United States Patent

Fischer

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[54] **METHOD FOR INHIBITING THE DEPOSITION OF WAX FROM A WAX-CONTAINING OIL**

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[52] **U.S. Cl.** ....**166/279,** 166/304, 252/8.3, 252/8.55 B, 134/40

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[58] **Field of Search**.................166/304, 279, 310, 303, 305; 252/8.55 B, 8.3, 56 R; 134/40; 137/15; 260/28.5 AV

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[57] **ABSTRACT**

A method for inhibiting the deposition of wax from wax-containing petroleum and other wax-containing oils in which a small amount of a wax deposition inhibitor comprised of a copolymer of ethylene and a monoethylenically unsaturated ester is added to the petroleum.

18 Claims, No Drawings

METHOD FOR INHIBITING THE DEPOSITION OF WAX FROM A WAX-CONTAINING OIL

This invention relates to the control of wax deposition from wax-containing oil, and more particularly to a method for inhibiting the formation of wax deposits in wells, tanks, pipelines, and other equipment used for handling crude petroleum and other wax-containing oils.

It is well known that when a crude petroleum or petroleum fraction containing paraffin wax is cooled below the solidification temperature of the wax, the wax solidifies and tends to deposit on the walls and other surfaces of equipment contacted by the cooled petroleum. The deposition and accumulation of wax-like substances on the walls and other surfaces of equipment contacted by wax-containing petroleum is a major problem in the production, transfer, storage and processing of crude petroleum and petroleum fractions containing significant amounts of wax, since the wax deposits often restrict or completely stop flow through this equipment, requiring costly cleaning to maintain the equipment in operation. More specifically, it is well known that wax-like substances deposit and accumulate on the surfaces of conduits and flow passages of wells operated for the production of wax-containing crude oils and that this wax deposition causes plugging that progressively decreases the rate of production from the well. Also, the wax-like substances deposit in pipelines, vessels and storage tanks handling wax-containing crude oil which results in a serious problem of plugging and clogging this equipment. Furthermore, deposition and accumulation of wax can cause plugging in heat exchangers and malfunctioning of valves in pumps and other apparatus employed in the treating and transportation of wax-containing crude oil and in the refining of such crude oil. The deposition and resulting accumulation of wax in well conduits and transportation, storage and treating equipment reduces the efficiency and capacity of the equipment, often necessitating frequent cleaning to maintain the equipment operational.

Various techniques for inhibiting the deposition of wax from wax-containing oils and for retarding its accumulation in wells and surface equipment have been proposed. Heretofore, the use of chemical additives to inhibit the deposition of wax from wax-containing oils has been largely unsuccessful. Mechanical devices such as scrapers and the like have been employed to maintain the interior surfaces of vessels and well conduits free of wax accumulations, but these devices are both costly and complex, and in many applications are only partially effective in preventing the accumulation of wax. Thus, need exists for a low cost, practical method for inhibiting the deposition and accumulation of wax from wax-containing petroleum and other wax-containing oils. In particular, a method for inhibiting wax deposition is desired that can be practical during normal operation and does not require the shutdown or interruption of these operations.

Accordingly, a primary object of this invention is to provide a method for inhibiting the deposition of wax from wax-containing petroleum and other wax-containing oils.

Another object of the invention is to provide a method for ameliorating the deposition of wax in wells, tanks, pipelines and other equipment handling wax-containing petroleum and liquid petroleum fractions.

Still another object of the invention is to provide a satisfactory technique for producing, storing, and transporting wax-containing crude oils.

A further object of the invention is to provide a method for inhibiting the agglomeration of solid wax particles in a wax-containing crude petroleum.

A still further object of the invention is to provide a method for inhibiting the agglomeration of solid wax crystals in a wax-containing oil.

A yet further object of the invention is to provide a method for removing accumulated wax deposits from equipment handling wax-containing oils.

Other objects and advantages of the invention will be apparent from the following description.

Briefly, this invention contemplates inhibiting the deposition of wax from wax-containing petroleum and other wax-containing oils by incorporating in the wax-containing oil a small amount of an oil-soluble or oil-dispersible copolymer of ethylene and a monoethylenically unsaturated ester. The wax deposition inhibitor may be admixed into the wax-containing oil directly, or as a solution of the inhibitor dissolved in an organic solvent. Low concentrations of the agent inhibits the deposition of wax and wax-like substances from wax-containing crude petroleum and other wax-containing oils and reduces the tendency of these substances to accumulate in wells, tanks, vessels, pipelines and other equipment contacted by the wax-containing oil.

