

SOLVENT-DEWAXING PROCESS USING COMBINATION DEWAXING AID OF
SUBSTANTIALLY PURE POLY (C₂₄) ALKYL METHACRYLATE POLYMER AND
POLY (C₈₋₂₀) ALKYL(METH-)ACRYLATE POLYMER

DESCRIPTION OF THE INVENTION

Solvent dewaxing processes wherein waxy hydrocarbons oils, preferably waxy petroleum oils such as lube oils, specialty oils such as white oils or turbine or refrigerator oils, are dewaxed by admixture with a dewaxing aid and a dewaxing solvent, which may involve either incremental dilution or total predilution, yielding a mixture of waxy oil dewaxing aid and solvent, and the mixture is chilled (e.g., in surface chiller exchangers such as scraped or unscraped surface chillers or other indirect heat exchange apparatus means) to a temperature sufficient to precipitate at least a portion of the wax therefrom or, alternatively, the waxy oil either with or without predilution (incremental or total) may be contacted with cold dewaxing solvent so as to be directly chilled to the dewaxing temperature by means of the cold solvent, are improved by using as the dewaxing aid a combination dewaxing aid consisting of (a) substantially pure poly (C₂₄) alkylmethacrylate polymer and (b) a lower melting point poly (C₈-C₂₀) alkyl(meth)acrylate polymer.

By use of this combination dewaxing aid the dewaxing process is improved insofar as the filter rate is increased and the liquids/solids ratio is improved.

This combination dewaxing aid assists in solvent dewaxing processes wherein a waxy hydrocarbon oil is mixed with a normally liquid dewaxing solvent and a quantity of the recited dewaxing aid combination to form a mixture which is chilled (e.g., either directly using cold dewaxing solvent or indirectly in heat exchange apparatus), to form a slurry comprising wax

particles and a solution of dewaxed oil and dewaxing solvent. The dewaxing aid components (a) and (b) may be precombined one with the other for addition to the waxy oil to be dewaxed, either as such or diluted in a suitable wax-free oil to improve flow properties. Alternatively, the components may be added separately and simultaneously or separately and sequentially at the same or separate points within the process. Even in this embodiment the individual components (a) and (b) may be employed as such or diluted in a suitable wax-free oil to improve flow properties. The wax particles which are precipitated are subsequently separated from the dewaxed oil by any of a number of typical liquid/solid separation processes exemplified by, but not limited to, filtration, settling, centrifugation, etc.

The use of the combination (a) plus (b) results in increased feed filter rates and liquids/solids ratios as compared to using no aid at all or using either component individually.

The solvent dewaxing processes benefited by the use of the present combination dewaxing aid are those using normally liquid solvent systems, such as C₃-C₆ ketones, aromatic hydrocarbons, halogenated hydrocarbons and mixtures thereof, as well as auto-refrigerative dewaxing processes employing normally gaseous hydrocarbons, such as propane, propylene, butane, butene, etc. and mixtures of said auto-refrigeration hydrocarbons with the aforesaid ketones, e.g., propane/MEK.

BACKGROUND OF THE INVENTION

Waxes in wax-containing hydrocarbon oils are removed therefrom by chilling the oil to precipitate out the wax and then separating the solid wax particles from the dewaxed oil by solid/liquid separation

procedures, such as filtration, centrifugation, settling, etc. Industrial dewaxing processes include press dewaxing processes wherein the wax-containing oil, in the absence of solvent, is chilled to crystallize out the wax particles, which are then pressed out by a filter. In general, only light hydrocarbon oil fractions are treated by press dewaxing processes due to viscosity limitations. More widely used are solvent dewaxing processes wherein a waxy oil is mixed with a solvent and then chilled to precipitate the wax as tiny particles or crystals, thereby forming a slurry comprising solid wax particles and a solution of dewaxed oil containing dewaxing solvent. The slurry is then fed to a wax separator (e.g., filter, centrifuge, settler) wherein the wax is removed from the dewaxed oil and dewaxing solvent. Solvent dewaxing processes are used for heavier oil fractions, such as lubricating oil fractions and Bright stocks. Typical dewaxing solvents include low boiling point, normally gaseous autorefrigerative hydrocarbons, such as propane, propylene, butane, pentane, etc., ketones such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) and mixtures thereof, aromatic hydrocarbons such as benzene, toluene and xylene, as well as mixtures of ketones and aromatic hydrocarbons, such as MEK/toluene and acetone/benzene.

