

58165.321

Field of the Invention

The invention relates to a process for dewaxing;
5 more particularly for dewaxing paraffin-containing crude oil products, by means of a solvent, using dewaxing aids based on polyacrylate.

Prior Art

10 Because of the presence of paraffin waxes in crude oil and in crude oil products, the treatment thereof is made considerably more difficult. This is mainly due to the fact that the waxes tend to crystallise below a certain temperature which varies for each product (cf.
15 Ullmanns Enzyklopädie der techn. Chemie 4th. ed., vol. 20, p. 548 ff, Verlag Chemie 1981). In lighter crude oil fractions, the wax may be removed by simply cooling it to the crystallisation temperature of the waxes and by pressing it out via filters.

20 The process, mainly employed in industry, for dewaxing paraffin-containing crude oils, uses solvents, mostly low-boiling aliphatic hydrocarbons such as pentane, hexane, heptane, octane etc., ketones such as acetone, methylethylketone, methylisobutylketone and the
25 like, also aromatic hydrocarbons such as benzene, toluene, xylene and the like, as well as mixtures of solvents. Here too, the wax-containing oil which had been mixed with solvents is cooled until the wax precipitates in the form of fine particles. The
30 isolated wax particles are supplied to a wax separator, i.e. a filter device, and are thus separated from the oil and the wax-removing solvent.

Difficulties in practical implementation are caused by the throughput capacity during the filtration which
35 is rarely constant and which is, for example, determined by the crystalline structure of the wax to be removed. This structure is influenced by various parameters of

the process, one of the most significant being the type of cooling. The nature of the waxes, the size and nature of the crystals thereof result in a relatively large variation of the texture and permeability of the filter cake, which naturally requires the filtration conditions to be adjusted. One of the undesired effects, is the formation of very fine wax crystallites which can only be filtered with difficulty and sometimes pass through the filters causing cloudiness in the oil.

10 In order to improve the filtration in general, in particular the rate of filtration and the oil yield, dewaxing aids, which are added to the oils during the dewaxing process have been developed in the industry.

Such dewaxing aids are normally polymers, for example of the α -olefin copolymer (OCP) type, ethylene-vinylacetate-copolymers (EVA) and polyalkyl(meth)acrylates of C_2 - C_{20} alcohols. US-A 4 451 353 discloses a dewaxing process, in which the wax-containing oil distillate is mixed with a solvent (dewaxing solvent) and a dewaxing aid based on polyacrylate, the mixture is cooled so that a thin pulp of solid wax particles is formed and the separation of the wax and the liquid parts from the dewaxed oil and solvent is carried out by filtration. Here, the dewaxing aid consists of:

- A. a polyacrylate and
- B. an n-alkylmethacrylate-polymer,

30 wherein the components (A) and (B) are used in a weight ratio of 1 : 100 to 100 : 1.

It is obvious from the claims and the specification of the US-A document that the methacrylate component must consist of esters of mainly linear i.e. unbranched C_{10} to C_{20} alcohols.

It was, therefore, apparent to the skilled man,

that this group of esters of methacrylic acid is particularly suitable as dewaxing aids. Though the existing theories on the effect of such polymer dewaxing aids try to give plausible explanations of how the polymer addition affects the crystallisation behaviour of the waxes, they do not offer any guidelines as to the choice of specific polymer compositions. (Cf. for example Ullmann, loc. cit. Vol. 20, Verlag Chemie 1981). It is therefore still the object to provide more effective dewaxing aids, possibly based on raw materials known per se, which do not produce, however, any significant changes in the implementation of the dewaxing technology of crude oils or crude oil products.

According to the present results, the process of the invention is able considerably to contribute to solving this problem.

The invention thus relates to a process for dewaxing paraffin-containing crude oil products, in particular mineral oil distillates, by means of a solvent, using at least one solvent suitable for dewaxing and a polymer dewaxing aid based on polyacrylate, whereby the products to be dewaxed are mixed with the solvent and the polymer dewaxing aid, the resultant mixture is cooled and the separated wax is removed, characterised in that a polymer mixture consisting of

I) a polymer P-1 of esters of acrylic acid having C₁₀-C₄₀ alcohols and

II) a polymer P-2 of esters of methacrylic acid having alkanols which consist of more than 10 wt.% of branched alkanol

is used as a dewaxing aid, with the proviso that the weight ratio of the components I) and II) in the mixture is 1 : 20 to 20 : 1,

preferably 1 : 10 to 10 : 1.