When crude petroleum or a petroleum fraction containing dissolved wax is cooled below the solidification temperature of the wax, solid wax precipitates are formed. These precipitates are mostly straight-chain paraffin hydrocarbons having emperical structures ranging from $C_{18}H_{38}$ to $C_{38}H_{78}$. While the solid precipitates can be either crystalline or amorphorous, it is generally believed that in most cases paraffins precipitate from crude oil as spiney crystals having arms radiating out from a central nucleus. These crystals agglomerate or bunch together because of their spiney structures, and oil can be occluded within this structure. It is known that wax tends to deposit more readily on rough surfaces than on a more smooth surface. Attachment to the rough metal surfaces on the interior of well conduits, pipelines, tanks, vessels and the like probably occurs through a somewhat similar process. Usually, once deposition starts, agglomeration continues until the conduit is completely plugged.

While the exact mechanism by which the wax deposition inhibitors of this invention inhibit the deposition of wax is not completely understood, it is believed that they function by reducing agglomeration of the wax crystals so that they are more readily kept in suspension and exhibit less tendency to adhere to solid surfaces. Also, these inhibitors may affect the deposition or attachment of the wax crystals to the metal surfaces which they contact. Thus, while it is believed that these inhibitors do not greatly affect the size and general appearance of individual wax crystals, they do affect the tendency of the crystals to agglomerate and to adhere to metal surfaces. However, although the exact mechanism by which the inhibitors of this invention inhibit wax deposition from a wax-containing oil may not be completely understood, it has nevertheless been conclusively demonstrated that low concentrations of these agents are effective in inhibiting the deposition of wax in well conduits, pipelines, tanks and like equipment handling wax-containing oil at a temperature below the solidification temperature of the wax. The term wax "deposition" is used herein to mean the precipitation and accumulation of wax and wax-like materials on the surfaces contacted by a wax-containing oil, and not merely the precipitation of wax crystals or particles that remain dispersed in the oil.

Also, it has been observed that the wax deposition inhibitors of this invention not only inhibit the deposition of wax and wax-like materials on metal surfaces which they contact, but also will in at least some cases disperse previously accumulated deposits of wax. Accordingly, the wax deposition inhibitors of this invention have utility both in inhibiting the deposition and accumulation of wax on surfaces contacted by a wax-containing oil and in removing previously deposited wax from such surfaces.

The wax deposition inhibitors useful in the practice of this invention are substantially linear addition copolymers of ethylene and a monoethylenically unsaturated esters such as the vinyl and allyl esters of saturated aliphatic carboxylic acids and the saturated aliphatic esters of monoethylenically unsaturated aliphatic carboxylic acids. The monoethylenically unsaturated esters that can be copolymerized with ethylene to produce the desired copolymers are characterized by the formula:

$$R-C(=O)-O-R_1$$

wherein (1) R is hydrogen or an alkyl group containing from about one to 25 carbon atoms and R_1 is a vinyl or allyl group, and preferably a vinyl group; or (2) R is an α,β-unsaturated alkylene and R_1 is an alkyl group containing from about one to 25 carbon atoms.

Exemplary monoethylenically unsaturated esters that are copolymerizable with ethylene to form the copolymers useful as wax deposition inhibitors are the vinyl and allyl esters of formic, acetic, propionic, butyric, lauryic, palmitic and stearic acids; and the saturated aliphatic esters of acrylic acid and α-alkyl substituted acrylic acids such as methacrylic acid and the like. Also, ethylene can be copolymerized with a mixture of two or more of these esters to yield an ethylene/mixed ester copolymer.

