfur-containing non-polar moieties may include—SO_3R, —SC(O)R, —SR, —SCl, etc. Typical phosphorous-containing non-polar moieties may include —PCl_2, —PCl_4, —PBr_2, etc. A preferred non-polar moiety X may be an oxygen-containing moiety, a hydrocarbon-containing moiety, a carbonyl-containing moiety, preferably —COOR′ or —OOCR″, etc.

In the preferred group of the non-polar moieties, R′ or R″ may be a hydrocarbon moiety, typically alkyl, aryl, alkaryl, or aralkyl. When R′ and R″ are alkyl, they may be methyl, ethyl, propyl, i-propyl, n-butyl, i-butyl, t-butyl, hexyl, cyclohexyl, octyl, etc. When R′ and R″ are aryl, they may be phenyl, naphthyl, etc. When R′ and R″ are alkaryl, they may be tolyl, xylenyl, etc. When R′ and R″ are aralkyl, they may be benzyl, beta-phenyl ethyl, etc. The R′ and R″ groups may be inertly substituted, i.e. they may bear a substituent which does not react with the other components of the process. Typical inert substituents may include nitro, ether, aryl, alkyl, etc. Typical inertly substituted R′ and R″ radicals may include nitrophenyl, 2-ethyl-hexyl, ethoxyethyl, methylcyclohexyl, etc. All the R′ and R″ groups in a particular structure need not be the same; preferably however, they may be the same. More preferably, R′ and R: may be alkyl and more preferably, lower alkyl having one to 10 carbon atoms. R″ may also be a hydrogen atom.

Among the preferred non-polar X moieties may be those selected from the group consisting of

Acetate	$CH_3COO—$
Propylate	$CH_3CH_2COO—$
Butyrate	$C_3H_7COO—$
Benzoate	$C_6H_5COO—$

Monofluoracetate	CH_2FCOO-
Cyclohexyl carboxylate	$C_6H_{11}COO$
Carbomethoxy	$-COOCH_3$
Carboethoxy	$-COOC_2H_5$
Carbopropoxy	$-COOC_3H_7$
etc.	

Typical moieties CH_2—CHX may thus include e.g. vinyl acetate, vinyl propylate, vinyl benzoate, methyl acrylate, ethyl acrylate, methyl methacrylate (in which one of the hydrogens of the formula is replaced by the methyl group), ethyl acrylate, etc.

The polar moiety Y may be a moiety containing carbon, oxygen, sulfur, nitrogen, phosphorous boron or their congeners.

The Y moiety contains a hydrogen atom which is capable of participating in hydrogen bonding.

In a preferred embodiment, the polar moiety, may be a moiety in which a non-carbon heteroatom is bonded directly to hydrogen. Typical of such groups may be —PH_2, —COOH, —NH_2, —NHR, —SH, —$S(O)_2OH$, —$P(O)_2OH$, —$B(OH)_3$, etc.

In a most preferred embodiment, the polar moiety Y may contain oxygen and may be —OH or —COOH.

Typical moieties CH_2—CHY may thus include vinyl alcohol (as a portion of the polymer structure), acrylic acid, methacrylic acid, ethyl amine, ethyl sulfonic acid, etc.

In practice of a preferred embodiment of this invention, the polar moiety Y may be derived from the non-polar group X as by hydrolysis, alcoholysis, hydrogenation, de-esterification, saponification, oxidation, ammonolysis, etc. Preferably the polar moiety Y may be derived from the non-polar moiety X by hydrolysis or alcoholysis, e.g. in the present of aqueous acids, bases, etc.

The polymers which may be used in the practice of this invention may be produced by various processes including cationic, anionic, free radical, and graft polymerization. Typical techniques may include the copolymerization of monomers including those which contain X and Y moieties, to form a polymer according to the following equations wherein, as elsewhere, the H atoms may be replaced by inert group

$$qm(CH_2CHR) + qn(CH_2CHX) + qp(CH_2CHY)$$
$$\downarrow$$
$$\left[-\left(CH_2CHR\right)_m -\left(CH_2CHX\right)_n\left(CH_2CHY\right)_p- \right]_q \qquad (III)$$

A typical example of polymers of this class is:

$$qmCH_2{=}CH_2 + qnCH_2{=}CHCOOR + qpCH_2{=}CHCOOH$$
$$\downarrow$$
$$[(CH_2CH_2)_m(CH_2CHCOOR)_n(CH_2CHCOOH)_p]_q \qquad (IV)$$