The amounts of polymers P1 and P2 to be added are in general 0.01 to 1 wt.%, based on the wax-containing substrates. This process is an advantageous direct
5 further development of prior art, e.g. US-A 4 451 353.

The process does not actually seem to be limited with regard to suitable wax-containing substrates based on crude oil, but from a practical point of view wax-containing distillation oils, in particular, are
10 suitable, more particularly those having a boiling range of from approx. 300 to approx. 600°C, a density of approx. 0.08 - 0.09 g/cc at 15°C, a viscosity of approx. 10 - 20 cS/100°C, a pour point of approx. 30 - 50°C and a wax content (dry) of approx. 10 - approx. 25 wt.%.

15 The distillation oils of those fractions which include lubrication oils and special oils in the boiling range of from 300 - 600°C, in particular those with an average boiling point of approx. 400 - 450°C, are of particular importance.

20 The solvents L used, according to the invention, for the dewaxing by means of a solvent, also correspond to those normally employed (see Prior Art). These include for example:

aliphatic hydrocarbons with a boiling point of <
25 150°C, inter alia the self-cooling gases such as propane, propylene, butane, pentane, also isooctane and the like, aromatic hydrocarbons such as for example toluene, xylene,

ketones such as for example acetone, dimethyl
30 ketone, methylethyl ketone, methylpropyl ketone, methylisobutyl ketone, optionally also

halogenated hydrocarbons, such as methylene chloride, dichloro ethane or N-alkyl pyrrolidone such as N-methyl pyrrolidone, N-ethyl pyrrolidone.

35 Mixtures of solvents e.g. of ketones and aromatic hydrocarbons such as methylethyl ketone/toluene or methyl isobutyl ketone/toluene are also advantageous.

The solvents L used in the process according to the invention are added in the usual amounts e.g. 0.5 - 10 parts by volume, preferably 2 - 7 parts by volume, based on the substrate to be dewaxed.

5

Polymers P-1 and P-2

The starting monomers for the polymerisation P-1 and P-2 (already used in industry for the preparation of polyalkyl(meth)acrylates (PMMA)) are known per se. The
10 polymerisation of monomers may also be carried out in a manner known per se.

The polyalkylacrylates P1 are synthesised from acrylic esters having from C_{10} - C_{40} alkanols, in particular, from acrylic esters having from C_{18} - C_{24}
15 alkanols, such as of the behenylalcohol type. The molecular weight M is, advantageously, within the range of from 10,000 to 1,500,000, preferably 50,000 to 500,000. It may be determined by means of gel permeation chromatography (cf. Kirk-Othmer Encyclopedia
20 of Chemical Technology, 3rd Ed., Vol. 18, pg. 209, 749, J. Wiley 1982).

The polyalkylmethacrylates P-2 have the characteristic feature that they contain more than 10 wt.%, preferably more than 15 wt.%, of esters of
25 methacrylic acid having branched alkyl groups.

The polymers P-2 are, in general, esters of from C_1 - C_{40} alkanols, preferably esters of from C_{10} - C_{24} , in particular C_{12} - C_{18} alcohols. Here, the polymer P-2 may contain 0.1 to 20 wt.%, in particular 1 - 15 wt.% of C_1 -
30 C_9 alkylmethacrylates. Special mention must be made of the alkanols having C_{12} - C_{18} hydrocarbon groups e.g. with an average C-number = 14, for example mixtures of ® DOBANOL 25L (Product of Shell AG) and tallow alcohol as well as mixtures of tallow alcohol and other alcohols,
35 such as i-decylalcohol.

The molecular weight M (see above) is generally within the range of from 3,000 to 500,000, preferably

50,000 to 300,000.

The radical polymerisation is, advantageously, carried out in a solvent e.g. a mineral oil which is compatible with the substrate to be dewaxed.

5 Conventional polymerisation initiators are used such as percompounds, in particular peresters, e.g. tert.butylperpivalate, tert.butylperoctoate, tert.butylperbenzoate and the like, in conventional amounts, for example 0.1 to 5, preferably 0.3 to 1 wt.%,
10 based on the monomers (cf. Th. Völker, H. Rauch-Puntigam, Acryl- und Methacrylverbindungen, Springer-Verlag 1967).

