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(72) Inventors ALBERT ROSSI, ERIK TORNQVIST, NORMAN JACOBSON and WON RYUL SONG

(54) A PROCESS FOR DEWAXING A PETROLEUM OIL

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for dewaxing a petroleum oil.

Various methods are known in the art for separating wax from petroleum oil. One such method, for instance, is chilling the wax-containing oil and filtering off the solid wax. One of the most commonly used methods of dewaxing oils is known as solvent dewaxing. This comprises diluting the oil with a solvent, heating until complete solution is obtained, and then chilling until the desired amount of wax has crystallized out. The wax crystals thus formed are separated from the slurry by means of filtration. The wax is then further purified, while the solvent is recovered for reuse and the dewaxed oil is sent to other refinery processes.

Although such solvent dewaxing has largely replaced other processes for the separation of wax from hydrocarbon oils, filtration of the wax crystals from the slurry formed during dewaxing is difficult and often the filtration rate of the slurry limits the capacity of the entire process. The slurry filtration rate is determined primarily by the size and shape of the wax crystals formed during the chilling step of the process. Very fine crystals tend to clog the filter media rapidly, reducing the filtration rate and eventually necessitating shutdown of the filters for removal of the accumulated wax. Very large crystals tend to form gel-like interlocking masses which do not form a compact filter cake, which contain a large amount of oil and solvent, and which are difficult to wash.

As a solution to this problem, it has become the practice in the art to incorporate in the wax-containing petroleum oil materials which modify the size and shape of wax crystals in such a manner as to permit more rapid separation of the wax during dewaxing operations. These materials are known as dewaxing aids. For example, U.S. Patent No. 3,355,379 discloses a dewaxing process employing a poly-alpha-olefin dewaxing aid having an average molecular weight of ten million or more. It is further disclosed therein that the molecular weight is critical since lower molecular weight polymers were found to be essentially inactive. In one aspect, the dewaxing aid of the present invention differs from the aforesaid patent in that it has been found that certain polymers of alpha-mono-olefins are very effective dewaxing aids when said polymers have relatively low molecular weights.

The present invention provides a process for the separation of wax from a petroleum oil, comprising chilling the oil to form solid wax crystals and removing said wax crystals, wherein there is incorporated into said oil prior to formation of said wax crystals a total of from 0.001 to 5.0 wt. %, based on the oil of

(a) an oil-soluble copolymer of at least two different C_{14} to C_{24} alpha monoolefins, or
(b) at least two oil-soluble homopolymers of different C_{14} to C_{24} alpha monoolefins, or
(c) an oil-soluble copolymer of at least one C_{14} to C_{24} alpha monoolefin with at least one C_3 to C_{12} alpha monoolefin and/or at least one C_5 to C_{12} diolefin, or
(d) both (1) an oil-soluble Friedel-Crafts condensation product of a halogenated paraffin with an aromatic hydrocarbon and (2) either a said material (a), (b), or (c), or an oil-soluble homopolymer of a C_{14} to C_{24} alpha monoolefin, said com-

ponents (1) and (2) being incorporated in a weight ratio of 1:3 to 3:1;

wherein the said homo- and copolymers have a number average mol. wt. not exceeding 200,000, and wherein said copolymer (c) contains at least 30 wt. % of said C_{12} to C_{24} alpha monoolefin.

In an embodiment of the invention the oil is mixed with a dewaxing solvent prior to the chilling to form sold wax crystals.

Desirably the said number average mol. wt. lies in the range of 1,000 to 200,000. Preferably the said alpha monoolefins are C_{14} to C_{20} monoolefins.

In the specification and claims the phrase the polymer "contains 'x' wt.% monoolefin or diolefin" means contains 'x' wt.% of units in the polymer which can be said to have been derived from the corresponding monomer. A copolymer comprised of 15 to 35 wt. % n-hexadecene-1, 15 to 30 wt. % n-octadecene-1, 10 to 20 wt. % n-eicosene-1 and 25 to 45 wt. % of a C_4—C_8 alpha monoolefin, e.g. n-hexene-1, is especially preferred.