One of the factors tending to limit the capacity of a solvent dewaxing plant is the rate of wax filtration (and separation in general) from the dewaxed oil, which in turn is strongly influenced by the crystal structure of the precipitated wax. Although the crystal structure of the precipitated wax is influenced by various operating conditions in the dewaxing process, for any given feed it is most strongly influenced by the chilling conditions. The

size and crystal structure of the precipitated wax, occlusion of oil in the wax crystal and the condition of the oil left in the crystal are extremely varied and depend on the wax composition and precipitation conditions. These conditions also affect the separation (filtration) rate of the dewaxed oil from the wax and the yield of dewaxed oil. In some cases, most notably when the waxy oil is Bright stock, the wax crystals are of an extremely fine size and not all are separated by filtration, but some leave the filter with the dewaxed oil component which creates an objectionable haze in the oil.

One way of improving the filtration rate and minimizing haze formation is to add a dewaxing aid to the wax containing oil during the dewaxing process.

PRESENT INVENTION

Solvent dewaxing processes wherein waxy hydrocarbon oils, particularly petroleum oils, more particularly waxy lube oil, turbine oil, refrigerator oils, or white oil base stocks, are dewaxed by combining said waxy oil with a dewaxing solvent (e.g., either by incremental dilution or total predilution) and chilling the mixture (e.g., either directly using cold dewaxing solvent or in indirect heat exchanger means), are improved by using a combination dewaxing aid comprising a combination of (a) substantially pure poly (C₂₄) alkylmethacrylate polymer and (b) lower melting point poly (C₈-C₂₀) alkylmethacrylate polymers. Component (a) may be substantially pure poly (n-C₂₄) alkylmethacrylate polymer.

These components (a) and (b) may be employed in (V/V) ratios of (a) to (b) ranging from 10:90 to 90:10, preferably 10:90 to 50:50, more preferably 10:90 to 30:70. Dose levels, based on the active ingredients (a) and (b), range from 0.01 to 2.0 weight percent, preferably 0.1 to 2.0 weight percent, more preferably 0.1 to 1.0 weight percent active ingredient, relative to the weight of waxy hydrocarbon oil.

Component (a) is a substantially pure poly (C₂₄) alkylmethacrylate, preferably derived from normal C₂₄ alcohol, preferably as pure as possible. This poly (C₂₄) alkylmethacrylate preferably has a number average molecular weight as determined by gel permeation chromatography, equivalent polystyrene molecular weight, ranging from 50,000 to 500,000 M_n, more preferably 50,000 to 200,000, most preferably 60,000 to 100,000 M_n, and preferably a melting point of from 50°C to 80°C, more preferably from 50°C to 70°C,, most preferably from 60°C to 70°C.

Component (b) is similar to component (a) insofar as it is a poly alkyl (meth-) acrylate, but differs in having carbon sidechains of 8-20 carbons. It may also differ in having a somewhat lower number average molecular weight, e.g., in the range of from 5,000 to 200,000 M_n, preferably 10,000 to 100,000 M_n, most preferably 5,000 to 50,000 M_n. Component (b) melts at lower temperatures than component (a), the melting point preferably being of the order of from -30°C to 50°C, preferably -20°C to 40°C, most preferably -10°C to 30°C. It is the melting point of the polymer that determines its solubility (higher melting point implies lower solubility) and the solubility of the polymer determines which particular waxes the polymer will modify in the dewaxing process. The molecular weight of the polymer determines how effective a polymer of a given melting point (i.e., solubility) is in modifying the morphology of the waxes. The lower melting poly alkyl (meth-) acrylate may possess mixed alkyl group side chains having from 8 to 20 carbons. Examples of such poly alkyl methacrylates are Acryloid 144 and Acryloid 150, produced by Rohm and Haas Company. Acryloid 150 is generally described as having an average side chain carbon number >50% C₁₄ and lower, and a number average molecular weight of from 5,000 to 200,000, preferably 10,000 to 100,000. Acryloid

150 is reported as having side chains of predominantly C₁₀-C₂₀, (2% C₁₀, 30% C₁₂, 27% C₁₄, 14% C₁₆, 16% C₁₈, 11% C₂₀). Acryloid 144 is generally described as having side chains of carbon number >50% C₁₆ and higher and a number average molecular weight of 5,000 to 200,000, preferably 10,000 to 100,000. Acryloid 144 is reported as having side chains predominantly C₁₆-C₁₈ (4% C₁₂, 7% C₁₄, 39% C₁₆, 45% C₁₈ and 5% C₂₀). A sample of Acryloid 144 was evaluated and found to have a number average molecular weight of about 23,000 and a melting point of about 29°C, while a sample of Acryloid 150 was also evaluated and found to have a number average molecular weight of about 45,000 and a melting point of about -4°C.