Among the agents useful for inhibiting the deposition of wax from petroleum are copolymer ethylene/vinyl formate, copolymer ethylene/allyl formate, copolymer ethylene/vinyl acetate, copolymer ethylene/allyl acetate, copolymer ethylene/vinyl propionate, copolymer ethylene/allyl propionate, copolymer ethylene/vinyl butyrate, copolymer ethylene/allyl butyrate, copolymer ethylene/vinyl laurate, copolymer ethylene/allyl laurate, copolymer ethylene/vinyl palmate, copolymer ethylene/allyl palmate, copolymer ethylene/vinyl stearate, copolymer ethylene/allyl stearate, copolymer ethylene/methyl acrylate, copolymer ethylene/ethyl acrylate, copolymer ethylene/butyl acrylate, copolymer ethylene/isobutyl acrylate, copolymer ethylene/2-ethylhexyl acrylate, copolymer ethylene/methyl methacrylate, copolymer ethylene/ethyl methacrylate, copolymer ethylene/butyl methacrylate, copolymer ethylene/isobutyl methacrylate, copolymer ethylene/isodecyl methacrylate, copolymer ethylene/lauryl methacrylate, copolymer ethylene/tridecyl methacrylate, and copolymer ethylene/stearyl methacrylate.

The ethylene copolymerized with the ester tends to increase the oil solubility of the resulting copolymer. Thus, it is preferred that the copolymer contain a sufficiently high ethylene content to render it oil soluble or oil dispersible at the concentration employed. However, it has been found that increased ethylene content tends to reduce the effectiveness of the copolymer as a wax deposition inhibitor. Accordingly, it is within the scope of this invention to employ as a wax deposition inhibitor an ester polymer containing sufficient copolymerized ethylene to render the copolymer soluble or dispersible in oil.

Generally, it is preferred that the copolymer contain at least about 10 weight percent ester, and more preferably at least about 35 weight percent ester with the maximum ester content of the polymer not exceeding that amount which renders the agent insoluble or difficult to disperse in oil under the conditions of use. Also, it is generally preferred that the copolymer exhibit a melt index between about 1 and 600 grams per 10 minutes. The term "melt index" as employed herein is the flow rate reported as the rate of extrusion in grams per 10 minutes as determined by ASTM test method D1238–65T entitled "Measuring Flow Rates of Thermoplastics by Extrusion Plastometer" and performed under Standard Test Condition E, ASTM Standards, American Society for Testing Materials, Part 27, June 1969, pages 455–466, which procedure is herein incorporated by reference.

Of the foregoing ethylene/ester copolymers useful in the practice of the invention, the lower vinyl esters and the lower alkyl acrylates and methacrylates are preferred in many applications.

Preferred copolymer combinations having a special utility as wax deposition inhibitors include copolymers of ethylene and vinyl acetate, ethyl acrylate and methyl methacrylate, i.e., copolymer ethylene/vinyl acetate, copolymer ethylene/ethyl acrylate and copolymer ethylene/methyl methacrylate.

One preferred class of agents particularly useful for inhibiting the deposition of wax from petroleum are ethylene/vinyl acetate copolymers containing from about 10 to 70 weight percent vinyl acetate, and more preferably containing about 35 to 55 weight percent vinyl acetate, and exhibiting a melt index between about 1 and 600 grams per 10 minutes.

A particularly preferred agent having a special utility as a wax deposition inhibitor for petroleum is an ethylene/vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index between about 45 to 70 grams per 10 minutes. An ethylene/vinyl acetate copolymer of this type especially useful as a wax deposition inhibitor is marketed by the E. I. duPont de Nemours Company under the trademark ELVAX 40.

The ethylene/ester copolymers useful as wax inhibitors are prepared by generally known techniques such as by copolymerizing ethylene and the ester monomer by free radical reaction at elevated temperatures and pressures. Any of a wide variety of free radical initiators such as small quantities of molecular oxygen or other known sources of free radicals including various peroxide compounds such as benzoyl peroxide, t-butyl hydroperoxide and the like can be employed to initiate the free radical reaction. Also, the catalyst can be activated by the addition of a reducing agent such as sodium bisulfite or ferrous salts.

In practicing the method of this invention, an effective amount of the aforementioned wax deposition inhibitor is incorporated into a wax-containing crude petroleum or petroleum fraction by any convenient mixing technique. It is to be recognized that the amount of wax deposition inhibitor required depends upon the properties of the particular crude petroleum or petroleum fraction, the amount and type of wax present in the oil, the temperature to which the oil is cooled, the particular type and physical arrangement of the equipment and the roughness of the interior surfaces contacted by the oil, the specific inhibitor employed, and the degree to which it is desired to inhibit wax deposition. Thus, the optimum amount of wax deposition inhibitor required in any particular application will depend upon these factors, the cost of the inhibitor, and the cost of cleaning and downtime due to wax plugging. Treatment at concentrations in excess of optimum is not only costly, but in some cases is less effective than the optimum concentration. The optimum treatment is best determined by actual field tests or by laboratory tests simulating field conditions.