The C_{14}—C_{24} alpha-monoolefin monomer which is used to prepare the dewaxing aid used in the invention may be represented by the following general formula: $H_2C{=}CHR$, wherein R is a substantially linear aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms. It is preferred, however, that R have the formula:

$$CH_3—(CH_2)_n—CH_2—,$$

wherein n is a whole number ranging from 10 to 20, for example 10 to 16, and more preferably, from 12 to 16. The term "substantially linear" is used herein to denote those aliphatic side chains, i.e. R, which contain no more than one lower alkyl (C_1 to C_6) side chain, such as methyl or ethyl, 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 12 carbon atoms. Examples of suitable monomers include n-tetradecene-1, n-hexadecene-1, 3-methylhexadecene-1, n-octadecene-1, n-eicosene-1, 4-methyl eicosene-1 and n-docosene-1.

The C_3—C_{12} alpha-olefins which can be methyl styrene. The aforedescribed C_{14}—C_{12} alpha-monoolefins may be represented by the following general formula: $H_2C{=}CHR'$, wherein R' is a hydrocarbon radical containing from 1 to 10 carbon atoms. There appears to 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-methyldecene-1, styrene and styrene derivatives such as p-methyl styrene, p-isopropyl styrene, and alpha-methyl styrene. The aforedescribed C_{14}—C_{24} alpha-monoolefins may be polymerized with various other monomers. For example, effective copolymers may comprise at least 30 wt. % of the C_{14}—C_{24} alpha-olefin used in the invention and up to 70 wt. % of a polymerizable C_3—C_{12} diolefin. Similarly, the polymers used in the invention may comprise 30 to 100 wt. % of the aforedescribed C_{14}—C_{24} alpha-monoolefin, and up to a total of 70 wt. % of the aforedescribed C_3—C_{12} alpha-olefin and/or a polymerizable C_3—C_{12} diolefin. These diolefins which are useful for polymerization with the aforedescribed alpha-olefins include the bicyclic, alicyclic or aliphatic diolefins containing from 5 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. 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 and 1,5-octadecadiene.

The preferred copolymer used in the invention is comprised of at least two unlike linear C_{14}—C_{20} alpha-monoolefins wherein at least two of said alpha-monoolefins each comprises 10 to 90 wt. % (but wherein the total of them is at least 30 wt. %), preferably 30 to 60 wt. % of the polymer. Of interest is a copolymer prepared from at least one, and preferably at least two, unlike linear C_{14}—C_{20} alpha-monoolefins having the aforesaid preferred formula and consisting essentially of 30 to 60 wt. % of a C_4—C_8 alpha-monoolefin (e.g. butene-1 or hexene-1), and 40 to 70 wt. % in total of at least one of tetradecene-1, hexadecene-1, octadecene-1 and eicosene-1. Of particular interest is a copolymer comprised of 15 to 60, preferably 25 to 45, wt. % hexene-1; 10 to 50, preferably 15 to 35, wt. % n-hexadecene-1; 10 to 40, preferably 15 to 30, wt. % n-octadecene-1; and 5 to 30, preferably 10 to 20 wt. % n-eicosene-1.

In another preferred embodiment, the dewaxing aid used in the present invention comprises a mixture of at least two unlike homopolymers prepared from the aforedescribed C_{14}—C_{20} alpha-monoolefins wherein no one homopolymer accounts for more than 80 wt. %, preferably no more than 60 wt. %, of the polymeric mixture. A particularly effective mixture comprises 0 to 70 wt. % (e.g. 40 wt. %) polyhexadecene, 0 to 70 wt. % (e.g. 30 wt. %) polyoctadecene and 0 to 70 wt. % (e.g. 30 wt. %) of polyeicosene.

The polymers used in the invention will have a number average mol. wt. not above 200,000 and generally within the range 1000 and 200,000. It is preferred, however, that the number average molecular weight range from 1500 to 100,000 more preferably 2000 to 30,000. In this connection, the number average molecular weights of up to 50,000 are measured by Vapor Phase Osmometry (for example, by using a Mechrolab Vapor Phase

Osmometer Model 310A) whereas higher number average molecular weights are measured by Membrane Osmometry.

