

## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Crude Oil with improved Flow Properties

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, 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 the improvement of the flow properties of waxy crude oils.

Dependent on the field of production, crude oils may contain considerable quantities of wax. This wax gradually separated when the oil is cooled to below a certain temperature. The coherence of the separated wax crystals in spatial structures imparts a certain stiffness to the oil. At sufficiently low temperatures the oil may even completely solidify. As will be explained below, the presence of crystallized wax in crude oil has a detrimental effect on the flow properties and handleability of the oil.

When crude oil is produced from a well which passes through strata of lower temperatures than that of the oil-bearing formation, the oil coming into contact with the cold wall of the well may stiffen, which interferes with its transport to the surface. If production is temporarily interrupted, the oil may even solidify completely, which involves serious problems when production is resumed.

When oil is stored in tanks which are not provided with heating facilities or insulation, the oil in contact with the cold walls and bottom of the tank will cool down and, as a result, may stiffen. This leads to difficulties in pumping the oil from the tank; in fact, considerable quantities of stiffened oil may remain behind, which reduces the effective capacity of the tank.

This problem acquires even greater importance during transport of waxy crude oil in unheated tankers, where the walls of the compartments are partly formed by the ship's hull,

which is in direct contact with the cold sea water. Large quantities of stiffened oil remaining behind when the tanker is discharged reduce the carrying capacity of the ship; in addition, subsequent cargoes of crude oil may become contaminated.

The poorer flow properties of the oil at lower temperatures may also considerably interfere with the transport of the oil through a pipeline, either by pumping or by flow under the influence of prevailing pressure or level differences.

When waxy crude oils are pumped through a pipeline, high flow resistances may build up, thus calling for very high pump power. This may lead to high cost of transport, particularly in long-distance pipelines. If the resistance is very high, the available discharge pressure of the pump or the maximum permissible pressure determined by the strength of the pipe may be insufficient, so that the crude oil cannot be pumped.

If pumping is interrupted while the waxy crude oil is in the pipeline and the oil is warmer than the surroundings, the oil will cool down. The wax separated during cooling can freely form a spatial structure, which may extend over the entire cross section of the pipe and requires a very high pump pressure to be broken. If this pressure exceeds the available or permissible discharge pressure, transport cannot be resumed.

When a waxy crude is pumped through a pipeline as well as when it remains still, the oil may solidify on the cold pipe wall to form a deposit which remains behind. This reduces the capacity of the pipeline and entails the risk of contamination of subsequent batches of crude oil which have to be pumped through the pipeline.

Certain operations of crude oil refining, such as separation of water or sediment, for example by means of settling, centrifuging, filtration or coalescence, require the oil to be a thin

liquid. If, owing to the presence of crystallized wax the flow of the oil is insufficient, there is a possibility that these operations cannot be carried out at all or only to a limited extent.

Good flow properties of a crude oil are desired not only for transport and storage but also for many other reasons, for example, sampling, the transmission of pressure signals through narrow lines and the proper functioning of automatic equipment installed in refineries and along pipelines for purposes such as temperature and density measurements.

As appears from the above, the flow properties of a crude oil play a great part both during production and upon storage, transport and refining of the oil. It is therefore very important to minimize the adverse effect of wax on the flow properties of the oil.

To predict the flow behaviour of a crude oil under operational conditions, laboratory-scale measurements are carried out of quantities which may be regarded as characteristic of the flow behaviour of the oil, viz. pour point, viscosity and yield stress. The pour point is a criterion of the lowest permissible temperature during storage or transport or during a possible interruption of transport. The yield stress gives an impression of the shear stresses which may be expected if a stagnant oil is to be set in motion again. The viscosity is particularly related to the resistance which the oil experiences during pumping.

In general, it may be said that the lower the pour point, the lower the yield stress and the lower the viscosity the more easily handleable will the crude oil be in practice.

It has now been found that the flow properties of waxy crude oils can be improved in a simple manner by adding to the oil a small quantity of certain polymeric compounds with a special structure. These compounds, even at a low concentration, are capable of effecting a considerable reduction in pour point, yield stress and viscosity of waxy crude oils.

According to the invention a crude oil composition comprises a waxy crude oil and a polymer containing aliphatic hydrocarbon side chains with at least 14 carbon atoms, which polymer may be taken to have been obtained by polymerization of olefinically unsaturated compounds.