Hence, broadly stated, this invention contemplates incorporating into a wax-containing crude petroleum, petroleum fraction, or other wax-containing oil an amount of the above-described ethylene/ester copolymer effective to inhibit the deposition of wax from the oil. While the exact amount of agent preferred in any particular application depends on the foregoing factors, nevertheless it has been found that the effective concentration of additive is between about 5 and 10,000 ppm based on the weight of oil, and in many applications the effective concentration is between about 5 and 200 ppm, and preferably less than about 60 ppm. Thus, it is within the scope of this invention to incorporate in a wax-containing oil an effective amount of the inhibitor between about 5 and 10,000 ppm, and preferably between about 5 and 200 ppm.

Although the wax deposition inhibitor can be added to the wax-containing oil directly, it is preferred that the additive be first dissolved or dispersed in an organic solvent such as naphtha, kerosene, diesel, gas oil, light crude oil, and other similar petroleum derivatives. Other suitable carriers include various alcohols, ketones, alkanes, cycloalkanes and aromatic solvents such as isopropyl alcohol, methyl ethyl ketone, hexane, cyclohexane, toluene, and the like. While the concentration of inhibitor in the solution can be varied over a wide range, the inhibitor solution generally contains between 10 and 50 weight percent of the wax deposition inhibitor.

It is preferred that the wax deposition inhibitor be added to the wax-containing oil before the oil has been cooled below the solidification temperature of the wax. While this temperature varies somewhat depending upon the particular waxes present in the wax-containing oil, it is generally preferred that the inhibitor be admixed into the wax-containing oil before the oil is cooled below a temperature of about 160° F.

While the inhibitor can be intermittently admixed with the wax-containing oil, it is preferred, particularly in continuous operations such as in the production of oil from a producing oil well, or the flow of oil through a pipeline, that the inhibitor be continuously added to the oil during the operation. However, where the inhibitor is added for the purpose of periodically removing accumulated wax deposits from equipment, the inhibitor can be effectively injected on an intermittant basis.

In a typical oil recovery operation, oil and other fluids flow from the producing earth formation into the well and accumulate in a reservoir therein, whereupon they are transported to the surface through production tubing, either under natural pressure or assisted by pumping or gas lift. Preferably, the inhibitor is added to the reservoir of oil in the well before it cools to a temperature below the solidification temperature of the wax. Wax deposition in a producing oil well can be inhibited by adding the wax deposition inhibitor to the reservoir of oil in the well either by pumping the inhibitor down the well through a separate tubing string, such as a small diameter macaroni tubing, or by merely injecting the inhibitor into the annulus at the top of the well and allowing it to fall by gravity into the reservoir of oil in the well.

In a preferred mode of practicing the invention, wax deposition from a wax-containing oil is inhibited by admixing a solution of an ethylene/vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index between about 45 to 70 grams per 10 minutes dissolved in an organic solvent with the wax-containing oil at a temperature above the solidification temperature of the wax in an amount to provide a concentration of copolymer in the oil between about 5 and 10,000 ppm, and more preferably between about 5 and 200 ppm, effective to inhibit the deposition and accumulation of wax in wells, pipelines, and other equipment contacted by the oil.

The invention is further described by the following examples which are illustrative of specific modes of practicing the invention and are not intended as limiting the scope of the invention defined by the appended claims.

EXAMPLE 1

A large number of materials of various types are tested to determine their effectiveness in inhibiting the deposition of wax from a wax-containing hydrocarbon solution. A standard solu-tion is prepared by dissolving 2 weight percent paraffin wax having a melting point of 140° F. in kerosene by heating the kerosene-wax mixture to a temperature of 160° F. and stirring until a clear homogeneous liquid solution is obtained.