Another technique which may be useful in producing polymers for use in this invention may be the polymerization of a monomer containing an X moiety (which is capable of being converted into a Y moiety) with another monomer to form a polymer as follows:

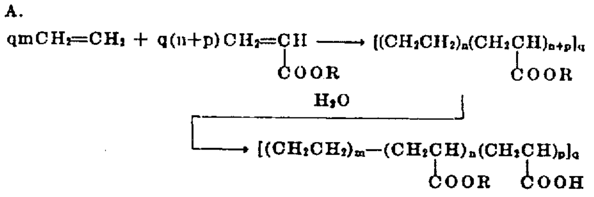
$$qm\,(CH_2CHR) + q(n{+}p)\,(CH_2CHX) \rightarrow [(CH_2CHR)_m(CH_2CHX)_{n+p}]_q \qquad (V)$$

If a polymer of this type is formed, subsequent reaction may convert at least some of the non-polar X moieties into polar Y moieties, e.g.

$$[(CH_2CHR)_m(CH_2CHX)_{n+p}]_q \rightarrow [(CH_2CHR)_m(CH_2CHX)_n(CH_2CHY)_p]_q \qquad (VI)$$

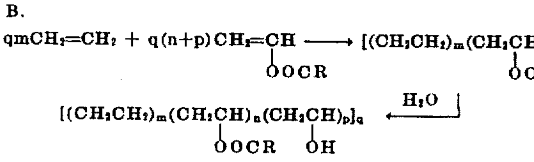
Specific examples of such polymers of this class include

A.



$$qmCH_2{=}CH_2 + q(n{+}p)CH_2{=}\underset{COOR}{CH} \longrightarrow [(CH_2CH_2)_n(CH_2\underset{COOR}{CH})_{n+p}]_q \xrightarrow{H_2O} [(CH_2CH_2)_m-(CH_2\underset{COOR}{CH})_n(CH_2\underset{COOH}{CH})_p]_q$$

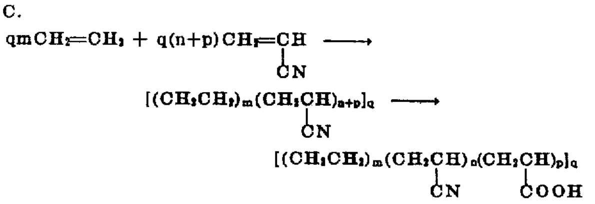
B.



$$qmCH_2{=}CH_2 + q(n{+}p)CH_2{=}\underset{OOCR}{CH} \longrightarrow [(CH_2CH_2)_m(CH_2\underset{OOCR}{CH})_{n+p}]_q \xrightarrow{H_2O} [(CH_2CH_2)_m(CH_2\underset{OOCR}{CH})_n(CH_2\underset{OH}{CH})_p]_q$$

(VII)

C.



$$qmCH_2{=}CH_2 + q(n{+}p)CH_2{=}\underset{CN}{CH} \longrightarrow [(CH_2CH_2)_m(CH_2\underset{CN}{CH})_{n+p}]_q \longrightarrow [(CH_2CH_2)_m(CH_2\underset{CN}{CH})_n(CH_2\underset{COOH}{CH})_p]_q$$

(VIII)

Alternatively, the polar Y moiety may be chosen to that by reaction with an appropriate reagent, it can be converted into a non-polar X moiety according to the following equation:

$$qm(CH_2CHR) + q(n{+}p)\,(CH_2CHY) \rightarrow [(CH_2CHR)_m(CH_2CHY)_{nc+p}]_q \rightarrow [(CH_2CHR)_m(CH_2CHX)_n(CH_2CHY)_{pcz}{}'_q \qquad (IX)$$

A typical example of this class of polymers may be that formed from monomers including $CH_2{=}CH_2$ and $CH_2{=}CHCOOH$; etc.