The term "a polymer" embraces a single polymer and a plurality of polymers. For the sake of brevity the terms "long hydrocarbon chains" and "long hydrocarbon side chains" will be used hereinafter to designate aliphatic hydrocarbon chains and aliphatic hydrocarbons side chains with at least 14 carbon atoms, respectively.

As the polymers are capable of improving the flow properties of waxy crude oils, the afore-mentioned problems which arise during production, storage, transport and refining of waxy crude oils owing to insufficient flow, can

be effectively solved by incorporating these polymers into the waxy crude oil.

When waxy crude oil is shipped, it is customary to keep the cargo during transport at an elevated temperature, for example by means of steam coils. The invention offers the possibility of shipping waxy crude oils without heating during the voyage. This means not only an appreciable saving for existing tankers, where the available energy can then be fully utilized to propel the ship, but particularly when constructing new tankers, where the installation of costly equipment for heating the cargo can be omitted. In spite of the cold shipment a low turn-out loss can be maintained. Shipment of unheated waxy crude oil compositions according to the invention permits the use of higher discharge pumping rates.

One of the most serious interruptions which may occur during transport of crude oil through a pipeline is line blocking after pumping at low temperatures or after the oil in the line has remained still. In this connection crude oils to be transported through pipelines have to meet stringent requirements as regards flow properties. It was for this reason that in the past various waxy crude oils were rejected for pipeline transport, so that these oils had to be transported in a different way. The present invention is preeminently suitable considerably to reduce the risk of line blocking during transport of such oils. The invention not only presents the possibility of reducing the required pump power, which will reduce the cost of pumping, but also the transport capacity of the line may be increased at the same pump power. Waxy crude oils which hitherto have been regarded as unacceptable for pipeline transport because of their flow properties, can now be rendered suitable for this purpose.

In contrast to known techniques to render waxy crude oils suitable for pipeline transport, which involve dilution of the waxy crude oil with a relatively large quantity of a thin oil with a low wax content as a carrier, the invention affords the advantage that, since only very small quantities of polymer are necessary, the waxy crude oil arrives, practically speaking, in its original condition at the destination. The use of carrier oils which afterwards cannot be separated from the original oil and may thus give rise to undesired contamination, is thus eliminated.

Some of the polymers have the characteristic feature of remaining as such in the distillation residue of the crude oil, and are capable also of improving the flow properties of this distillation residue. This is an important advantage of the invention, as these residues may be employed, for instance, as fuel oil for heating purposes and as fuel for low-speed diesel engines. In these applications the flow properties play a very important part.

In preferred polymers the long hydrocarbon

side chains are unbranched and saturated; that is, the long hydrocarbon side chains can be represented by the formula  $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_2-$ , in which  $n$  is at least 12. Preferably polymers are chosen with long hydrocarbon side chains having at least 16 and at most 30, in particularly at least 18 and at most 26, carbon atoms.

The polymers consist of a main chain built up of carbon atoms, which main chain carries long hydrocarbon side chains. These long hydrocarbon side chains may be attached either directly or indirectly to the main chain. In the former case there are no further atoms between the first carbon atom of the long hydrocarbon side chain and the carbon atom of the main chain to which the side chain is attached. If the long hydrocarbon side chain is attached indirectly to the main chain, one or more other atoms such as carbon, oxygen, sulphur, nitrogen or phosphorus atoms are present between the first carbon atom of the long hydrocarbon side chain and the carbon atom of the main chain to which the side chain is attached. Preferably the long hydrocarbon side chains are attached indirectly to the main chain, via one or more oxygen and/or carbon atoms. Some examples of polymers wherein the aliphatic hydrocarbon side chains are attached indirectly to the main chain via one or more oxygen and/or carbon atoms are polymers wherein the aliphatic hydrocarbon side chains are attached to the main chain via a carboxyl group or via an oxygen atom.

The preparation of such polymers may basically be carried out in two ways. In the first way, these polymers can be prepared by polymerization of olefinically unsaturated compounds, of which at least a proportion consists of olefinically unsaturated compounds containing, in addition to a polymerizable  $>\text{C}=\text{C}<$  group, a long hydrocarbon chain. Olefinically unsaturated compounds of this type will hereinafter be termed olefinically unsaturated compounds containing a long hydrocarbon chain. A second way in which these polymers can be prepared is by polymerization of olefinically unsaturated compounds containing no long hydrocarbon chain, and after-treatment of the polymer by means of which the long hydrocarbon chains are introduced into the polymer as side chains.

The polymers may be either homopolymers or copolymers.