In conducting these tests, an amount of the additive to be tested that produces a desired additive concentration is added to the hot kerosene-wax solution and thoroughly admixed therein. The solution is then transferred to a 1-inch diameter by 12-inch long test tube and the test tube mounted in a rack adapted to support it at an angle of 15 degrees from vertical. The rack containing one or more of the test tubes is placed in a cooling chamber maintained at a temperature of 35° F. for a period of one hour to allow it to reach thermal equilibrium. The physical appearance of the test solution is then noted and the rack transferred to a cold chamber maintained at a temperature of 0° F. for an additional period of one hour and its physical appearance again noted.

The physical state of the test solution at each observa-tion is rated by the following standard:

% Liquid — Material contains approximately the indicated percentage of liquid with the balance being precipitated solids. Liquid contents of less than about 5 volume percent are designated "some liquid".

Light mush — Material is a semi-solid that exhibits a high solids content with no separate liquid phase, however, the material will flow fairly readily.

Mush — Material exhibits a high solids content with no separate liquid phase, but flows more slowly than the light mush.

Heavy mush — Material is a semi-solid that exhibits a high solids content with no separate liquid phase, and flows quite slowly.

Almost solid — Material is a solid, but an inverted sample will flow on light impact.

Just solid — Material is a solid, but an inverted sample will flow on heavy impact.

Solid — Material is solid.

The results of the foregoing tests are reported in Table 1. It has been determined that additives that maintain the standard test solution in a semi-solid or liquid state will inhibit the deposition of wax in wells, pipelines, tanks and other equipment at comparable temperatures, and that the effectiveness of an additive as a wax deposition inhibitor correlates generally with its ability to maintain the standard test solution in the liquid state at a specified temperature. Thus, those agents that maintain the test solution in the liquid state of 0° F. are preferred, although those that maintain the solution in the semi-solid state will at least retard the deposition of wax.

TABLE 1

Run number	Additive			Additive concentration, p.p.m.	Appearance after one hour	
	Composition	Melt index, grams./10 min.	Ester content, weight percent		35° F.	0° F.
Blank	None			0	Solid	Solid.
1	Ethylene/ethyl acrylate copolymer.	18	20	300	Mush	Do.
2	do	18	30	300	Mush, some liquid	Solid.
3	Ethylene/vinyl acetate copolymer.	335–465	17–19	50	Mush	Do.
4	do	335–465	17–19	100	Mush, some liquid	Mush.
5	do	335–465	17–19	150	20% liquid	Mush, some liquid.
6	do	335–465	17–19	200	40% liquid	Do.
7	do	2.1–2.9	17–19	50	Almost liquid	Solid.
8	do	2.1–2.9	17–19	100	Mush, some liquid	Just solid.
9	do	2.1–2.9	17–19	150	do	Do.
10	do	2.1–2.9	17–19	200	do	Do.
11	do	0.7	18	50	Almost solid	Solid.
12	do	0.7	18	100	do	Do.
13	do	0.7	18	150	Mush	Do.
14	do	0.7	18	200	do	Almost solid.
15	do	300	10	50	Just solid	Solid.
16	do	300	10	100	Almost solid	Do.
17	do	300	10	150	Mush	Just solid.
18	do	300	10	200	do	Almost solid.
19	do	0.8	9.5	50	Solid	Solid.
20	do	0.8	9.5	100	do	Do.
21	do	0.8	9.5	150	Heavy mush	Do.
22	do	0.8	9.5	200	do	Do.

EXAMPLE 2

The effectiveness of a preferred wax deposition inhibi-tor is demonstrated by this series of tests. The additive is an ethylene vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index between about 45 to 70 grams per 10 minutes marketed by E. I. duPont de Nemours Company under the trademark ELVAX 40. A standard kerosene-wax test solution is prepared and the test conducted substantially as des-cribed in Example 1. The effectiveness of the additive is deter-mined at various concen-tration levels and the results tabulated in Table 2.

TABLE 2

Additive Concentration, ppm	Sample Appearance 35° F.	0° F.
0	Solid	Solid
10	Almost solid	Just solid
20	Mush	Almost solid
30	Mush	Almost solid
40	Mush, some liquid	Mush
50	20% liquid	Mush, part liquid
60	30% liquid	Mush, part liquid
80	50% liquid	Light mush, some liquid[1]
100	75% liquid	Light mush, some liquid[1]
120	80% liquid	Light mush, some liquid[1]

[1]The amount of liquid increased at each successively higher addition concentration, but did not exceed about 10 percent.