Still another method of preparing a polymer which may be used in the practice of this invention is through the use of graft polymerization technique wherein the X and Y groups are introduced into the polymer backbone through simultaneous or sequential reactions of the backbone polymer with reagents which contain an X or a Y moiety. This technique may be illustrated by the following equation:

$$[(CH_2CHR)_m(CH_2CH_2)_n(CH_2CH_2)_p]_q \xrightarrow{2x} [(CH_2CHR)_m(CH_2CHX)_n(CH_2CHX)_{pq} \longrightarrow [(CH_2CHR)_m(CH_2CHX)_n(CH_2CHY)_{pq} \qquad (X)$$

In the grafting, an X moiety may be chosen so as to be capable of being converted into a Y moiety through subsequent reactions. Conversely a Y moiety convertible to an X moiety may be chosen.

In the formula

$$[(CH_2CHR)_m(CH_2CHX)_n(CH_2CHY)_{pq} \qquad (XI)$$

m may be 1.5–3, preferably 1.5–2.5, say 2.

n may be 0.1–0.8, preferably 0.2–0.5, say 0.2.

p may be 0.01–0.5, preferably 0.02–0.4, say 0.2.

q may be 2–500, preferably 5–100, typically 10–50, say 50.

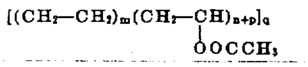
$m/m{+}n{+}p)$ is 0.65–0.97, say 0.80.

$p/n{+}p$ is 0.1–0.85, say 0.50 and

$\overline{M}_n$ is 500–100,000, preferably 1,00–10,000, typically 1,500–4,000 say 2,000

A preferred polymer useful in practice of the process of this invention may be that derived by free radical copolymerization of ethylene and vinyl acetate at 105°

C. and 60 atmospheres in the presence of lauroyl peroxide in inert diluent cyclohexane to yield a copolymer of molecular weight $\overline{M}_n$ 2,000 having the following formula:



$$[(CH_2-CH_2)_m(CH_2-\underset{\underset{OOCCH_3}{|}}{CH})_{n+p}]_q \qquad \text{(XII)}$$

wherein *m* is 2, and *n*+*p* is 0.4, and *q* is 25.

In a preferred embodiment of the process of this invention, the conversion of a first polymer containing non-polar X moieties into a second polymer bearing non-polar X and polar Y moieties may be accomplished by reacting the first polymer with a conversion agent preferably in a reaction medium in the presence of a reaction adjuvant.

The reaction medium within which the X-bearing polymer may be converted to the Y-bearing polymer may include a liquid in which the reactants and/or the products may be at least partially soluble or miscible. Preferably it may be a liquid in which both are substantially to completely soluble under the conditions of reaction. The preferred reaction medium may include oxygenated or semi-polar liquids having a boiling point of 50° to 250° C., preferably 50° to 150° C., say 82° C. Typically the reaction medium may include alcohols, preferably lower (e.g. C_{1-4}), aliphatic alcohols such as methanol, propanol, isopropanol, ethanol, etc., glycols such as ethylene glycol, propylene glycol, etc., ketones such as acetone, methyl ethyl ketone, methyl butyl ketone, etc. preferably lower (e.g. C_{1-5} total) aliphatic ketones, ethers such as dibutyl ether, etc. and particularly cyclic ethers such as tetrahydrofuran, dioxane, etc. A preferred reaction medium may be an aqueous medium, optionally containing at least one of the other components noted supra. A preferred reaction medium may include water. Another preferred reaction may include isopropanol.

The preferred reaction medium may be one in which the first polymer and the conversion agent may be at least partially soluble under the conditions of reaction. Preferably, the reaction medium may be present in amounts of 150–15,000 parts, typically 500–1,000 parts, say 770 parts.

In practice of the preferred aspects of this invention, the reaction medium may contain a reaction adjuvant. The reaction adjuvant will preferably be a liquid which is inert in that it exerts no undesirable effect on the reaction. Preferably the adjuvant will be a composition which assists in the reaction typically by raising the solubility of the polymer or product or conversion agent in the reaction medium. In the preferred embodiment the adjuvant will be miscible with the reaction medium and the reflux temperature of the mixture at which the reaction is preferably carried out may thus be intermediate the boiling point of the reaction medium and that of the adjuvant.

In the most preferred embodiment, the reaction adjuvant may be a liquid in which the product of the reaction may be usable, i.e. preferably the product may be handled and marketed as a combination of product and adjuvant. Typical adjuvants may include aromatic solvents such as toluene or xylene, a refinery stream such as a gas oil, a heavy aromatic naphtha, crude oil, etc. The preferred adjuvant is one in which the charge polymer is soluble.