The polymers used in this invention may be conventionally prepared by polymerizing the monomers under relatively mild conditions of temperature and pressure in the presence of catalysts generally known as coordination catalysts. These catalysts are made of components of two types, namely, compounds of the heavy transition metals of Groups IV, V and VI of the Periodic System beginning with titanium, vanadium, and chromium and organometallic compounds and hydrides of metals of Groups I, II and III of the Periodic System wherein the amount of the compounds derived from a Group IV—VI metal may range from 0.01 to 2.0 moles per mole of the organometallic compound.

The compounds of the first type are preferably halides, oxyhalides and mixtures thereof, while titanium, and vanadium deserve preference as metals. The second component is preferably an organometallic compound of lithium, sodium, magnesium, or aluminum, in which the organic portions are preferably alkyl radicals. In these organometallic compounds, the valence of the metal can be partially saturated by halogens or alkoxyls, provided, naturally, that at least one bond binds the metal directly to a carbon atom. Mixtures of two or more compounds of the type described above can often be used to advantage.

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; titanium tetrachloride and aluminium 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 and heptane, and then adding the monomers to the catalyst mixture at atmospheric or superatmospheric pressures and temperatures within the range of 50° and 180°F. Usually atmospheric pressure is employed when polymerizing the monomers containing more than 4 carbon atoms in the molecule and elevated 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, the pressure employed and the monomer conversion desired. In general, however, 1/2 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.

The polymeric additive used in this invention functions effectively as a dewaxing aid and filtration aid in those dewaxing processes involving chilling the oil to form solid wax crystals and subsequently removing the wax crystals. Particularly good results are secured in the conventional solvent dewaxing processes. It has been found that in these dewaxing operations the removal of precipitated wax from a petroleum oil can be substantially improved by the incorporation of from 0.001 to 5 wt. %, e.g. 0.01 to 0.06 wt. % (based on weight of wax-containing oil) of the polymers or mixtures thereof used in the invention.

While the polymeric additive may be used to separate wax from a number of petroleum stocks, such as residua, middle distillates and the like, it has special application to waxy distillate and residual lubricating oil fractions such as solvent neutrals and bright stocks. These fractions generally range in boiling points from about 400° to about 1100°F. and contain from about 5 to about 30 wt. % wax.

Various methods may be used to effect the blending of the wax crystal modifier, the wax-containing oil, and the dewaxing solvent, where used. For example, the wax crystal modifier and the wax-containing petroleum oil may be combined prior to the addition of a dewaxing solvent or alternatively, the dewaxing solvent can be admixed with the oil prior to the addition of the wax crystal modifier. Broadly, the admixing temperature should be above the cloud point of the wax-containing petroleum oil. For example, admixing temperatures of about 120°F. to about 250°F. may be used. It is preferred, however, that the temperature be from about 160° to 200°F.

Particularly desirable results are obtained when the polymeric additive is utilized in a conventional dewaxing process. For example, admixtures of the afore-described polymer, dewaxing solvent and wax-containing oil may be processed by chilling said admixture in any suitable manner to a wax precipitation temperature. The precipitated wax may then be removed by centrifugation or filtration, preferably the latter. Dewaxing operations are preferably conducted at a temperature within the range of −40° to +20°F., and more preferably, at a temperature within the range of −30 to 15°F. Among the dewaxing solvents which may be advantageously employed, a large number are well known in the art and include benzene, toluene, acetone, methylethyl ketone, methylisobutyl ketone, propane, hexane, ethylene dichloride, aliphatic alcohols, naphtha, and mixtures thereof such as a 45/55 blend of methylethyl ketone and toluene, and a 30/70 blend of methylethyl

ketone and benzene. The amount of solvent used will usually range from 0.5 to 3.5 volumes of solvent per volume of oil to be dewaxed.