If the preparation is carried out by direct polymerization, that is, without an after-treatment, the material to be polymerized invariably contains olefinically unsaturated compounds with long hydrocarbon chains. When homopolymers are prepared in this manner, the starting material is one specific olefinically unsaturated monomer with a long hydrocarbon chain. When copolymers are prepared in this manner, the starting material is a monomer mixture which, in addition to a specific ole-

finically unsaturated monomer with a long hydrocarbon chain, contains one or more other monomers which may or may not contain a long hydrocarbon chain.

If the preparation is carried out by indirect polymerization, i.e. including an after-treatment, the material to be polymerized need not contain any olefinically unsaturated compounds with long hydrocarbon chains. When homopolymers are prepared in this manner, the starting material is one specific olefinically unsaturated monomer from which a polymer can be prepared that is suitable for the desired after-treatment. When copolymers are thus prepared, the starting material may be, for example, a mixture of monomers which, in addition to one specific monomer from which can be prepared a polymer that is suitable for the desired after-treatment, contains one or more other monomers which may or may not contain a long hydrocarbon chain.

The molecular weight of the polymers may vary between wide limits. It is preferable to choose polymers whose number average molecular weight (number average  $M_n$ ) ranges between 1,000 and 1,000,000, in particular between 4,000 and 100,000, as determined by the osmometric method.

Depending upon the nature of the waxes present in the crude oil, it may be preferable to incorporate in this crude oil polymers wherein the long hydrocarbon side chains differ in chain length by a number of carbon atoms.

Some examples of olefinically unsaturated compounds containing long hydrocarbon chains, suitable for the preparation of the polymers, are: vinyl esters and allyl esters of saturated monocarboxylic acids, such as vinyl esters and allyl esters of arachidic acid and behenic acid; alkyl esters of unsaturated monocarboxylic acids, such as *n*-octadecyl acrylate and *n*-eicosyl methacrylate; alkyl amides of unsaturated monocarboxylic acids such as *n*-eicosyl acrylamide and *n*-docosyl methacrylamide; dialkyl esters of unsaturated dicarboxylic acids, such as di-*n*-octadecyl maleate and di-*n*-tetracosyl fumarate; dialkylamides of unsaturated dicarboxylic acids, such as di-*n*-eicosylmaleic diamide and di-*n*-docosylfumaric diamide; alkyl imides of unsaturated dicarboxylic acids, such as *n*-octadecylmaleic acid imide and *n*-eicosylmaleic acid imide; alkyl vinyl ethers, such as *n*-docosylvinyl ether and *n*-tetracosyl vinyl ether; and mono-olefins such as 1-octacosene and 1-docosene.

Some examples of olefinically unsaturated compounds which have no long hydrocarbon chains and with which the compounds which do possess such long hydrocarbon chains can be copolymerized are: vinyl esters of saturated monocarboxylic acids, such as vinyl acetate; alkyl esters of unsaturated mono- and dicarboxylic acids, such as methyl methacrylate and diethyl maleate; alkyl vinyl ethers, such as

octyl vinyl ether; and mono-olefins, such as ethylene and isobutylene.

Some examples of polymers obtained by direct polymerization of olefinically unsaturated compounds of which at least a proportion consists of olefinically unsaturated compounds with long hydrocarbon chains, are:

Copolymers of vinyl esters of saturated monocarboxylic acids with one another.

Copolymers of allyl esters of saturated monocarboxylic acids with one another.

Homopolymers of alkyl esters of unsaturated monocarboxylic acids.

Copolymers of alkyl esters of unsaturated monocarboxylic acids with one another.

Copolymers of alkyl esters of unsaturated monocarboxylic acids with dialkyl esters of unsaturated dicarboxylic acids or with mono-olefins.

Homopolymers of dialkyl esters of unsaturated dicarboxylic acids.

Copolymers of dialkyl esters of unsaturated dicarboxylic acids with mono-olefins.

Homopolymers of alkyl vinyl ethers.

Copolymers of alkyl vinyl ethers with one another.

If the polymers are copolymers they may be built up either of two or of more than two different monomers.

Examples of terpolymers are terpolymers obtained by copolymerization of a vinyl ester of a saturated monocarboxylic acid with a dialkyl ester of an unsaturated dicarboxylic acid and an alkyl ester of an unsaturated monocarboxylic acid.