The conversion agent which may be employed in practice of the process of this invention may be an agent which may effect conversion of the X moiety to the Y moiety under the conditions of reaction. Typically the conversion agent may be a hydrolyzing agent, an alcoholyzing agent, a hydrogenating agent, a de-esterifying agent, a saponifying agent, an oxidation agent, a peroxidizing agent, etc.

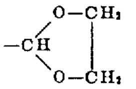
When the conversion agent is an alcoholizing agent, it may typically be sodium methoxide, sodium ethoxide, potassium isopropoxide, etc. When the conversion agent is a hydrogenating agent, it may typically be hydrogen in the presence of Raney nickel, etc. When the conversion agent is a de-esterifying agent, it may typically be water, etc. When the conversion agent is a saponifying agent, it may typically be aqueous sodium or potassium hydroxide, etc.

It will be apparent that hydrolysis may be employed to convert the —COOR group to the —COOH group or the —OOCR group to the —OH group, that alcoholysis may be employed to convert the —OOCR group to the —OH group, that de-esterification may be employed to convert the —COOR group to the —COOH group, that saponification may be employed to convert the —OOCR group to the —OH group, that oxidation may be employed to convert the $—C_2H_5$ to the —COOH group, etc.

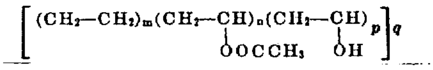
In a typical example the X moiety may be a C_{1-4} carboxylic acid ester moiety such as acetate, formate, butyrate, etc. The conversion agent may be an alkali metal hydroxide or alcoholate such as sodium hydroxide or potassium methoxide, the reaction medium may be a C_{1-4} alcohol such as methanol or isopropanol, and the adjuvant may be an aromatic hydrocarbon solvent such as xylene or heavy aromatic naphtha.

Illustrative examples of non-polar X moieties which may be converted to polar Y moieties by hydrolysis, alcoholysis, hydrogenation, etc. may be as set forth in the following Table.

TABLE

X	Y
—Cl	—OH
—COOR	—COOH
—OOCR	—OH
$-\overset{\underset{\|}{O}}{\underset{\overset{\|}{O}}{S}}OR$	$-\overset{\underset{\|}{O}}{\underset{\overset{\|}{O}}{S}}-OH$
$-O-\overset{\underset{\|}{O}}{\underset{\overset{\|}{O}}{S}}-R$	—OH
$-PCl_2$	$-\overset{\underset{\|}{O}}{\underset{\overset{\|}{O}}{P}}-OH$
—CN	—COOH
—CN	$—CONH_2$
—CN	$—CH_2NH_2$
$-\underset{\underset{O}{\|}}{C}NR_2$	—COOH
	—CHO

In practice of a preferred embodiment, the copolymer may be hydrolyzed in aqueous medium containing sodium hydroxide, isopropyl alcohol (reaction medium) and heavy aromatic naphtha (adjuvant) at 85°–88 C. for 120—240 minutes to yield



$$\left[(CH_2—CH_2)_m(\underset{OOCCH_3}{CH_2—CH})_n(\underset{OH}{CH_2—CH})_p\right]_q$$

wherein m is 2, n is 0.2, p is 0.2, and q is 25.

In practice of the process of this invention, according to certain of its aspects, there may be added to a reaction vessel the following components (all parts, as elsewhere in this specification being parts by weight):

TABLE

Component	Typical	Preferred
Polymer	500—1000	730
Reaction Medium	150—15,000	770
Adjuvant	0—15,000	810
Conversion Agent	5—500	70

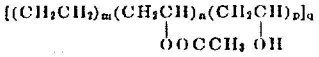
The reaction mixture so formed, preferably a homogeneous mixture, may be maintained at 20°-250° C., preferably 100°-150° C. at 0.2-5 atmospheres, say 1 atmosphere for 1-10 hours, say 6 hours. During this period the reaction may preferably be maintained at reflux temperature at which the reaction may proceed. At the end of the reaction period, the product may be recovered. Typically the reaction medium may be stripped off as by distillation or by the use of e.g. a stream of gas such as nitrogen. The conversion agent may be extracted as by water washing, or filtered. In a preferred embodiment, the product polymer may be recovered in high yield in solution or suspension in the adjuvant.