As indicated hereinbefore, mixtures of the aforedescribed polyolefins and the well-known class of wax crystal modifiers made by the Friedel-Crafts condensation of a halogenated paraffin with an aromatic hydrocarbon synergistically improve the separation of wax from petroleum oils. The halogenated paraffin may, for example, contain from 8 to 60 carbon atoms, preferably from 16 to 44, and from 5 to 25 wt. % chlorine, preferably from 10 to 18 wt. %. Typically, the halogenated paraffins used to prepare this well-known class of wax modifiers are themselves prepared by chlorinating to the above recited chlorine content a paraffin wax having a melting point within the range between 105° and 190°F, preferably 120°F to 190°F. The aromatic hydrocarbon used herein contains a maximum of three substituent groups and/or condensed rings and may be a hydroxy compound such as phenol, cresol, xylenol, or an amine such as aniline, but is preferably naphthalene, phenanthrene or anthracene. The Friedel-Crafts condensation products used in the present invention are prepared in accordance with well-known techniques, e.g. British Patents 511,207 and 562,714.

The syngeristic wax crystal modifier composition may comprise various amounts of the aforedescribed polyolefin and Friedel-Crafts condensation product; the amounts employed will produce a mixture containing 25 to 75 wt. % (e.g. 50 wt. %) of the condensation product and 25 to 75 wt. % (e.g. 50 wt. %) of the polyolefin.

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

The polymeric additive is found to be compatible with other additive materials and may be blended successfully with petroleum oils containing minor amounts of viscosity index improvers, rust inhibitors, lubricity agents, oxidation inhibitors and the like. The invention can be more fully understood by reference to the following three examples, which contain comparative data, and which are preceded by a typical preparation of a polymer for use as a dewaxing aid in the process of the present invention.

Preparation

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

Into a 500 milliliter 4-neck flask fitted with a mechanical stirrer, heating mantle, thermometer, condenser and gas inlet were charged under anhydrous conditions, 0.11 gram of a cocrystallized titanium trichloride-aluminum trichloride catalyst ($TiCl_3 . 1/3AlCl_3$), 75 milliliters of xylene as solvent and 0.41 gram of triethylaluminum. 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 19 grams of n-tetradecene-1 was added thereto. After addition of the alpha-olefin was completed, the reaction mixture was heated to 70°—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 10 volumes of methanol to precipitate the solid tetradecene 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 13 grams and had a number average molecular weight of about 5000 as measured by Vapor Phase Osmometry (VPO).

Example 1

Following the general procedure of the Preparation, various homopolymers and copolymers were prepared from normal C_{14} to C_{20} alpha-monoolefins. The resulting homopolymers and copolymers were then tested as dewaxing aids in a distillate lube stock and a residual lube stock. The properties of these oils are shown in Table I and hereinafter referred to as Test Oil A and Test Oil B.

TABLE I

Properties of Test Oils

Inspection	Test Oil A (1)	Test Oil B (2)
ASTM Viscosity @ 210°F., SUS	27.9	160
Gravity, API	31.76	26.7
ASTM Pour Point, °F.	120	125
Wax Content, Wt. %	23.9	15

(1) A distilled lube stock from Texas Panhandle crude.

(2) A residual lube stock from Louisiana crude.

Test Oil A was dewaxed by diluting with a solvent consisting of 55 volume % methyl-ethyl ketone and 45 volume % toluene at a solvent/oil ratio of 3.1/1 and then chilling at the rate of 3°—6°F. per minute from a feed temperature of 140°F. to a filter temperature of 0°F. The chilled mixture was then continuously filtered through a refrigerated circular leaf filter at a pressure differential of 22 inches of mercury. The filtration cycle consisted of a filtration time of 28 seconds, a drying time of 5 seconds, a wash time of 22 seconds and a second drying time of 8 seconds.

In a similar manner, Test Oil B was dewaxed by diluting with hexane at a solvent/oil ratio of 3/1 and then chilling at the rate of 3°—6°F. per minute from a feed temperature of 140°F. to a filter temperature of −30°F. The chilled mixture was then continuously filtered through a refrigerated circular leaf filter at a pressure differential of 20 inches of mercury. The filtration cycle consisted of a filtration time of 36 seconds, a drying time of 9 seconds, a wash time of 27 seconds and a second drying time of 8 seconds.