From the foregoing, it is apparent that this ethylene/vinyl acetate copolymer is effective in inhibiting wax deposition at concentrations in excess of about 10 ppm.

EXAMPLE 3

The effectiveness of several ethylene/vinyl acetate copolymers as wax deposition inhibitors is illustrated by the following tests. The additives are (1) an ethylene/vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting melt index of between 45 to 70 grams per 10 minutes marketed by the E. I. duPont de Nemours Company under the trademark ELVAX 40; (2) an ethylene vinyl acetate copolymer containing about 32 to 34 weight percent vinyl acetate and exhibiting a melt index of between about 22 to 28 grams per 10 minutes marketed by the E. I. duPont de Nemours Company under the trademark ELVAX 150; and (3) an ethylene/vinyl acetate copolymer containing about 27 to 29 weight percent vinyl acetate and exhibiting a melt index of between about 22 to 28 grams per 10 minutes marketed by the E. I. duPont de Nemours Company under the trademark ELVAX 240.

A standard kerosene-wax test solution is prepared and the test conducted substantially as described in Example 1. The effectiveness of each additive is determined at various concentration levels and the results tabulated in Table 3.

TABLE 3

Additive Concentr-ation, ppm	Vinyl Acetate Content of Polymer, Wt. %	Sample Appearance 35° F.	0° F.
Blank	—	Solid	Solid
10	27–29	Almost solid	Solid
10	32–34	Almost solid	Just solid
10	39–42	Almost solid	Just solid
20	27–29	Mush	Almost solid
20	32–34	Mush	Heavy mush
20	39–42	Mush	Heavy mush
40	27–29	Mush, some liquid	Almost solid
40	32–34	Mush, some liquid	Mush
40	39–42	Mush, some liquid	Mush
60	27–29	Mush, some liquid	Mush
60	32–34	Mush, some liquid	Mush, some liquid
60	39–42	Mush, some liquid	Mush, some liquid
80	27–29	5% liquid	Mush, some liquid
80	32–34	20% liquid	Mush, some liquid
80	39–42	40% liquid	Mush, some liquid
100	27–29	10% liquid	Mush, some liquid
100	32–34	30% liquid	Mush, some liquid
100	39–42	50% liquid	Mush, some liquid

From the foregoing, it is apparent that the effective-ness of these ethylene/vinyl acetate copolymers in inhibiting wax deposition is generally enhanced as the vinyl acetate content of copolymers is increased, with the copolymer containing 39 to 42 weight percent vinyl acetate providing the greatest improvement in wax deposition.

EXAMPLE 4

The effectiveness of an optimum concentration of a preferred wax deposition inhibitor is demonstrated by the following series of tests. The additive is an ethylene/vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index of between 45 to 70 grams per 10 minutes marketed by the E. I. duPont de Nemours Company under the trademark ELVAX 40. The optimum additive concentration is determined by measuring the filtration rate of a wax-containing crude oil containing various amounts of the additive.

The additive is prepared by dissolving the ethylene/vinyl acetate copolymer in kerosene to obtain a solution containing 10 weight percent copolymer. 100 ml of a wax-containing Louisiana crude is placed in a water bath and heated to a temperature of 130° F. A measured quantity of the additive solution is added to the crude oil with a microsyringe and thoroughly admixed by shak-ing it about 100 times. After an additional 20 minutes in the water bath, the sample is removed and allowed to cool to room temperature. A 50 ml portion of the sample is then filtered through API Fluid Loss Test filter paper at a pressure of 100 psig, and the filtration rate determined. The measured filtration rates at various additive concentrations are reported in Table 4.

TABLE 4

Additive Concentration, ppm	Filter Time, minutes
0	55
5	19.5
10	5.33
20	0.25
30	0.97
40	0.58
50	0.75
60	0.86
70	0.75
80	0.92
90	1.17
100	1.17

EXAMPLE 5

The effectiveness of a preferred wax deposition inhibitor in reducing wax deposition from exemplary wax-containing crude oils is demonstrated by the following series of tests. The additive is an ethylene/vinyl acetate copolymer containing about 39 to 42 percent vinyl acetate and exhibiting a melt index of between about 45 to 70 grams per 10 minutes marketed by E. I. duPont de Nemours Company under the trademark ELVAX 40.