Molecular weight regulators may also be added to the preparation mixtures, in a manner known per se.
15 These regulators include, in particular, sulphur regulators, special mercaptans such as dodecylmercaptans, in conventional amounts such as 0.01 to 2 wt.%, based on the monomers.

The work is, advantageously, carried out under a protective gas such as CO₂.
20

In a suitable polymerisation vessel equipped with stirrer, the monomers are suitably dissolved in the solvent, optionally together with a regulator and initiator, and are firstly de-gassed e.g. by means of CO₂ snow and then heated. As a guide, they may, for
25 example, be heated to $80 \pm 10^\circ\text{C}$. In certain instances, the initiator may also be added to the heated mixture.

Optionally, further amounts of the monomer and initiator as well as of the regulator may be added. The
30 temperature normally rises e.g. to $140^\circ \pm 10^\circ\text{C}$. By supplying heat and/or further initiator, suitable conditions may, optionally, be created for the subsequent polymerisation. The total polymerisation takes just under 12 hours.

35 It may be of advantage if the polymer components P-1 and P-2 are used as preparations which have been individually prepared. They are then added, in the

above weight ratio and intended proportions, to the substrates to be dewaxed, either in substance or in a compatible solvent such as a wax-free mineral oil or one of the solvents L or mixtures thereof, whereby it is
5 important that the cloud point of the oils to be dewaxed is exceeded, for example by heating to 50 - 120°C. The polymers P-1 and P-2 may either be added jointly or separately. They may be added either before or during the cooling, but always in solvents which have been
10 cooled. The cooling may be carried out for example according to US-A 3 773 650. The mixture of the polymers P-1 and P-2 is advantageously added, together with the dewaxing solvent L, in a cooling zone and at a temperature adjusted to the pour point of the dewaxed
15 oil to be obtained.

The cooling step results in the formation of a slightly liquid pulp which, apart from solid wax particles, contains dewaxed oil and solvent L. The wax particles contain, as a rule, polymer P-1 and P-2. The
20 nature of the substrate to be dewaxed and the total method determine the temperature of cooling to be reached. The dewaxing is generally carried out in a temperature range of from 0°C to -50°C. If a solvent mixture L consisting of a ketone and an aromatic
25 hydrocarbon is used, then the dewaxing must be carried out at a temperature between -10°C and -30°C.

Special Effects

The results obtained with the mixtures of the
30 polymers P-1 and P-2 show unexpectedly that, when PAMA blend components having a greater or lower degree of branching of the alkyl groups are used, the effectiveness is clearly better and the synergistic effects are more obvious than with
35 polyalky(meth)acrylates which are largely linear. The results were obtained using very different dewaxing solvents and paraffin-containing substrates i.e. "Feedstocks", as demonstrated by the following Examples.

It can thus be assumed that they have general validity.

The following Examples serve to explain the invention. The determination of the specific viscosity η_{sp}/c is carried out according to DIN 7745 in chloroform

5 as the solvent, at 20°C.

Examples

A. Preparing polymers P-1 and P-2

5 Example 1

Preparing poly(behenylacrylate) P-1

51 kg of behenylacrylate (C_{18} - C_{24} acrylate), 9 kg of
10 100 N-oil and 0.051 kg of dodecylmercaptan are
introduced to a 100 l stirring vessel, de-gassed with CO_2
ice and heated to $70^\circ C$. Then, 0.191 kg of t-
butylperpivalate and 0.115 kg of t-butylperbenzoate are
added in order to start polymerisation. One hour after
15 reaching the temperature peak of $134^\circ C$, 0.077 kg of
dodecylmercaptan and 0.051 kg of t-butylperbenzoate are
added to the mixture, and a second polymerisation is
carried out for 3 hours at $130^\circ C$.

