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54 **A wax-containing crude oil or fuel oil comprising a pour point depressant.**

57 **A wax-containing crude oil or a wax-containing fuel oil, in particular a wax-containing residual fuel oil, comprising a small amount of a polymer having predominantly aliphatic hydrocarbon side chains of at least 14 carbon atoms, characterized in that the polymer has a branched backbone. This polymer shows an excellent pour point depression at low concentrations.**

A WAX-CONTAINING CRUDE OIL OR FUEL OIL COMPRISING  
A POUR POINT DEPRESSANT

This invention relates to a wax-containing crude oil or a wax-containing fuel oil, in particular a wax-containing residual fuel oil, comprising a small amount of a polymer having predominantly aliphatic hydrocarbon side chains of at least 14 carbon atoms, as pour point depressant.

Such oils are known from British patent specifications 1,161,188 and 1,154,966. The polymers described in this literature are linear polymers and although they show an excellent pour point depressing and flow improving effect, it has now been found that a still better pour point depressing, and flow improving effect can be obtained, in particular at low concentrations, if these polymers have a branched backbone.

This invention therefore relates to the above-mentioned crude oils or fuel oils, characterized in that the polymer has a branched backbone.

Such a polymer is especially suitable for depressing the pour point of crude oils and fuel oils containing at least 3%w of waxes with a melting point above 35°C and a boiling point above 350°C; such as the crude oils described in British patent specification 1,161,188 and the fuel oils described in British patent specification 1,154,966.

Suitable proportions of polymer are 0.001 to 2%w, preferably 0.005 to 0.05%w, on total oil composition.

Suitable polymers are copolymers of (A) at least one monoolefinically unsaturated aliphatic monomer having a saturated, preferably unbranched, hydrocarbon chain of at least 14 carbon atoms, optionally (B) a small amount, preferably up to 10%w on total monomers, of at least one other monoolefinically unsaturated monomer, preferably having a nitrogen-containing polar group, and (C) a controlled small amount, e.g. 0.01 to 1, preferably 0.01-0.5%w

on total monomers, of at least one polyolefinically unsaturated monomer which during polymerization results in a polymer having a branched backbone and substantially having no cross-linking.

Suitable monomers (A) are described in the above-mentioned  
5 British patent specification 1,161,188, in particular those having a saturated unbranched hydrocarbon chain of 18-30 carbon atoms as described in British patent specification 1,154,966.

Particularly preferred monomers (A) are alkyl(meth)acrylates, such as n-octadecyl- and n-eicosyl( $C_{20}$ ) (meth)acrylate, and  
10 dialkyl esters of unsaturated dicarboxylic acids, such as di-n-behenyl ( $C_{21}$ ) esters of maleic fumaric and itaconic acid.

Suitable monomers (B) are styrene, methyl styrene, tert. butyl styrene, vinyltoluene and mono-olefins, such as ethylene, propylene and butylene, and preferably are monoolefinically,  
15 unsaturated compounds having nitrogen-containing groups, such as acrylonitrile, acrylamide, p-aminostyrene, in particular those having heterocyclic nitrogen-containing groups, such as vinylpyridine, in particular 4-vinylpyridine, and N-vinylpyrrolidone.

Suitable monomers (C) are polyesters of alkanepolyols, such  
20 as diols, triols and tetraols, and unsaturated monocarboxylic acids, such as alkanediol di(meth)acrylates, trimethylolpropane tri(meth)acrylate and pentaerythritol tetra(meth)acrylate. Suitable polyols have 1 to 12 carbon atoms, such as ethanediol, propane-  
25 diol, butanediol, in particular 1,4-butanediol; polyvinyl compounds, such as divinylesters of saturated or unsaturated dicarboxylic acids such as succinic, maleic, fumaric and itaconic acids and polyvinyl aromatic compounds, in particular divinyl benzene. These and other suitable monomers (C) are described in British  
patent specification 1,575,507.

30 Suitable molecular weights of the present polymers are 10,000 to 1,000,000 preferably 20,000 - 250,000 (number average).

Other additives may additionally be used, such as other pour point depressants, anti-oxidants, anti-corrosion agents, metal deactivators, additives for preventing filter clogging and emul-  
35 sion formation.