Simulated high wax content crude oils are prepared by dissolving about 2.5 weight percent 140° F. melting point wax in a wax-containing Texas crude oil and about 3.0 weight percent of the wax in a wax-containing Illinois crude oil. The wax deposition tendency of these crude oils at various additive concentrations is determined by adding a desired amount of a 10 weight percent solution of the additive in an organic solvent to the crude oil and testing these mixtures substantially as described in Example 1. The results of these tests are tabulated in Table 5.

TABLE 5

Additive Concentration, ppm	Appearance of Oil 35° F.	0° F.
Texas Crude plus 2.5 wt. % wax		
0	Solid	Solid
40	Just solid	Just solid
60	Mush	Almost solid
80	Mush	Mush
100	Light mush	Mush
120	Liquid	Liquid
Illinois Crude plus 3 wt. % wax		
0	Solid	Solid
40	Mush	Mush
60	Liquid	Liquid
80	Liquid	Liquid
100	Liquid	Liquid
120	Liquid	Liquid

EXAMPLE 6

This example illustrates the practice of the invention in inhibiting wax deposition in a producing oil well and the associated surface production facilities handing a wax-containing East Texas crude oil. The well bottom hole temperature is approximately 130° F., but the crude oil is cooled to about 110° F. on reaching the surface. Wax deposition is experienced in the well and, to an even greater extent, in the surface production pipeline used for transporting the crude oil from the well. When the production pipeline is clean, a pressure of approximately 55 psig is required at the well head to move the produced crude oil through the pipeline. However, after two or three weeks of operation wax deposition in the pipeline plugs it to the extent that the discharge pressure builds up to the maximum allowable pressure of 300 psig, thus necessitating a costly cleaning operation.

Wax deposition in the crude oil is inhibited by adding a wax inhibitor to the well. The additive is an ethylene/vinyl acetate copolymer containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index of between about 45 to 70 grams per 10 minutes, and is dissolved in kerosene to provide a solution containing 40 weight percent additive. A concentrate is prepared at the well site by admixing two gallons of the additive solution and approximately one barrel of the produced crude oil. The well is treated by continuously pumping this concentrate into the well annulus at the rate of about one barrel per day so as to provide in the produced crude oil an additive concentration of about 40 ppm. The additive admixes with the oil in the well in a region that the oil is above the wax solidification temperature and is ultimately produced with the crude wax.

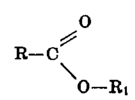
Although the initial quantity of additive is introduced into the well immediately after cleaning the well and pipeline to remove deposited wax, a large pressure increase is noted within only a few days and the pipeline is plugged with wax indicating that the inhibitor removed previously deposited quantities of wax not removed by the usual cleaning process. The loosened wax is again cleaned from the pipeline and the well returned to production with a well head pressure of about 55 psig. The well is produced for a period of three months with no significant increase in well head pressure.

Various embodiments and modifications of this invention have been described in the foregoing description and examples, and further modifications will be apparent to those skilled in the art. Such modifications are included within the scope of this invention as defined by the following claims.

Having now described the invention, I claim:

1. A method for inhibiting the deposition of wax from wax-containing oil comprising incorporating into said oil a wax deposition inhibitor comprising a copolymer of ethylene and a monoethylenically unsaturated ester selected from the group consisting of (1) vinyl and allyl esters of saturated aliphatic carboxylic acids and (2) saturated aliphatic esters of unsaturated aliphatic carboxylic acids.

2. The method in accordance with claim 1 wherein said monoethylenically unsaturated ester is characterized by the formula:



wherein (1) R is hydrogen or an alkyl group containing from about one to 25 carbon atoms and R_1 is a vinyl or allyl group, or (2) R is an α,β-unsaturated alkylene and R_1 is an alkyl group containing from about one to 25 carbon atoms.

3. The method in accordance with claim 1 wherein said inhibitor is copolymer ethylene/vinyl acetate, copolymer ethylene/ethyl acrylate or copolymer ethylene/methyl methacrylate.

4. The method in accordance with claim 1 wherein said inhibitor is incorporated into said wax-containing oil as a solution of the copolymer dissolved in an organic solvent.

5. The method defined in claim 1 wherein the inhibitor is incorporated into said wax-containing oil at an oil temperature sufficiently high to maintain the wax dissolved in the oil, and wherein said oil is thereafter cooled to a temperature below the solidification temperature of the wax.