It is a feature of this invention that additional quantities of adjuvant may be added to the product recovered.

It is a feature of this invention when the reaction is carried out in the presence of the adjuvant that the product mixture obtained, containing product polymer and adjuvant, may be characterized by an unexpectedly low pour point. Typically the preferred concentrates containing product polymer and adjuvant may be found to have a pour point of −30° to −15° C. say −21° to −18° C. as determined by ASTM D-97-57. It is an unexpected characteristic of these compositions that they have such an outstandingly low pour point; this facilitates handling and use, particularly under ambient conditions in cold areas.

Typically the preferred products may contain 100 parts of polymer together with 0–10,000, preferably 0–5,000, say 1,000 parts of adjuvant.

A preferred composition, for example, having a pour point of 0° F. may contain 800 parts of heavy aromatic naphtha, 2,200 parts of aromatic solvent having an initial boiling point of 400° C., 3,000 parts of xylene, and 680 parts a polymer formed from an ethylene-vinyl acetate copolymer by partial hydrolysis with sodium hydroxide to yield a product characterized by the following formula:

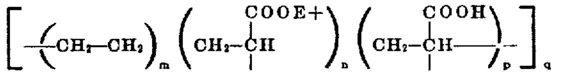


$$[(CH_2CH_2)_m(\underset{OOCCH_3}{CH_2CH})_n(\underset{OH}{CH_2CH})_p]_q \qquad (XIIa)$$

Where m is 2, n is 0.2, p is 0.2, $m/(m+n+p)$ is 0.83, $p/n+p$ is 0.5, q is 22 and $\overline{M}_n$ is 2,000.

Typical further formulations may include:

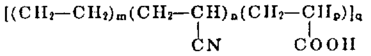
A. A composition containing 500 parts of kerosene and 200 parts of a polymer formed by reaction of a polymer of ethylene-ethyl acrylate, $\overline{M}_n$ of 1,500 with sodium methoxide (alcoholyzing agent), the product polymer typically being



$$\left[\left(CH_2—CH_2\right)_m\left(CH_2—\overset{COOEt}{\underset{|}{CH}}\right)_n\left(CH_2—\overset{COOH}{\underset{|}{CH}}\right)_p\right]_q \qquad (XIII)$$

wherein m is 2.5, n is 0.4, p is 0.3, and q is 10.

B. A composition containing 400 parts of a heavy gas oil and 500 parts of a polymer formed by reaction of a polymer of ethylene-acrylonitrile, $\overline{M}_n$ is of 2,500 with aqueous caustic soda, the product polymer typically being



$$[(CH_2—CH_2)_m(\underset{CN}{CH_2—CH})_n(\underset{COOH}{CH_2—CH})_p]_q \qquad (XIV)$$

wherein m is 1.5, n is 0.1, p is 0.1, and q is 50.

Practice of this invention may include addition of the oil-soluble polymer in wax-deposit-inhibiting amount, preferably in the form of a concentrate, to a crude petroleum oil at a point at which the crude petroleum oil is above its wax deposition temperature.

The wax deposit inhibiting amount may be 5–500 parts, preferably 10–50 parts, say 20 parts per 1,000,000 parts of crude petroleum oil.

Addition of the polymer to the crude petroleum oil may be affected by injecting the polymer, preferably as a concentrate or solution, directly into a body of crude petroleum oil typically in subsurface reservoir or by injecting the polymer into the crude petroleum oil within the well casing or at a point immediately adjacent to the lower end of the wall or tubing.

Other addition techniques may be employed including injection into the gas stream which is fed to the bottom of gas lift wells.

Performance of wax deposit inhibiting formulations of this invention may be determined by wax deposition test which includes mixing 0.03% active ingredient in 100 parts of crude petroleum oil. The mixture may then be placed within a test cell containing a preweighed, removable standard water chilled deposition steel plate, a stirrer thermometer, and an electrical heater. The test cell is placed in an insulated bath together with an identical reference cell containing the untreated base crude oil. The temperature of the oils in both cells is maintained at 2° to 5.5° C. above the known cloud point temperature of the oil (as determined by ASTM D-97-57). The test may be continued for 3–24 hours and then each deposition plate is removed, weighed, and the amount of wax deposited thereon calculated. The results are expressed in terms of inhibitor efficiency (I.E.) which is calculated according to the following expression:

$$\text{I.E.}=\frac{\text{Wt. of deposit from untreated oil}-\text{wt. of deposit from treated oil}}{\text{Wt. of deposit from untreated oil}}$$

When there is complete inhibition of wax deposition, the wt. of deposit from treated oil is zero and the I.E. of the inhibitor is 1.0. When there is no inhibition of wax deposition, the weight of deposit from the treated oil equals that from the untreated oil and the numerator in the above expression become zero and the I.E. of the inhibitor is also zero.