A useful and easily reproducible identification of the polymers is made by relying on their melting points. Component A, the substantially pure C₂₄ alkylmethacrylate polymer, will preferably have a melting point of between 50°C to 80°C, more preferably 50°C to 70°C, most preferably 60°C to 70°C as determined by differential scanning calorimetry, while the commercially available component B, such as Acryloid 150 and Acryloid 144, will preferably have melting points in the -30°C to 50°C range, more preferably -20°C to 40°C, most preferably -10°C to 30°C as determined by differential scanning calorimetry (DSC).

The components (a) and (b) of the dewaxing aid are mixed together in the previously recited ratios and added at the desired dose level, either as such or dissolved in a suitable wax-free oil, such as mineral oil or other suitable solvent, such as toluene, benzene, propane, methylene chloride and the like, which imparts to the additive improved flow properties, pumpability, etc. Alternatively, the individual components (a) and (b) can be

employed separately (either as such or dissolved in a solvent as previously indicated) and introduced to the dewaxing process simultaneously or sequentially at separate points within the process. The aid, regardless of whether both components are pre-mixed one with the other, or employed separately/simultaneously or separately/ sequentially, with or without dilution, may be either mixed with the waxy oil prior to chilling or introduced during the chilling process, in either indirect chilling means, such as scraped surface chillers, or, alternatively, direct chilling means employing cold solvent. Preferred direct chilling means employing cold solvent injected along a number of stages therein, a number of which stages are highly agitated insuring instantaneous mixing, is the DILCHIL[®] (registered service mark of Exxon Research and Engineering Company) process as presented in U.S. Patent No. 3,773,650, hereby incorporated herein by reference.

The normally liquid dewaxing solvent that may be used in the present invention is not particularly critical; thus, any of the well-known, normally liquid dewaxing solvents can be used. For example, ketones having from 3 to 6 carbon atoms, such as acetone, dimethyl ketone, methyl ethyl ketone, methyl propyl ketone and methyl isobutyl ketone and mixtures thereof, aromatic hydrocarbons, such as benzene, xylene or toluene, mixtures of ketones and aromatic hydrocarbons, such as methyl ethyl ketone/toluene or methyl isobutyl ketone/toluene. Also useful are halogenated hydrocarbons, such as methylene chloride. Further, N-alkyl-pyrrolidones, such as N-methyl-pyrrolidone and N-ethyl-pyrrolidone may be used as the dewaxing solvent. Solvents which may be especially preferred for practicing the process of the present invention include aromatic hydrocarbon, such as

toluene, C₃-C₆ ketones, such as MEK, MIBK and mixtures thereof, mixtures of a ketone and an aromatic hydrocarbon, such as MEK/toluene, halogenated hydrocarbons, such as methylene chloride, and mixtures of acetone and methylene chloride.

Other dewaxing solvents which can be employed are the low boiling point, normally gaseous autorefrigerative hydrocarbons, such as C₂-C₅ alkanes and alkenes, including propane, propylene, butane, pentane and mixtures of such autorefrigerative hydrocarbons with the aforementioned ketones, propane/MEK, propane/MIBK, etc.

In an embodiment of the process of this invention a solution of dewaxing aid comprising components (a) and (b) is dissolved in an appropriate solvent, such as a light heating oil or a light dewaxed mineral oil fraction, is mixed into the wax-containing oil and the mixture heated to a temperature higher than the cloud point of the oil (typically about 50°C to 120°C). The mixture is introduced, along with the dewaxing solvent, into a chilling zone and chilled to a temperature necessary to yield the desired pour point for the resulting dewaxed oil. The chilling produces a slurry comprising dewaxed oil and solvent, along with solid particles of wax which contain the dewaxing aid. This slurry is then sent to a filter to separate the dewaxed oil and solvent from the wax particles. The dewaxing temperature to which the slurry is chilled varies depending on the feed and conditions. In general, this temperature will range from about 0°C to about -50°C. In the case where the dewaxing solvent comprises a mixture of a ketone and an aromatic hydrocarbon, such as methyl ethyl ketone/toluene, the dewaxing temperature will range from about -10°C to about -30°C.

Preferred dewaxing solvents used in the process of this invention include mixtures of ketones, such as MEK/MIBK, mixtures of a ketone and an aromatic hydrocarbon, as well as mixtures of a ketone and methylene chloride. The ratio of solvent to waxy oil would generally range from about 0.5 to 10 and preferably from about 2 to 7, by volume. The optimum amount of dewaxing solvent employed is, of course, determined by the wax content of the oil, viscosity, pretreatment and dewaxing conditions.