The test oils were also dewaxed in the same manner as above except that 0.02—0.12 wt. % (based on weight of wax-containing oil) of a homopolymer, copolymer or mixture of homopolymers set forth below were each added to a separate oil sample prior to chilling. The feed mixtures comprising the individual polymers or mixtures thereof were then separately processed under the same dewaxing conditions as used in the above operation wherein no wax crystal modifier was employed.

The data obtained from the dewaxing of Test Oil A are shown below in Table II.

TABLE II

Dewaxing of Test Oil A

Dewaxing Aid Used	Relative Filtration Rate (1)
None	1.00
0.06 wt. % of n-tetradecene-1 homopolymer(2)	1.91
0.06 wt. % of n-hexadecene-1 homopolymer(3)	3.56
0.06 wt. % of n-octadecene-1 homopolymer(4)	2.09
0.03 wt. % of n-tetradecene-1 homopolymer(2) + 0.03 wt. % of n-octadecene-1 homopolymer(4)	4.23
0.03 wt. % of n-hexedecene-1 homopolymer(3) + 0.03 wt. % of n-octadecene-1 homopolymer(4)	4.46

(1) Ratio of filtration rate for oil containing additive to filtration rate for oil with no additive.

(2) Homopolymer of the preparation.

(3) Number average molecular weight of about 6,800 (VPO).

(4) Number average molecular weight of about 7,300 (VPO).

The data obtained from the dewaxing of Test Oil B are shown below in Table III.

It can be seen from the data in the Tables that the alpha-olefin polymers used in the invention are very effective for improving the oil filtration rate in a conventional solvent dewaxing operation. Further, the data demonstrate that copolymers of C_{14}—C_{20} alpha-monoolefins and mixtures of unlike homopolymers of said monoolefins are more effective than an equivalent weight amount of a homopolymer or copolymer comprised of only one of said monoolefins.

TABLE III

Dewaxing of Test Oil B

Dewaxing Aid Used	Relative Filtration Rate
None	1.0
0.05 wt. % of n-tetradecene-1 homopolymer(1)	1.91
0.05 wt. % of n-hexadecene-1 homopolymer (2)	1.98
0.05 wt. % of n-octadecene-1 homopolymer(3)	1.81
0.05 wt. % of n-tetradecene-1/ n-octadecene-1 copolymer(4)	2.67
0.05 wt. % of n-hexadecene-1/ n-octadecene-1 copolymer(5)	2.86
0.05 wt. % of n-butene-1/ n-hexadecene-1 copolymer(6)	2.53
0.05 wt. % of n-hexene-1/C_{16}—C_{20} copolymer(7)	2.92

(1) Homopolymer of the Preparation.

(2) Number average molecular weight of about 6,600 (VPO).

(3) Number average moelcular weight of about 4,900 (VPO).

(4) Copolymer comprising 38 wt. % tetradecene and 62 wt. % octadecene and having a number average molecular weight of about 2,450 (VPO).

(5) Copolymer comprising 40 wt. % hexadecene and 60 wt. % octadecene and having a number average molecular weight of about 2,350 (VPO).

(6) Copolymer comprising 40 wt. % butene and 60 wt. % hexadecene and having a number average molecular weight of about 9,200 (VPO).

(7) Interpolymer comprising 38 wt. % hexene, 26 wt· % n-hexadecene-1, 21 wt. % of n-octadecene-1, 15 wt. % n-eicosene-1 and having a number average molecular weight of about 28,000 (VPO).

Example 2

This Example serves to illustrate the effect which the molecular weight of the polymeric dewaxing aid has on its ability to improve the oil filtration rate obtained in a dewaxing operation.

A copolymer prepared in the manner of the Preparation by polymerizing a monomer mixture consisting of 38 wt. % hexene-1, 26 wt. % hexadecene-1, 21 wt. % octadecene-1 and 15 wt. % eicosene-1 was fractionated into several fractions of various molecular weights by fractional precipitation using methanol addition to a polymer-benzene solution. Each of the polymer fractions was blended at 0.06 wt. % concentration (based on oil) with separate samples of Test Oil A and evaluated for dewaxing effectiveness in accordance with the test procedure of Example 2. The results given in Table IV show that more effective polymers have relatively low molecular weights.