Some examples of polymers obtained by polymerization of olefinically unsaturated compounds containing no long hydrocarbon chains and where, by after-treatment of the polymer, long hydrocarbon chains are introduced into the polymer as side chains, are:

Copolymers of unsaturated monocarboxylic acids, dicarboxylic acids or anhydrides thereof with mono-olefins, vinyl esters of saturated monocarboxylic acids or dialkyl esters of unsaturated di-carboxylic acids, which polymers have been after-treated with an aliphatic alcohol containing a long hydrocarbon chain.

Homopolymers of unsaturated alcohols, which polymers have been after-treated with an aliphatic carboxylic acid or aliphatic carboxylic chloride containing a long hydrocarbon chain.

Homopolymers of alkyl esters of unsaturated monocarboxylic acids or copolymers of alkyl esters of unsaturated monocarboxylic acids with one another or with mono-olefins, which polymers have been after-treated with an aliphatic amine containing a long hydrocarbon chain.

Copolymers of anhydride of unsaturated dicarboxylic acids with mono-olefins or other olefinically unsaturated compounds, which polymers have been after-treated with an ali-

phatic amine containing a long hydrocarbon chain.

Although polymers which contain aliphatic hydrocarbon side chains with at least 14 carbon atoms and which may be taken to have been obtained by polymerization of olefinically unsaturated compounds are in general suitable for improving the flow properties of waxy crude oils, preference is given to polymers which may be taken to have been obtained by polymerization of olefinically unsaturated compounds which consist at least partly of olefinically unsaturated aliphatic compounds containing a saturated hydrocarbon chain with at least 14 carbon atoms.

Particularly favourable results can be obtained by the use of the polymers mentioned below.

Homo- or copolymers of alkyl esters of unsaturated carboxylic acids, such as homo- or copolymers of alkyl esters of unsaturated monocarboxylic acids, in particular homo- or copolymers of alkyl acrylates. Examples of very suitable homopolymers of alkyl acrylates are homopolymers of n-tetradecyl acrylate, homopolymers of n-hexadecyl acrylate, homopolymers of n-octadecyl acrylate and homopolymers of n-eicosyl acrylate.

Homo- or copolymers of alkyl vinyl ethers, in particular homo-polymers of n-octadecyl vinyl ether.

Copolymers of a mono-olefin and a dialkyl ester of an unsaturated dicarboxylic acid with at least 14 carbon atoms in the alkyl groups, in particular copolymers of ethylene and di-n-octadecyl maleate.

Homo- or copolymers of vinyl esters of saturated monocarboxylic acids, in particular copolymers of vinyl esters of hydrogenated rape-seed oil fatty acids.

Homo- or copolymers of alkyl esters of unsaturated carboxylic acids, such as homo- or copolymers of alkyl esters of unsaturated monocarboxylic acids, in particular homo- or copolymers of alkyl acrylates, are preferred. Most preferred are homo- or copolymers of alkyl acrylates having 18 to 26 carbon atoms in the alkyl group, in particular a homopolymer of n-octadecyl acrylate and a homopolymer of n-eicosyl acrylate.

The concentration in which the polymers may be applied may vary between wide limits, depending upon the nature, the structure and the molecular weight of the polymer to be employed, the nature of and the quantity of the paraffin waxes present in the crude oil, and the improvement of the flow properties desired. In some instances a quantity of 0.001 %w, calculated on the crude oil composition, is sufficient for attaining the desired improvement in flow properties. In most cases, a quantity of 2.0 %w is amply sufficient. Preferably, from 0.002 %w to 0.2 %w of the polymers is incorporated into the crude oil.

The polymers have so far been referred to

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as flow improvers of waxy crude oils. Their properties include the ability to reduce the pour point, the viscosity and the yield stress of waxy crude oils. With regard to each of these properties separately they can, if desired, also be designated as pour point depressants, viscosity depressants and yield stress depressants. In this connection it should be observed that a compound may in general be regarded as belonging to the class of pour point depressants only if it is capable of effecting a pour point reduction of at least 6°C when it is applied in a concentration of at most 0.2 %w.

The waxy crude oil to which the polymers may be added may consist of one waxy crude oil or a mixture of waxy crude oils. If desired, the polymers can also be incorporated in mixtures consisting of one or more waxy crude oils and one or more non-waxy crudes.

The present polymers are particularly important as additives to ease the transport of waxy crude oils. This can take place at least partly by pumping. It can also take place at least partly through a pipeline, by tankers or by other means. The polymers can also be used in oil wells producing waxy crude to prevent the formation of waxy deposits or to dissolve such deposits formed on the walls of the well.