Typical oils, therefore, include distillates, preferably medium to heavy distillates, in the 400 neutral to 1,000 neutral range and Bright stocks. These waxy distillates may come from any natural or synthetic sources, such as from tar sands, shale oil, coal liquids, etc.

Preparation of C₂₄

(Lignoceryl) Methacrylate

Into a 250 ml, four-necked flask fitted with a mechanical stirrer, nitrogen inlet, thermometer port, syringe septum, and a Dean-Stark trap equipped with a reflux condenser, was charged 17.2 g. of methacrylic acid, 70.8 g. of lignoceryl (C₂₄) alcohol, and 0.1 g. of phenothiazine. While stirring, the mixture was heated to reflux under a blanket of nitrogen. By means of a syringe, 0.5 g. of tetraisopropyl titanate was added dropwise. Heating was continued until the evolution of water ceased. The infrared spectrum of the product confirmed the conversion of acid to ester.

Preparation of Poly

(Lignoceryl Methacrylate)

Into a 250 ml, four-necked flask fitted with a mechanical stirrer, nitrogen inlet, thermometer port, and a reflux condenser, was charged 50.0 g. of the above product and 100.0 g. of cyclohexane. With

stirring, the mixture was heated to reflux under a blanket of nitrogen. 0.3 g. of Lucidol 70[®]* was added. After three hours, the mixture had become very viscous and 0.1 g. of p-methoxy phenol was added. The reaction mixture was then poured into 500 ml of methanol and the polymer, poly (lignoceryl methacrylate) was isolated by vacuum filtration.

EXAMPLES

Four different dewaxing aids were evaluated in varying combinations in two different chilling process sequences. In one sequence (Process I) an incremental dilution procedure was employed utilizing a scraped surface chiller wherein the scraper revolved at 24 rpm, while in the other sequence (Process II) a total predilution procedure was employed using agitated chilling at 200 rpm in an indirect heat exchanger (no scraping). The procedure of Process II is the subject of a separation application, OP-3021, U. S. Serial No. 867,141, filed May 27, 1986 in the name of Theodore H. West. In Process II a 5.25 inch (13.335 cm) internal diameter scraped surface chiller is modified so that the scraper blades no longer touch the internal walls of the chilling unit. In the procedure used in this particular experiment the blades are one-half inch away from the chiller walls and are rotating at the aforementioned 200 rpm. Conditions for Process I and Process II are reported in Table A. The oil employed is described in Table I, while the aids employed are listed in Table II, with the results reported in Table III.

* "Lucidol" is a trade mark.

TABLE A

RUN CONDITIONS FOR PROCEDURES:
PROCESS I AND PROCESS II

1. Incremental Dilution (Process I)

Lab simulation of plant scraped surface chilling using a 5.25" (13.335 cm) diameter twin-bladed scraper in a 5.25" (13.335 cm) diameter vessel. Scraper speed is 24 revolutions per minute. Solvent addition is as follows :

	<u>Dilution</u> <u>V/V</u>	<u>Temperature</u> <u>°C</u>
Predilution	.6	60
1st Increment	.47	35
2nd Increment	.57	5
3rd Increment	.57	-10
Total Dilution	2.21 Solvent/Feed	-10

2. Predilution (Process II)

Lab simulator using a 4.25" (10.795 cm) diameter twin-bladed paddle in a 5.25" (13.335 cm) vessel. Paddle speed is 200 revolutions per minute.

Total predilution: 2.2 V/V at 50°C

Common Conditions to Both Processes:

Solvent - 40/60 V/V MEK/MIBK

Filter Temperature - -10°C

Chilling Range - 3°C/Minute

Performance evaluations by standard filter leaf.

TABLE I

FEED CHARACTERISTICS

Feed: Strathcona MCT 30 (600N)

Typical Properties

Feed Cloud - 51°C

Dis. Range - 393-582°C

Viscosity @ 100°C - 9.56 cst ($9.56 \times 10^{-6} \text{ m}^2/\text{s}$)

R.I.* @ 75°C - 1.4596

API Gravity - 28.8 (equivalent
to a specific gravity of 0.8827)

* R.I. signifies "refractive index"

TABLE II

DEWAXING AID COMPONENTS IN LABORATORY PROCESS
SIMULATIONS ON STRATHCONA 600N OIL.