The present invention furthermore relates to the polymers per se, to their preparation and to their use as dewaxing agents.

The present polymers can be prepared by radical polymerization in a solvent such as benzene, toluene or the xylenes with the aid of an initiator, e.g. dibenzoyl peroxide or azo-bis-isobutyronitrile (AIBN) and optionally a chain-transfer agent, such as an alkyl mercaptan or other mercaptan.

#### Examples 1, 2 and 3

A 300 ml 3-necked flask fitted with stirrer, thermometer and heating/cooling device was charged with: (in grams):

	1	2	3
behenyl acrylate	83.08	83.37	82.94
tert.-dodecylmercaptan	0.182	0.182	0.197
divinylbenzene (tech. grade)	0.042	-	-
butylene 1,4-dicrylate	-	0.101	0.233
toluene	68.47	67.87	67.65
AIBN	0.061	0.061	0.060

After replacing the air by nitrogen ( $O_2 < 25$  ppm) and heating to 69°C the polymerization was initiated by adding the AIBN as a solution in part of the toluene. The reaction temperature was controlled at  $70 \pm 1^\circ C$ . Duration of the copolymerization: 21 hours. Conversion:  $\geq 95\%$  (by  $O_3$ -titration)

Molecular weight distribution (by GPC (Gel Permeation Chromatography), applying the polyacrylate scale):

	1	2	3
$\bar{M}_n$	67800	71200	55200
$\bar{M}_w$	412000	400000	1030000

Example 4

In a 300 ml 3 necked flask fitted with stirrer thermometer and heating/cooling device were placed:

- 71.6 g behenyl acrylate
- 5 0.206 g butylene-1,4-diacrylate
- 3.53 g 4-vinyl pyridine
- 55.85 g toluene (part of)

After replacing the air by nitrogen ( $O_2 < 25$  ppm) and heating to  $70^\circ C$  copolymerization was initiated by adding a solution of 0.328 g of AIBN in part of the toluene. The temperature was controlled at  $71^\circ C \pm 1^\circ C$ . During the copolymerization the following solutions were added at programmed rates:

Solution A: containing 55%w of 4-vinylpyridine plus 0.673%w  
15 t-dodecyl mercaptan in toluene

Solution B: Containing 4%w of AIBN in toluene

Rates of addition:

Solution A:

Starting immediately after initiation this solution was added:

- 20 1) at rate of 11.8 ml/hr for 1.5 hours
- 2) " " " 3.93 "/ " 4.5 "
- 3) " " " 2.21 "/ " 4.0 "

Solution B:

Starting after 3 hours of reaction this solution was added at  
25 a rate of 3.78 ml/hr for 8 hours.

Duration of copolymerization: 21 hrs.

Conversion (by  $O_3$ -titration): 92.1%

Molecular weight distribution (by GPC applying the polyacrylate scale):

30  $M_n = 43700$ ;  $M_w = 212000$

TESTSI Pour point response

A

- 1) Swedish trial fuel (viscosity at 50°C 79 mm<sup>2</sup>/s, wax content 7.7%w, melting point of wax 63°C)

5 The ASTM D97 maximum pour points are shown in the following table. Undoped pour point 24°C. Additives added at 65°C.

Conc. ppm.w.	Pour point °C			
	X*	1	2	3
25	21	18	18	15
50	12	6	6	3
75	6	3	-6	-6
100	-3	-6	-9	-6
125	-6	-6	-9	-9
150	-9	-9	-12	-9
200	-9	-9	-15	-12
400	-12	-12	-15	-15

\* similar pour point depressant with linear backbone

- 2) Bombay High crude oil (Density at 15°C, 0.833 kg/l, viscosity at 40°C 3.2 mm<sup>2</sup>/s and at 60°C 2.2 mm<sup>2</sup>/s, wax content 16%w, melting point of wax 54°C).

5 The ASTM D97 pseudo-actual pour points are shown in the following table.

Undoped pour point 27°C. Additives added at 50°C.