The invention is illustrated by the following experiments:

Seven polymers were mixed in various different concentrations with the following six crude oils.

#### CRUDE OIL I

A crude oil originating from South America, with a kinematic viscosity of 8.8 cS at 37.8°C, a wax content of 9.7 %w (setting point of the wax 58.5°C), a pour point of -10°C, determined according to method A, and a pour point of -4°C, determined according to method C. The methods of pour point determination are described below.

#### CRUDE OIL II

A crude oil originating from South America, with a kinematic viscosity of 1.82 cS at 60°C, a wax content of 17.5 %w (setting point of the wax 54.5°C), a pour point of 26°C, determined according to method A, and a pour point of 29°C, determined according to method C.

#### CRUDE OIL III

A crude oil originating from North Africa, with a kinematic viscosity of 5.13 cS at 37.8°C, a wax content of 7.0 %w (setting point of the wax 58.0°C), a pour point of -4°C, determined according to method A, and a pour point of +2°C, determined according to method C.

#### CRUDE OIL IV

A crude oil originating from North Africa, with a kinematic viscosity of 3.66 cS at

37.8°C, a wax content of 7.8 %w (setting point of the wax 51.5°C), a pour point of +2°C, determined according to method A, and a pour point of +5°C, determined according to method C.

#### CRUDE OIL V

A crude oil originating from West Africa, with a kinematic viscosity of 15.0 cS at 50°C, a wax content of 17.8 %w (setting point of the wax 56.0°C), a pour point of 20°C, determined according to method B, and a pour point of 32°C, determined according to method D.

#### CRUDE OIL VI

A crude oil originating from West Africa, with a kinematic viscosity of 2.70 cS at 50°C, a wax content of 7.0 %w (setting point of the wax 54.0°C), a pour point of 11°C, determined according to method A, and a pour point of 14°C, determined according to method C.

As regards the methods for the determination of the pour point of waxy crude oils, the following points should be noted.

The pour point of a waxy crude oil is often dependent upon the thermal pre-treatment to which the oil has been subjected.

On the basis of whether or not a thermal pre-treatment is carried out, the methods suitable for the determination of the pour point of waxy crude oils may be divided into two groups, viz.:

(1) methods where the pour point is determined on a sample that is not reheated before the determination;

(2) methods where the sample is heated to 46°C just before the determination.

Although the thermal treatment is some instances results in a higher pour point, it is perhaps less realistic, as the pertaining crude oil is not subjected to this thermal cycle in actual practice.

From the experiments described it appears that the polymers are capable of depressing the pour point in a general sense, i.e. independent of whether or not the thermal pre-treatment is carried out.

The pour point determination methods A, B, C, and D, mentioned above, were carried out as follows.

#### METHOD A

Two samples of a crude oil are heated to 65°C, at which temperature the desired quantity of polymer is added to one of the samples. After cooling the samples to room temperature the pour point is determined as described in ASTM D 97-66/IP 15/67, but without the reheating to 46°C.

#### METHOD B

As described under method A, but with initial heating to 100°C instead of 65°C.

## METHOD C

Two samples of a crude oil are heated to 65°C, at which temperature the desired quantity of polymer is added to one of the samples. After cooling to room temperature the samples are stored at room temperature for a least 24 hours. Subsequently, the pour point is determined as described in ASTM D 97-66/IP 15/67. This pour point is usually specified as the ASTM maximum pour point or the IP maximum pour point.

## METHOD D

As described under method C, but with initial heating to 100°C instead of 65°C. The results of the experiments are given in Table I, in which the number of degrees Centigrade is specified at which the pour point determined according to any one of methods A-D is depressed after addition of the various polymers.

For comparison two related polymers (a poly-n-C<sub>10</sub> alkyl methacrylate and a poly n-C<sub>12</sub> alkyl methacrylate) were tested as pour point depressants in crude oil III. The results of these experiments (with polymers outside the scope of the present invention) are also incorporated in Table 1.

## YIELD STRESS

A sample of crude oil is heated to 65°C, at which temperature the desired quantity of polymer is added to the sample. After cooling to room temperature a metal U-tube with a length of 54 cm and an inside diameter of 3.8 mm is filled with the oil to be tested. Subsequently, the oil in the tube is cooled

down to the determination temperature, after which the pressure on one of the U-tube limbs is gradually raised.