Component Identification	Description	Molecular Weight*		Polymer Melting Point °C by DSC
		Number	Average	
(a)	Dialkylfumarate/vinyl acetate copolymer made from 70% C22, 15% C20 and 15% C18 alcohols.	8,600		49
(b)	Rohm and Haas Acryloid 144, a polyalkylmethacrylate polymer made from 4% C12, 7% C14, 39% C16, 45% C18, 5% C20 alcohols (average 16.5).	23,000		29
(c)	Rohm and Haas Acryloid 150, a polyalkylmethacrylate polymer made from 2% C10, 30% C12, 27% C14, 14% C16, 16% C18 and 11% C20 alcohols (average 12.5).	45,000		-4
(d)	Experimental polyalkylmethacrylate polymer made from a single carbon number normal C24 alcohol.	88,000		65

*Determined by gel permeation chromatography, equivalent polystyrene molecular weight.

TABLE III
DEWAXING PERFORMANCE FOR GOON OIL

Process	Dewaxing Aid		Wt. % Active Ingredient On Feed	Melting Point of Dewaxing Aid Mixture	Feed Filter Rate m^3/m^2-d	Wax Cake Liquids/ Solids	DNO Yield Wt. %	No Wash	Relative Feed Filter Rate
	Components	v/v Ratio							
I	-	Base Case	-		5.8	7.9	52.1	38.4	1.0
I	a/b	1/3	0.7		10.8	3.4	78.1		1.86
I	d/b	1/3	0.7		12.6	3.2	78.1	59.2	2.17
II	-	Base Case	-		10.0	6.6	59	40.	1.0
II	a/b	1/3	0.5	49 to 29	10.7	1.3	78.1	70.4	1.07
II	d/b	1/3	0.5	65 to 29	20.6	1.6	77.4	68.9	2.06
II	d/b/c	1/4/5	0.18		18.6	2.7	78.7		1.86
II	d/b/c	1/4/5	0.45	65 to 4	32	1.7	78.8		3.2
II	a/b/c	1/4/5	.47	49 to -4	14.8	2.3	78.8		1.5
II	d		.1	65	14.5	3.4	76.9		1.45

From this it is seen that the combination of substantially pure poly C₂₄ alkyl methacrylate with Acryloid 144/150 is significantly superior in performance as a dewaxing aid as compared to the combination of dialkylfumarate/vinyl acetate copolymer with Acryloid 144 or dialkylfumarate/vinyl acetate with Acryloid 144/150. The high melting point experimental substantially pure poly C₂₄ alkylmethacrylate (component D) extends the solubility range of the dewaxing aid mixture toward the first paraffin crystallizing out of solution (the high melting point waxes) and increases the temperature range within which crystal modification of the dewaxing aid is exerted on the wax/solvent/dewaxing aid mixture.

U.S. patent application Serial No. 867,141 filed 27 May 1986, referred to herein, corresponds to European Patent Application No. 87306510.6 (EP-A-0252761).

Length expressed in inch(") is converted to cm by multiplying by 2.54.

Kinematic viscosity expressed in cSt is converted to m²/s by multiplying by 1×10^{-6} .

CLAIMS

1. A solvent dewaxing process wherein a waxy hydrocarbon oil is contacted with a dewaxing solvent and a combination dewaxing aid and chilled so as to precipitate at least a portion of the wax present in said waxy hydrocarbon oil and the precipitated wax is removed by means of liquid/solid separation means yielding a dewaxed oil, wherein the combination dewaxing aid is a combination of component (A) which is substantially pure poly-(C₂₄) alkylmethacrylate polymer, and component (B) which is a lower melting point poly (C₈-C₂₀) alkyl(meth)acrylate polymer.

2. The process of claim 1 wherein the said dewaxing aid comprising components (A) and (B) is used in a (V/V) ratio of A/B in the range of from 10/90 to 90/10.

3. The process of claim 1 or claim 2 wherein component (A) has a number average molecular weight ranging from 50,000 to 500,000.

4. The process of any one of claims 1 to 3 wherein component (A) has a melting point of from 50°C to 80°C.

5. The process of any one of claims 1 to 4 wherein component (B) has a number average molecular weight ranging from 5,000 to 200,000.

6. The process of any one of claims 1 to 5 wherein component (B) has a melting point of from -30°C to 50°C.

7. The process of any one of claims 1 to 6 wherein the said dewaxing aid is used at a dose level of from 0.01 to 2 weight percent, based on the weight of waxy hydrocarbon oil.



8. The process of any one of claims 1 to 7 wherein component ^A(a) is substantially pure poly(n-C₂₄) alkylmethacrylate polymer.