TABLE IV

Dewaxing of Test Oil B

Number Average Molecular (VPO) of Polymer Fraction	Relative Filtration Rate(1)
13,000	2.13
28,000	2.28
37,600	1.35

(1) Ratio of filtration rate for oil containing additive to filtration rate for oil with no additive.

Example 3

The following example illustrates the synergistic effect between (a) a commercial Friedel-Crafts condensate wax crystal modifier (i.e. a condensation product of 4 moles of chlorinated 123°F. melting point paraffin wax containing 12 wt. % chlorine with 1 mole of naphthalene) and (b) a homopolymer of n-octadecene-1 prepared in the manner of the Preparation and having a number average molecular weight of about 8,600 (VPO).

Using the test procedure of Example 1, the wax-naphthalene condensation product, the polyoctadecene and mixture thereof were blended with separate samples of Test Oil A prior to dewaxing. The results given below in Table V show that the combination of the additives imparts an improvement which is significantly greater than that which could be obtained by the use of an equivalent weight amount of either material alone.

TABLE V

Dewaxing of Test Oil A

Dewaxing Aid Used	Relative Filtration Rate (1)
None	1.00
0.06 wt. % of wax-naphthalene condensate	1.71
0.06 wt. % of polyoctadecene	2.52
0.03 wt. % of wax-naphthalene condensate + 0.03 wt. % of polyoctadecene	3.16

(1) Ratio of filtration rate for oil containing additive to filtration rate for oil with no additive.

WHAT WE CLAIM IS:—

1. A process for the separation of wax from a petroleum oil, comprising chilling the oil to form solid wax crystals and removing said wax crystals, wherein there is incorporated into said oil prior to formation of said wax crystals a total of from 0.001 to 5.0 wt. %, based on the oil of

(a) an oil-soluble copolymer of at least two different C_{14} to C_{24} alpha monoolefins, or

(b) at least two oil-soluble homopolymers of different C_{14} to C_{24} alpha monoolefins, or

(c) an oil-soluble copolymer of at least one C_{14} to C_{24} alpha monoolefin with at least one C_3 to C_{12} alpha monoolefin and/or at least one C_5 to C_{12} diolefin, or

(d) both (1) an oil-soluble Friedel-Crafts condensation product of a halogenated paraffin with an aromatic hydrocarbon and (2) either a said material (a), (b), or (c), or an oil-soluble homopolymer of a C_{14} to C_{24} alpha monoolefin, said components (1) and (2) being incorporated in a weight ratio of 1:3 to 3:1;

wherein the said homo- and copolymers have a number average mol. wt. not exceeding 200,000, and wherein said copolymer (c) contains at least 30 wt. % of said C_{12} to C_{24} alpha monoolefin.

2. A process as claimed in claim 1, where-

TABLE IV

Dewaxing of Test Oil B

Number Average Molecular (VPO) of Polymer Fraction	Relative Filtration Rate(1)
13,000	2.13
28,000	2.28
37,600	1.35

(1) Ratio of filtration rate for oil containing additive to filtration rate for oil with no additive.

Example 3

The following example illustrates the synergistic effect between (a) a commercial Friedel-Crafts condensate wax crystal modifier (i.e. a condensation product of 4 moles of chlorinated 123°F. melting point paraffin wax containing 12 wt. % chlorine with 1 mole of naphthalene) and (b) a homopolymer of n-octadecene-1 prepared in the manner of the Preparation and having a number average molecular weight of about 8,600 (VPO).

Using the test procedure of Example 1, the wax-naphthalene condensation product, the polyoctadecene and mixture thereof were blended with separate samples of Test Oil A prior to dewaxing. The results given below in Table V show that the combination of the additives imparts an improvement which is significantly greater than that which could be obtained by the use of an equivalent weight amount of either material alone.

TABLE V

Dewaxing of Test Oil A

Dewaxing Aid Used	Relative Filtration Rate (1)
None	1.00
0.06 wt. % of wax-naphthalene condensate	1.71
0.06 wt. % of polyoctadecene	2.52
0.03 wt. % of wax-naphthalene condensate + 0.03 wt. % of polyoctadecene	3.16

(1) Ratio of filtration rate for oil containing additive to filtration rate for oil with no additive.