The pressure (P<sub>o</sub>) at which the first flow is observed is used for calculating the yield stress. The yield stress (defined as the shear stress required for setting a congealed oil into motion) is calculated from the observed P<sub>o</sub>, with the aid of the equation:

$$\gamma_o = \frac{P_o D}{4 L},$$

where:

$\gamma_o$  = yield stress, dyn/cm<sup>2</sup>

P<sub>o</sub> = pressure at which the first flow is observed, dyn/cm<sup>2</sup>

D = diameter of the tube, cm

L = length of the tube, cm

The yield stress of a sample of crude oil VI to which 0.005 %w of poly n-C<sub>10</sub> alkyl acrylate had been added was determined at two different temperatures in the manner described above, and was compared with the yield stress of a sample of crude oil VI which had been subjected to a similar thermal pre-treatment without any additive. The results obtained are given below:

## CRUDE OIL VI:

yield stress at 8°C: 302 dyn/cm<sup>2</sup>

Crude oil VI + 0.005 %w of poly-n-C<sub>10</sub> alkyl acrylate:

yield stress at 8°C: <10 dyn/cm<sup>2</sup>

yield stress at 0°C: 17 dyn/cm<sup>2</sup>.

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### Depression of the pour

[illegible]

point in °C

[illegible]

*Behaviour during distillation*

To two samples of crude oil VI (pour point as determined according to method A +11°C) was added 0.03%w of poly-n-C<sub>18</sub> alkyl acrylate and 0.03%w of poly-n-C<sub>20</sub> alkyl acrylate, respectively. In each case the pour point, determined according to method A, dropped to -19°C.

In order to determine the behaviour of

the polymers during distillation, a 300°C<sup>+</sup> residue was prepared according to ASTM D 86-66 (atmospheric distillation to a maximum vapour temperature of 300°C) from the untreated crude oil and from the two crude oil samples to which polymer had been added. The residues showed the following pour points (determined according to ASTM D 97-66).

Residue from untreated crude oil VI

Residue from crude oil VI + 0.03%w of poly-n-C<sub>18</sub> alkyl acrylate

Residue from crude oil VI + 0.03%w of poly-n-C<sub>20</sub> alkyl acrylate

maximum pour point 38°C  
minimum pour point 35°C  
maximum pour point 32°C  
minimum pour point 17°C  
maximum pour point 23°C  
minimum pour point 17°C

**VISCOSITY**

Since waxy crude oils at lower temperatures behave as non-Newtonian liquids, the viscosity of such oils can be determined in a realistic manner only in a viscometer wherein either the shearing stress or the rate of shear can be adjusted between narrow limits and be kept constant. Very suitable for determining viscosities of waxy crude oils is the Ferranti Portable Viscometer, Model VL, a so-called Couette coaxial-cylindrical viscometer of the constant - shear - rate type.

A sample of crude oil is heated to 65°C, at which temperature the desired quantity of polymer is added to the sample. After cooling down to room temperature the reservoir of the viscometer is filled with the oil to be tested.

The viscosity of a sample of crude oil VI to which 0.005%w of poly-n-C<sub>18</sub> alkyl acrylate had been added was determined in the manner described above, and was compared with the viscosity of a sample of crude oil VI which had been subjected to a similar thermal pre-treatment without any additive. The results obtained are given below.

Crude oil VI + 0.005%w of poly-n-C<sub>18</sub> alkyl acrylate

Equilibrium viscosity at 5°C and shear rate of 318 s<sup>-1</sup> = 12 cP.

**DEMULSIBILITY**

The influence of the demulsifying properties of the present polymers on emulsions of crude oil and water was studied by means of the following experiment.

A crude oil sample was heated to 65°C, at which temperature the desired quantity of polymer was added. The oil was then cooled to 18°C at a rate of 3°C per minute. Finally the oil was emulsified with 1 part of water per 4 parts of oil. The water contained 1.5%w sodium chloride and 0.34%w sodium bicarbonate. The demulsifying properties of the oil were measured on the basis of the quantity of water separated from the emulsion after a given time (expressed as percentage of the quantity of water added).

A sample of crude oil VI to which 0.005%w of poly-n-C<sub>18</sub> alkyl acrylate had been added, was compared in this experiment with a sample of crude oil VI without polymer.

**CRUDE OIL VI**

Equilibrium viscosity at 5°C and shear rate of 318 s<sup>-1</sup> = 30 cP.