6. The method defined in claim 1 wherein said inhibitor is incorporated into said wax-containing oil in an amount to provide therein an effective concentration of said inhibitor between about 5 and 2,000 ppm.

7. A method for inhibiting the deposition and accumulation of wax in wells, tanks, pipelines and like equipment handling a wax-containing oil, which comprises incorporating into said oil a wax deposition inhibitor comprising a copolymer of (1) ethylene and (2) a lower vinyl ester or a lower alkyl acrylate or methacrylate, said inhibitor being added to said oil in an amount to provide therein a concentration of said copolymer between about 5 and 2,000 ppm effective to inhibit the deposition and accumulation of wax in said equipment.

8. The method defined in claim 7 wherein said inhibitor is added to said oil as a solution containing about 10 to 50 weight percent of said copolymer dissolved in an organic solvent.

9. The method defined in claim 7 wherein said inhibitor is a copolymer of ethylene and vinyl acetate containing from about 10 to 70 weight percent vinyl acetate and exhibiting a melt index between about 1 and 600 grams per 10 minutes.

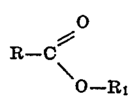
10. The method defined in claim 7 wherein the inhibitor is incorporated into said wax-containing oil at an oil temperature sufficiently high to maintain the wax dissolved in the oil, and wherein said oil is thereafter cooled to a temperature below the solidification temperature of the wax.

11. A method for inhibiting the deposition of wax from a wax-containing oil comprising admixing into said oil at an oil temperature sufficiently high to maintain the wax dissolved in the oil an amount of a solution of about 10 to 50 weight percent of a wax deposition inhibitor dissolved in an organic solvent to provide in said wax-containing oil an effective concen-

tration of said inhibitor between about 5 and 2,000 ppm, said wax deposition inhibitor comprising a copolymer of ethylene and vinyl acetate containing about 35 to 55 weight percent vinyl acetate and exhibiting a melt index between about 1 and 600 grams per 10 minutes.

12. The method defined in claim **11** wherein said wax deposition inhibitor is a copolymer of ethylene and vinyl acetate containing about 39 to 42 weight percent vinyl acetate and exhibiting a melt index between about 1 and 600 grams per 10 minutes.

13. In a method for operating a well for the produc-tion of wax-containing petroleum from a subterranean formation wherein the petroleum flows from the formation into the well and is accumulated therein at a temperature sufficiently high to maintain the wax dissolved in the petroleum and wherein said petroleum is transported to the surface through a production tubing, said petroleum being cooled to a temperature below the solidification temperature of the wax whereupon wax participates from the petroleum and tends to deposit on the interior surface of the production tubing and on the interior surfaces of surface equipment causing them to become plugged with wax, the improvement which comprises adding to the wax-containing petroleum in the well a wax deposition inhibitor comprising a copolymer of ethylene and a monoethylenically unsaturated ester characterized by the following formula:



wherein (1) R is hydrogen or an alkyl group containing from about one to 25 carbon atoms and R is a vinyl or allyl group, or (2) R is an α,β-unsaturated alkylene and R_1 is an alkyl group containing from about one to 25 carbon atoms.

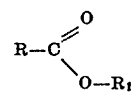
14. The method defined in claim **13** wherein said inhibitor is incorporated into said petroleum in an amount to provide therein an effective concentration between about 5 and 2,000 ppm.

15. The method defined in claim **14** wherein said wax deposition inhibitor is added to said petroleum as a solution of the copolymer dissolved in an organic solvent.

16. The method defined in claim **15** wherein said monoethylenically unsaturated ester is vinyl acetate.

17. The method defined in claim **16** wherein said copolymer contains from about 10 to 70 weight percent vinyl acetate.

18. A method for removing accumulated wax deposits from surfaces contacted by a wax-containing oil which comprises periodically adding to said oil an effective concentration of a copolymer of ethylene and a monoethylenically unsaturated ester characterized by the formula:



wherein (1) R is hydrogen or an alkyl group containing from about one to 25 carbon atoms and R_1 is a vinyl or alkyl group, or (2) R is an α,β-unsaturated alkylene and R_1 is an alkyl group containing from about one to 25 carbon atoms.

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