Alternatively the results may be expressed in grams (gm.) of wax deposited on the plate.

The addition of the oil-soluble polymer to the crude petroleum oil may modify the properties of the oil and/or of the waxy components; and it may be found that deposits of waxy components on the surface with which the oil comes into contact may be minimized or eliminated. A typical well may thus be able to operate at full capacity for indefinitely long periods of time without the need for shutdown for cleaning.

The crude petroleum oil may be collected at full rate of flow at the collection point - typically the well-head. It may be found that the properties of the oil are substantially improved, i.e. in addition to being obtained at full flow rates, it may be found that the oil has been improved with respect to pour point, flow properties, etc., as well as bacteriocidal properties and solids carrying capacity. Sand, silt and inorganic solids will be carried with the suspended wax rather than adhering to pipe walls with the wax.

Practice of this invention may be apparent to those skilled in the art from inspection of the following examples wherein, as elsewhere in this specification unless specifically indicated otherwise, all parts are parts by weight.

DESCRIPTION OF PREFERRED EMBODIMENT

EXAMPLE I

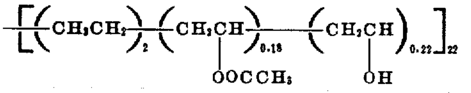
In this example which illustrates practice of the invention, the oil-soluble polymer may be prepared by reacting ethylene with vinyl acetate. Reaction may be carried out by adding 100 parts of vinyl acetate and 25 parts of lauroyl peroxide catalyst to 250 parts of cyclohexane solvent in a reaction vessel. The vessel may be pressurized to 60 atmospheres at 105° C. by ethylene; and this pressure maintained over 2 hours until no more ethylene is absorbed, i.e. reacted.

The product polymer may be worked up by distilling off the reaction solvent and excess vinyl acetate.

The polymer so obtained in amount of 130 parts (49% yield based upon vinyl acetate) may have an average molecular weight $\overline{M}_n$ of 2,000, a vinyl acetate content of 38 wt.%, an ethylene content of 62 wt. %, and a kinematic viscosity at 43° C. of 100 centistokes when dissolved in 120 parts kerosene per 100 parts polymer.

This charge polymer may be partially hydrolyzed by addition of 730 parts thereof to 810 parts of adjuvant heavy aromatic naphtha, 770 parts of solvent isopropyl alcohol reaction medium, and 70 parts of sodium hydroxide conversion agent. The reaction mixture may be maintained for 6 hours under reflux at 90°-100° C. Alcohol may then be stripped by passing nitrogen through the reaction medium. 2,160 parts aromatic solvent (IBP 400° C.), 2,970 parts of xylene, and 150 parts of filter aid may be added and the mixture filtered.

Analysis of the filtrate may indicate that it may contain 10 wt. % of polymer in which 55% of the ester moieties in the initial polymer have been converted to hydroxyl moieties. The polymer may have a molecular weight $\overline{M}_n$ of 2,000 and corresponding to the following formula:



$$-\!\!\left[\left(CH_2CH_2\right)_2\left(\underset{\substack{|\\OOCCH_3}}{CH_2CH}\right)_{0.18}\left(\underset{\substack{|\\OH}}{CH_2CH}\right)_{0.22}\right]_{22}\qquad XV$$

The pour point of this filtrate may be −18° C. When this composition is tested in the standard wax deposition inhibitor test supra using a Grand Isle T-1 crude, it may be found that the inhibitor efficiency of the system is 0.56, i.e. the amount of wax deposited from the treated experimental may desirably be only 56% as great as that deposited from the untreated control. This example clearly demonstrates the wax deposit inhibiting effect of the polymer of this invention.