20 Mw (GPC, PMMA-calibration) = 560,000 g/mol
 η_{sp}/c ($CHCl_3$, $20^\circ C$) = 48 ml/g

Example 2

25 Preparing poly(C_{12} - C_{18} alkylmethacrylate) P-2-1

2.967 kg of a C_{12} - C_{18} alkylmethacrylate (average C-
number 14, 17.9% branched e.g. based on a mixture of
Dobanol 25 L[®] of Shell and tallow alcohol), 26.7 kg of
30 N-oil and 0.083 kg of t-butylperoctoate are introduced
to a 150 l stirring vessel, de-gassed with CO_2 ice and
heated to $85^\circ C$. Then, 37.033 kg of C_{12} - C_{18}
alkylmethacrylate and 0.0741 kg of t-butylperoctoate are
added within 3.5 hours. Two hours after the addition,
35 another 0.08 kg of t-butylperoctoate are added. After
another 5 hours, the mixture is diluted with 33.3 kg of
100 N-oil.

Mw (GPC, PMMA-calibration) = 410,000 g/mol

η_{sp}/c (CHCl₃, 20°C) = 65 ml/g

part by weight of branched esters = 17.9%.

5 Examples 3 - 5

Preparing poly(C₁₂-C₁₈ alkylmethacrylates) having different degrees of branching of the alkyl groups.

The preparation is carried out as described in Example 2. Instead of Dobanol/tallow alcohol, other alcohol mixtures are used. The subsequent table lists the characteristics of the polymers.

Example	Alkyl groups C-number	Parts by weight branched ester %	η_{sp}/c (20°C CHCl ₃)	
3	13 - 18	27.2	62	P-2-2
4	13 - 18	38.9	64	P-2-3
5	12 - 18	46.7	63	P-2-4
Comparison example	12 - 18	0	61	V-2-1

25 Example 6

Preparing a copolymer from i-C₁₀ methacrylate and tallow methacrylate P-2-5

37 kg of 100 N-oil, 4.111 kg of a methacrylic acid ester of an alcohol mixture consisting of 57.9 wt.% of tallow alcohol and 42.1 wt.% of i-decylalcohol are introduced to a 100 l stirring vessel and heated to 85°C. Then, the mixture is de-gassed by adding CO₂ ice and 0.016 kg of dodecylmercaptan and 0.032 kg of t-butylperoctoate are added. Within 3.5 hours, another 58.889 kg of methacrylic acid ester, 0.236 kg of dodecylmercaptan and 0.177 kg of t-butylperoctoate are added. Two hours after the addition, another 0.126 kg

of t-butylperoctoate is added. After another 5 hours, the polymerisation is finished.

η_{sp}/c (CHCl_3 , 20°C) = 22 ml/g

5 part by weight of branched esters = 45.2%

Example 7

Preparing poly($\text{C}_1\text{-C}_{18}$ alkylmethacrylate) P-2-6

10

1.976 kg of $\text{C}_{12}\text{-C}_{18}$ alkylmethacrylate (average C-number 14, 17.9% branched, e.g. based on a mixture of Dobanol 25 L[®] of Shell and tallow alcohol), 0.0297 kg of methylmethacrylate, 17.8 kg of 100 N-oil and 0.0551
15 kg of t-butylperoctoate are introduced into a 100 l stirring vessel, de-gassed with CO_2 ice and heated to 85°C . Then, within 3.5 hours, 24.664 kg of $\text{C}_{12}\text{-C}_{18}$ alkylmethacrylate, 6.223 kg of methylmethacrylate and 0.0494 kg of t-butylperoctoate are added. Two hours
20 after the addition, another 0.053 kg of t-butylperoctoate are added. After another 5 hours, the mixture is diluted with 22.18 kg of 100 N-oil.

η_{sp}/c (CHCl_3 , 20°C) = 34 ml/g

25 part by weight of branched esters = 14.5%

Comparison Example 2

Preparing an unbranched poly($\text{C}_{16}\text{-C}_{18}$ alkylmethacrylate) V2-2

30

4.889 kg of $\text{C}_{16}\text{-C}_{18}$ alkylmethacrylate (e.g. based on Alfol 1618 S[®] alcohol of Condea), 44.0 kg of 100 N-oil and 0.172 kg of t-butylperoctoate are introduced to a
35 150 l stirring vessel. After de-gassing with CO_2 ice, the mixture is heated to 85°C . Then within 3.5 hours, 51.111 kg of $\text{C}_{16}\text{-C}_{18}$ alkylmethacrylate and 0.153 kg of t-

butylperoctoate are added by means of a metering pump. Two hours after the addition, another 0.112 kg of t-butylperoctoate is added. After another 5 hours, the polymerisation is finished.