WHAT WE CLAIM IS:—

1. A process for the separation of wax from a petroleum oil, comprising chilling the oil to form solid wax crystals and removing said wax crystals, wherein there is incorporated into said oil prior to formation of said wax crystals a total of from 0.001 to 5.0 wt. %, based on the oil of

(a) an oil-soluble copolymer of at least two different C_{14} to C_{24} alpha monoolefins, or

(b) at least two oil-soluble homopolymers of different C_{14} to C_{24} alpha monoolefins, or

(c) an oil-soluble copolymer of at least one C_{14} to C_{24} alpha monoolefin with at least one C_3 to C_{12} alpha monoolefin and/or at least one C_3 to C_{12} diolefin, or

(d) both (1) an oil-soluble Friedel-Crafts condensation product of a halogenated paraffin with an aromatic hydrocarbon and (2) either a said material (a), (b), or (c), or an oil-soluble homopolymer of a C_{14} to C_{24} alpha monoolefin, said components (1) and (2) being incorporated in a weight ratio of 1:3 to 3:1;

wherein the said homo- and copolymers have a number average mol. wt. not exceeding 200,000, and wherein said copolymer (c) contains at least 30 wt. % of said C_{12} to C_{24} alpha monoolefin.

2. A process as claimed in claim 1, where-

* C L M S *

in the oil is mixed with a dewaxing solvent prior to the chilling to form solid wax crystals.

3. A process as claimed in claim 1 or claim 2, wherein said number average mol. wt. lies in the range 1,000 to 200,000.

4. A process as claimed in any preceding claim, wherein each said alpha-monoolefin is a C_{14} to C_{20} alpha monoolefin represented by the formula:

$$H_2C=CH—CH_2—(CH_2)_n—CH_3$$

wherein n is a whole number from 10 to 16 and wherein the said number average molecular weight is in the range of 1500 to 100,000.

5. A process as claimed in any preceding claim, wherein the said number average molecular weight is in the range of 2000 to 30,000.

6. A process as claimed in claim 4 or claim 5 when dependent on claim 4, wherein there is incorporated an oil-soluble copolymer of at least two unlike alpha-olefins defined by said formula and wherein at least two of said alpha-monoolefins each comprises 10 to 90 wt. % of the polymer, their total being at least 30 wt. %.

7. A process as claimed in any preceding claim, wherein said polymer (c) consists essentially of 30 to 60 wt. % of a C_4—C_8 alpha-monoolefin, and 40 to 70 wt. % in total of at least one of tetradecene-1, hexadecene-1, octadecene-1 and eicosene-1.

8. A process as claimed in claim 7, wherein said polymer consists essentially of 15 to 60 wt. % hexene-1, 10 to 50 wt. % n-hexadecene-1, 10 to 40 wt. % n-octadecene-1 and 5 to 30 wt. % n-eicosene-1.

9. A process as claimed in claim 8, wherein said polymer consists essentially of 25 to 45 wt. % hexene-1, 15 to 35 wt. % n-hexadecene-1, 15 to 30 wt. % n-octadecene-1, and 10 to 20 wt. % n-eicosene-1.

10. A process as claimed in any one of claims 1 to 5, wherein there are employed at least two oil-soluble homopolymers of different C_{14} to C_{20} alpha monoolefins, wherein no one of the homopolymers comprises more than 80 wt. % of the total wt. employed.

11. A process as claimed in any preceding claim, wherein the said halogenated paraffin of the Friedel-Crafts condensation product is a paraffin wax having a melting point in the range of 120°F to 190°F and chlorinated to contain 5 to 25 wt. % chlorine.

12. A process as claimed in any of claims 1 to 11 and substantially as herein described.

13. A process as claimed in claim 1 and substantially as herein described with reference to any one of the Examples.

14. A petroleum oil from which wax has been separated by a process as claimed in any of claims 1 to 13.

K. J. VERYARD,
15, Suffolk Street,
London, SW1Y 4HS.
Agent for the Applicants.

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