Conc. ppmw.	Pour point, °C	
	X*	3
200	12	3
250	12	6
300	6	3
400	3	0
500	0	-3
700	-3	-3

\* Similar pour point depressant with linear backbone.

B

- 1) Swedish trial fuel (see IAl)

Conc. ppmw	Pour point, °C	
	Y*	4
75	18	12
100	12	0
125	3	-3
150	0	-6
400	-6	-6

\* similar pour point depressant with linear backbone.

- 2) Assam crude oil (Density at 15°C 0.878 kg/l, viscosity at 50°C 4.1 mm<sup>2</sup>/s, wax content 14%w, melting point of wax 57°C).

5 The ASTM D97 pseudo actual pour points are shown in the following table. Undoped pour point 33°C. Additives added at 50 and 60°C.

Pour point, °C

Conc.	Doping at 50°C		Doping at 60°C	
ppm w.	Y <sup>**</sup>	4	Y <sup>**</sup>	4
100	33	33	-	-
200	33	30	27	27
300	30	27	27	15
400	30	24	24	12
600	-	-	18	9

\*\* comparative pour point depressant with linear backbone.

## II Dewaxing performance

10 The oil was a bright stock waxy raffinate. This oil was dewaxed with a solvent mixture of methylethylketone and toluene (volume ratio 1:1), at a solvent/feed weight ratio of 3.85, a doping temperature of 70°C, a dewaxing temperature of -20°C, a cooling rate of 3.5°C/min and a filter vacuum of 0.2 bar.



Additive	Conc. ppmw.	Filtr. rate g/s m <sup>2</sup>	oil content wax %w	oil yield %w
none	-	80	28.4	4.9
X	200	141	16.8	8.4
	400	184	14.1	9.0
3	200	157	18.7	7.9
	400	195	11.1	9.8
Y	200	102	15.6	8.7
	400	137	11.5	9.7
4	200	115	12.9	9.3
	400	143	11.2	9.7

From the above data there appears to be a better performance with the branched polymers than with the corresponding linear polymers. The beneficial effect of branching is observed for pour point depression with both residual fuels and crude oils and for the

5 improvement in the bright stock dewaxing process.

C L A I M S

1. A wax-containing crude oil or a wax-containing fuel oil, in particular a wax-containing residual fuel oil, comprising a small amount of a polymer having predominantly aliphatic hydrocarbon side chains of at least 14 carbon atoms, characterized in that the  
5 polymer has a branched backbone.
2. An oil as claimed in claim 1, wherein the proportion of polymer is 0.001 to 2%w, in particular 0.005 to 0.05%w, based on the total oil composition.
3. An oil as claimed in claim 1 or 2 wherein the polymer is a  
10 copolymer of (A) at least one monoolefinically unsaturated aliphatic monomer having a saturated, preferably unbranched, hydrocarbon chain of at least 14 carbon atoms, optionally  
(B) a small amount of at least one other monoolefinically unsaturated monomer, and  
15 (C) a controlled small amount of at least one diolefinically unsaturated monomer which during polymerization results in a polymer having a branched backbone.
4. An oil as claimed in claim 3, wherein monomer (A) is an alkyl(meth)acrylate.
- 20 5. An oil as claimed in claim 3 or 4, wherein the amount of monomer (B) in the copolymer is 0-10%w on total monomers.
6. An oil as claimed in any one of claims 3-5, wherein monomer (B) has a nitrogen-containing polar group.
7. An oil as claimed in claim 6, wherein monomer (B) has a  
25 heterocyclic nitrogen-containing group.
8. An oil as claimed in any one of claims 3-7, wherein the amount of monomer (C) in the copolymer is 0.01 to 1%w on total monomers.
9. An oil as claimed in any one of claims 3-8, wherein monomer  
30 (C) is an alkanepolyol poly(meth)acrylate or a polyvinyl aromatic compound.
10. An oil as claimed in claim 1, substantially as hereinbefore described with special reference to the Examples.

11. A polymer as defined in any one of claims 1-10.
12. A process for the preparation of the polymer of claim 11, wherein the polymer is prepared by radical polymerization in a solvent with the aid of an initiator.
- 5 13. Use of the polymer of claim 11 as dewaxing agent.