5

Mw (GPC, PMMA-calibration) = 220,000 g/mol

η_{sp}/c (CHCl_3 , 20°C) = 44 ml/g

part by weight of branched esters = 0%

- 10 B. Carrying out a laboratory filtration test for determining the oil yield and rate of filtration

The filtering apparatus consists of a steel filter with cover and cooling jacket and is cooled in rotation by means of a cryostat. Filter cloth from the dewaxing plant of the corresponding refinery is used. The volume of filtering is 100 ml. The filter is connected to a measuring cylinder via a glass attachment with two-way cock. A set vacuum may be applied to the filtering apparatus by means of a rotary vane oil pump, a pressure-reducing valve and a pressure gauge. The mineral oil distillate to be dewaxed is mixed, when heated (above the cloud point), with the dewaxing solvents and stirred until a clear solution is obtained. This mixture is cooled to the required filtering temperature by means of a cryostat controlling the temperature at a set speed. The filter is cooled to this temperature.

All the conditions of filtering such as the ratio between solvent and feedstock, the ratio between the solvents in mixtures, the rates of cooling and the filtering temperature correspond to the conditions used in the relevant refinery. Since working with propane causes problems in the laboratory, isooctane is used where appropriate instead of propane.

After reaching the filtering temperature, the mixture is supplied to the pre-cooled filter and a

vacuum is applied. The volume of the filtrate is measured as a function of the time, and the rate of filtering S is determined as a gradient of the linear plot of $V/2S^2$ relative to t/V , whereby V is the volume of
5 the filtrate, t the time in seconds and S the filter surface in cm^2 .

After distilling off the solvent by means of a rotary evaporator, optionally azeotropically, by means of a further solvent, the resultant dewaxed oil is dried to
10 weight constancy and the oil yield is determined gravimetrically. The determination of the oil content in the filtered-off paraffin is carried out according to ISO 2908.

Example 8

Dewaxing of Heavy Neutral 95 of a Spanish refinery

Solvent = isooctane, HN 95 : solvent = 1 : 4 (wt.). Cooling from +60°C to +5°C was carried out, whilst stirring, by placing the mixture into a cold bath of 0°C and cooling from +5°C to -20°C by placing the mixture into a cold bath of -22°C. Thereafter, the mixture was stirred for a further 20 minutes, then filtered.

Dewaxing additive				Dewaxing		
Polyalkyl-acrylate	Polyalkyl-methacrylate	% branched	Ratio of mixing	Filtering property F (cm ² /s)	Filtering time (sec.)	Oil yield %
-	-	-	-	1.1 x 10 ⁻²	2460	73.7
P-1	-	-	-	9 x 10 ⁻²	300	83.0
P-1	P-2-1	17.9	1 : 1	26 x 10 ⁻²	90	83.9
P-1	P-2-1	17.9	2 : 1	47 x 10 ⁻²	70	85.4
P-1	P-2-2	27.2	1 : 1	48 x 10 ⁻²	60	84.6
P-1	P-2-3	38.9	1 : 1	70 x 10 ⁻²	40	84.7
P-1	V-2-1	0	1 : 1	18 x 10 ⁻²	150	83.7

Example 9

Dewaxing of Bright Stock 95 of a Spanish refinery

Solvent: Isooctane

Conditions of the laboratory test as described in Example 8

Dewaxing additive				Dewaxing		
Polyalkyl- acrylate	Polyalkyl- methacrylate	% branched	Ratio of mixing	Filtering property F (cm ² /s)	Filtering time (sec.)	Oil yield %
-	-	-	-	0.09×10^{-2}	3 300	83
P-1	-	-	-	14×10^{-2}	180	83.4
-	P-2-1	17.9	-	4×10^{-2}	480	82.8
P-1	P-2-1	17.9	1 : 1	24×10^{-2}	90	83.2
P-1	P-2-1	17.9	3 : 1	25×10^{-2}	120	83.2
P-1	P-2-1	17.9	5 : 1	28×10^{-2}	90	83.4
P-1	P-2-1	17.9	10 : 1	23×10^{-2}	120	83.3
P-1	P-2-2	27.2	1 : 1	28×10^{-2}	90	82.8
P-1	P-2-3	38.9	1 : 1	23×10^{-2}	90	82.6
P-1	P-2-6	14.5	1 : 1	23×10^{-2}	100	83.3
-	V-2-2	0	-	4×10^{-2}	420	82.9
P-1	V-2-2	0	1 : 1	14×10^{-2}	180	82.8
P-1	V-2-1	0	1 : 1	22×10^{-2}	140	82.8

Example 10

Dewaxing of 500 N feedstock of a German refinery

Solvent ethylmethyl ketone : toluene = 1 : 1 (vol). The ratio between feedstock and solvent is 1 : 3. The mixture was cooled from +70°C to -17°C by 3.5°C/min. The filtration was carried out at -17°C.