EXAMPLES II-V

In Examples II—V the charge ethylene-vinyl acetate polymer of Example I was used as a charge polymer. Reaction mixtures containing 50 parts of this charge polymer were made up in 50 parts of isopropyl alcohol together with varying amounts of sodium hydroxide which were calculated to give varying percentages of acetate moieties hydrolyzed as indicated in the following Table by the expression $p/(n+p)$. The hydrolyzed polymers were tested at 0.03 parts per 100 parts oil as before in the Grand Isle T-1 crude heretofore described in the standard wax deposition inhibitor test. Results are summarized in the Table.

TABLE

Example	Length of Test (Hrs)	$\frac{p}{n+p}$*	Wax Deposited (gm) Untreated Oil	Wax Deposited (gm) Treated Oil	I.E.
II	18	.50	—	0.45	—
III	18	.75	—	0.50	—
IV	4	.50	0.62	0.23	0.63
V	4	.75	0.62	0.25	0.60

*i.e., fraction of acetate moieties hydrolyzed)

These results show, particularly in Examples IV and V that practice of this invention reduces to 60% the amount of wax deposited by a crude oil.

EXAMPLE VI

The polymers made in Examples II-V were blended at 0.03 parts per 100 parts in the Eugene Island 126 crude heretofore described. The blends were then tested for five hours in the standard wax deposition inhibition test described above and their pour points determined according to ASTM D-97-57. The results are summarized in the following Table:

Example	p/n+p	Wax Deposited (gm) Untreated Oil	Treated Oil	ASTM* Pour Pt., °C.
VI	0.25	—	0.78	−26
VII	0.50	—	0.40	−32
VIII	0.75	—	0.37	−29
IX	1.0	—	0.35	−26
X	0.50	0.74	0.39	—
XI	0.75	—	0.39	—

*Untreated oil pour point −12° C.

These results show that wax deposit inhibitors useful in Grand Isle T-1 crude oil are also useful in a different crude, Eugene Island 126. It can also be seen that while partially hydrolyzed ethylene-vinyl acetate copolymers are effective as pour point depressants regardless of the percentage of hydrolyzed acetate moieties, they need not all be equally effective as wax deposit inhibitors. Thus the inhibitor of Example VI is effective as a pour point depressant but ineffective as a wax deposit inhibitor.

EXAMPLES XII–XIX

The wax deposit inhibitors prepared in Examples II–V were blended at a ratio of 0.03 parts per 100 parts oil in Examples XII–XV with a Powell 15 crude heretofore described and in Examples XVI–XIX with a Yarbrough-Allen 69 crude having a cloud point of 24° C., pour point −15° C., and obtained from a flowing well of Monahans District of Texas.

These blends were tested in the standard wax deposit inhibition test described supra for 16 hours. The results are summarized in the following Table:

Example	p/n+p	Crude Oil Base	Gm. Deposit from Tested Oil	Pour Point*, °C
XII	0.25	Powell 15	1.13	−43
XIII	0.50	"	0.89	>−45
XIV	0.75	"	0.88	−45
XV	1.00	"	1.15	>−45
XVI	0.25	Yarbrough -Allen 69	0.75	>−45
XVII	0.50	"	0.35	−43
XVIII	0.75	"	0.27	>−45
XIX	1.00	"	0.45	>−26

*The Powell 15 untreated oil had a pour point of −7°C.; the Yarbrough-Allen 69 untreated oil had a pour point of −15°C.

From these results it is clear that wax deposit inhibitors containing between 25–75 percent hydrolyzed acetate moieties (e.g. Examples XIII, XIV, and XVII, XVIII) are preferred in inhibiting wax deposition over inhibitors containing lesser or greater percents of hydrolyzed acetate moieties, i.e. $p/(n+p)$ ratios of less than 0.25 or more than 0.75 (e.g. Examples XII, XV and Examples XVI, XIX). From a comparison of the pour points of all these oil blends, it is apparent that there is no correlation between wax deposit inhibitor efficiency and pour point depressant efficiency.

Thus while there is a 20% decrease in the amount wax deposited when the polymers of Examples XIII and XIV are used, as compared to those of Examples XII and XV, there is no change in the pour point. Similarly, while the compositions of Examples XVII and XVIII exhibit a 50% decrease in wax deposition as compared to that of Example XVI there is no change in the pour points of these blends.