The results are given below.

|                                                                      | % water separated |                |
|----------------------------------------------------------------------|-------------------|----------------|
|                                                                      | after 24 hours    | after 48 hours |
| Crude oil VI                                                         | 0                 | 0              |
| Crude oil VI +<br>0.005 %w poly-n-<br>C <sub>18</sub> alkyl acrylate | 16                | 42             |

- To determine the influence of the present polymers on the pumpability of waxy crude oil under practical conditions, some field trials were carried out. The oil used for this purpose was a waxy crude from North Africa with a kinematic viscosity of 8.5 cS at 50°C, a wax content of 14.0 %w (setting point of the wax 56°C) and an ASTM maximum pour point of +23°C (crude oil VII). Two cargoes of this crude were shipped from North Africa to West Europe by a 50,000-ton tanker.

## 1ST VOYAGE

20,000 tons of unheated doped crude oil VII and

30,000 tons of unheated undoped crude oil VII.

The flow improver used was 0.015 %w poly-n-C<sub>18</sub> alkyl acrylate.

Temperature during loading in North Africa: 100°F.

Temperature of the cargo on arrival in West Europe: 75°F.

Average rate of cooling: 3°F per day.

*Properties of the undoped oil*

(a) Actual pour point: 20°C. (The actual pour point is determined as described in ASTM D 97-66/IP 15/67, but without the reheating to 46°C.)

## (b) Yield stress

| Test temperature<br>°C | Yield stress<br>dyn/cm <sup>2</sup> |
|------------------------|-------------------------------------|
| 13.1                   | 83                                  |
| 9.8                    | 286                                 |
| 7.1                    | 900                                 |

## (c) Viscosity (Ferranti viscometer)

| rate of<br>shear,<br>sec <sup>-1</sup> |        |       |        |
|----------------------------------------|--------|-------|--------|
| test<br>tempera-<br>ture, °C.          | 36.9   | 318   | 628    |
| 22.1                                   | 113 cP | 44 cP | 39 cP  |
| 18.9                                   | 154 cP | 56 cP | >47 cP |
| 15.8                                   | 196 cP | 64 cP | >47 cP |

*Note:* The yield stress and viscosity (Ferranti viscometer) values for crude oil VII mentioned in this specification were determined as described above for crude oil VI, but without heating to 65°C.

*Properties of the doped oil*

- (a) Actual pour point: 2°C.  
(b) Yield stress

| Test temperature<br>°C | Yield stress<br>dyn/cm <sup>2</sup> |
|------------------------|-------------------------------------|
| 9.8                    | 17                                  |
| 7.1                    | 43                                  |
| 3.8                    | 54                                  |
| 0.0                    | 74                                  |

- (c) Viscosity (Ferranti viscometer)

| rate<br>shear,<br>sec <sup>-1</sup><br>test<br>tempera-<br>ture, °C | 36.9   | 164   | 628    |
|---------------------------------------------------------------------|--------|-------|--------|
| 21.4                                                                | 56 cP  | 34 cP | 32 cP  |
| 18.3                                                                | 82 cP  | 46 cP | 37 cP  |
| 15.5                                                                | 110 cP | 52 cP | 41 cP  |
| 9.7                                                                 | 159 cP | 69 cP | >47 cP |
| 5.2                                                                 | 223 cP | 87 cP | >47 cP |

When the cargo was loaded in North Africa for the 1st voyage, three samples of crude oil VII were taken. Two of these samples were doped with polymers to form compositions according to the invention; the third sample was not doped. The samples were kept in dewar vessels, which were stored during the voyage in an insulated wooden case. On arrival in West Europe the samples were stored in a space at a temperature of about 13°C. After being stored for about 1 week the yield stress and viscosity of the samples were deter-

mined. The results are given below.

- Sample 1: crude oil VII.  
Sample 2: crude oil VII + 0.02%w poly-n-C<sub>18</sub> alkyl acrylate.  
Sample 3: crude oil VII + 0.02%w poly-n-C<sub>20</sub> alkyl acrylate.  
(a) Yield stress (test temperature 5°C).  
Sample 1: 467 dyn/cm<sup>2</sup>.  
Sample 2: 398 dyn/cm<sup>2</sup>.  
Sample 3: 143 dyn/cm<sup>2</sup>.  
(b) Viscosity (Ferranti viscometer)

15

25

|          | rate of<br>shear,<br>sec <sup>-1</sup><br>test<br>tempera-<br>ture, °C | 36.9   | 164     | 328   |
|----------|------------------------------------------------------------------------|--------|---------|-------|
| Sample 1 | 13.6                                                                   | 342 cP | >230 cP |       |
| Sample 2 | 13.2                                                                   | 206 cP | 90 cP   | 63 cP |
| Sample 3 | 13.0                                                                   | 131 cP | 80 cP   | 63 cP |

5 On arrival of the tanker in West Europe restart trials were made with the doped and the undoped crude oil in a pipe circuit consisting of 2000 m 2" non-insulated pipe and 2000 m 24" insulated pipe. The trials were performed as follows.