Dewaxing additive					Dewaxing			
Poly-acrylate	Polymeth-acrylate	% branched	Ratio of mixing	Metering	Filtering Property F (cm ² /s)	Filtering time (sec.)	Oil Yield %	Oil content of paraffin %
-	-	-	-	-	1.5 x 10 ⁻²	1 100	42.4	63.4
P-1	-	-	-	250	3.6 x 10 ⁻²	420	57.3	-
				500	3.6 x 10 ⁻²	480	57.4	58
-	P-2-1	17.9	-	250	1.8 x 10 ⁻²	840	43.2	-
				500	1.4 x 10 ⁻²	1 260	44.9	-
P-1	P-2-1	17.9	1 : 1	250	4.1 x 10 ⁻²	420	57.1	-
				500	3.8 x 10 ⁻²	440	57.5	-
P-1	P-2-1	17.9	2 : 1	250	4.1 x 10 ⁻²	420	58.1	-
				500	4.5 x 10 ⁻²	380	59.2	55.3
P-1	P-2-1	17.9	1 : 2	250	3.6 x 10 ⁻²	480	53.5	-
				500	3.95 x 10 ⁻²	420	57.2	56
P-1	P-2-1	17.9	1 : 3	500	3.9 x 10 ⁻²	420	55.1	-
P-1	P-2-2	27.2	1 : 1	250	3.5 x 10 ⁻²	480	55.4	-
P-1	P-2-3	38.9	1 : 1	250	3.1 x 10 ⁻²	540	54.8	-
				500	3.8 x 10 ⁻²	420	58.0	-
P-1	P-2-4	46.1	1 : 1	250	3.4 x 10 ⁻²	540	53.2	-
				500	4.2 x 10 ⁻²	420	58.1	-
P-1	P-2-5	45.2	1 : 1	250	3.6 x 10 ⁻²	420	55.6	-
P-1	V-2-2	0	1 : 1	500	2.8 x 10 ⁻²	600	54.5	-
-	V-2-2	0	-	500	2.2 x 10 ⁻²	660	43.5	-
P-1	V-2-1	0	1 : 1	500	3.6 x 10 ⁻²	420	55.9	-



Claims

1. A process for dewaxing paraffin-containing crude oil products, by means of a solvent, using at least one solvent suitable for dewaxing and a polymer dewaxing adjuvant based on polyacrylate, whereby the products to be dewaxed are mixed with the solvent and the polymer dewaxing adjuvant, the resultant mixture is cooled and the separated wax is removed, and whereby a polymer mixture consisting of

- I a polymer P-1 of esters of acrylic acid having $C_{10}-C_{40}$ alkanols and
- 15 II a polymer P-2 of esters of methacrylic acid having alkanols

is used as dewaxing adjuvant, with the proviso that the weight ratio of the components I) and II) is 1 : 20 to 20 : 1, characterised in that the alkanols of the polymer P-2 contain branched alkanols in an amount of more than 10 wt.%. .

2. A process according to claim 1, characterised in that the weight ratio of the components I) and II) is 1 : 10 to 10 : 1.

3. A process according to claims 1 and 2, characterised in that the polymers P-1 are composed of acrylic esters having $C_{18}-C_{24}$ alkanols.

4. A process according to claims 1 and 2, characterised in that the polymers P-2 are composed of esters of methacrylic acid having C_1-C_{40} alkanols.

5. A process according to claim 4, characterised in that the polymer P-2 is composed of at least 80 wt.% of



esters of methacrylic acid having $C_{10}-C_{24}$ alkanols.

6. A process according to claim 5, characterised in
that the polymer P-2 is composed of up to 20 wt.% of
5 esters of methacrylic acid having C_1-C_9 alkanols.