EXAMPLE XX

In Example XX the unhydrolyzed polymer prepared in Example I was blended in the ratio of 0.03 parts per 100 parts oil with Grand Isle T-1 crude. This blend was tested in the standard wax deposit inhibition test described above for three hours. The untreated oil was tested at the same time in the reference cell of the apparatus. Both the treated and untreated oil deposited essentially the same amount of wax, 0.39 and 0.37 gm., respectively, demonstrating that the unhydrolyzed polymer, a known pour point depressant, is totally ineffective as a wax deposit inhibitor.

Although this invention has been illustrated by reference to the above specific embodiments, it will be obvious to those skilled in the art that various changes and modifications may be made which clearly fall within its scope. The extent of the invention is intended to be limited only by the appended claims.

It will be apparent to those skilled in the art that the polymer formulas are schematic and average, and in particular, that the subscripts *m*, *n*, *p*, and *q* represent average values.

What is claimed is:

1. The method of recovering a crude petroleum oil containing waxy components, from a reservoir wherein the oil is at a temperature above its wax deposition temperature which comprises:
   a. passing a portion of said crude petroleum oil from said reservoir to a first central collection point;
   b. passing said oil from said first central collection point to a second collection point at a temperature below the wax deposition temperature of said oil whereby the temperature of said oil decreases and passes through a wax-deposition temperature at which the waxy components begin to precipitate and to deposit on surfaces with which said oil comes in contact as it passes to said second collection point;
   c. collecting said crude petroleum oil at said second collection point; and
   d. adding to said crude petroleum oil before the temperature of said oil decreases to said wax-deposition temperature a wax-deposit-inhibiting amount of a polymer

$$+\!+\mathrm{CH_2CHR}+_m +\mathrm{CH_2CHX}+_n +\mathrm{CH_2CHY}+_p+_q$$

wherein X is a non-polar moiety, Y is a polar moiety, R is H, alkyl, aryl, aralkyl, or alkaryl moiety, m is 1.5–3, n is 0.1–0.8, p is 0.01–0.5, $m/(m+n+p)$ is 0.65–0.97, $p/(n+p)$ is 0.1–0.85, q is 2 to 500, and the molecular weight $\overline{M}_n$ of said polymer is 500–100,000.

2. The method claimed in claim 1 wherein said Y moiety is a hydrolyzed X moiety.

3. The method claimed in claim 2 wherein R is hydrogen, X is —CN and Y is —COOH.

4. The method claimed in claim 1 wherein X is a carboxylic acid ester moiety of a C_{1-8} acid, Y is a hydroxyl moiety, and R is a hydrogen atom.

5. The method claimed in claim 1 wherein said polymer is added as a mixture with inert diluent-solvent.

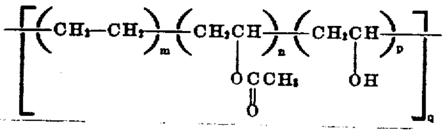
6. The method claimed in claim 5 wherein said inert diluent-solvent is selected from the group consisting of xylene, heavy aromatic naphtha, gas oil, and processing oil and is present in 5 to 50 parts by weight per part by weight of polymer.

7. The method of recovering crude petroleum oil containing waxy components which comprises adding down an oil well, a wax deposit inhibiting amount of a polymer

$$-\!\!\left[-\!\left(CH_2CHR\right)\!-_m -\!\left(CH_2CHX\right)\!-_n -\!\left(Ch_2CHY\right)\!-_p\right]\!-_q$$

wherein X is a non-polar moiety, Y is a polar moiety, R is H, alkyl, aryl, aralkyl, or alkaryl moiety, *m* is 1.5–3, *n* is 0.1–0.8, *p* is 0.01–0.5, $m/(m+n+p)$ is 0.65–0.97, $p/(n+p)$ is 0.1–0.85, *q* is 2 to 500, and the molecular weight $\overline{M}_n$ of said polymer is 500–100,000.

8. The method claimed in claim 7 wherein the polymer is



$$-\!\!\left[\left(CH_2-CH_2\right)_m\left(\begin{array}{c}CH_2CH\\ |\\ OCCH_3\\ \|\\ O\end{array}\right)_n\left(\begin{array}{c}CH_2CH\\ |\\ OH\end{array}\right)_p\right]\!-_q$$

and *m* is 1.5–2.5, *n* is 0.2–0.5, *p* is 0.02–0.4, *q* is 10–50, and the molecular weight $\overline{M}_n$ is 1,500–4,000.

* * * * *