10 The oil under test was pumped at its temperature of arrival into the circuit, after which the pump was stopped for some days (shut-in time), so that the oil was allowed to cool down. Subsequently the pressure at the inlet of the circuit was raised by means of a pump in

steps until the oil began to flow. The yield stress was calculated from the highest pressure drop over the non-insulated (i.e. cooled) pipe section by means of the afore-mentioned formula:

$$\gamma_0 = \frac{P_0 D}{4L}$$

The results of the restart trials are mentioned below.

#### Restart trials with undoped and doped crude

|                                                          | undoped<br>crude | doped<br>crude |
|----------------------------------------------------------|------------------|----------------|
| Shut-in time, h                                          | 78               | 102            |
| Average temperature non-insulated pipe, °C.              | 9                | 3              |
| Ambient temperature, °C                                  | 4                | 0              |
| Pressure drop in non-insulated pipe, kgf/cm <sup>2</sup> | 6.3              | <0.75          |
| Yield stress related to pipe wall, dyn/cm <sup>2</sup>   | 400              | <47            |

#### 2ND VOYAGE

25 20,000 tons of unheated doped crude oil VII and 30,000 tons of unheated undoped crude oil VII.

The flow improver used was 0.015%w poly-n-C<sub>18</sub> alkyl acrylate.

Temperature during loading in North Africa: 102°F.

Temperature of the cargo on arrival in West Europe: 78°F.

Average rate of cooling: 3°F per day.

*Properties of the undoped oil*

- (a) Actual pour point: 20°C.  
 (b) Yield stress

| Test temperature<br>°C | Yield stress<br>dyn/cm <sup>2</sup> |
|------------------------|-------------------------------------|
| 17.1                   | 118                                 |
| 13.6                   | 302                                 |
| 10.4                   | 415                                 |

- (c) Viscosity (Ferranti viscometer)

| rate of<br>shear,<br>sec <sup>-1</sup><br>test<br>tempera-<br>ture, °C | 36.9   | 164   | 328   |
|------------------------------------------------------------------------|--------|-------|-------|
| 15.0                                                                   | 192 cP | —     | —     |
| 22.7                                                                   | 114 cP | 57 cP | 45 cP |

*Properties of the doped oil*

- (a) Actual pour point: 2°C.  
 (b) Yield stress

| Test temperature<br>°C | Yield stress<br>dyn/cm <sup>2</sup> |
|------------------------|-------------------------------------|
| 6.0                    | 37                                  |
| 1.4                    | 76                                  |
| -3.1                   | 206                                 |

- (c) Viscosity (Ferranti viscometer)

| rate of<br>shear,<br>sec <sup>-1</sup><br>test<br>tempera-<br>ture, °C | 36.9   | 164    | 328   |
|------------------------------------------------------------------------|--------|--------|-------|
| 22.7                                                                   | 37 cP  | 30 cP  | 29 cP |
| 10.2                                                                   | 131 cP | 81 cP  | 65 cP |
| 4.8                                                                    | 210 cP | 119 cP | 93 cP |

It was found that the rate of discharge of the doped oil from the tanker was 15% higher than that of the undoped oil.

- 5 After discharge of the undoped oil stored on arrival in West Europe in unheated floating-roof tanks a solid wax-oil mixture remained behind on the tank wall. This was not the case with the doped oil.

WHAT WE CLAIM IS:—

- 10 1. A crude oil composition comprising a waxy crude oil and a polymer containing aliphatic hydrocarbon side chains with at least 14 carbon atoms, which polymer may be taken to have been obtained by polymerization of olefinically unsaturated compounds.

- 15 2. A crude oil composition as claimed in claim 1, in which the polymer may be taken to have been obtained by polymerization of olefinically unsaturated compounds which consist at least partly of olefinically unsaturated aliphatic compounds containing a saturated hydrocarbon chain with at least 14 carbon atoms.

- 20 3. A crude oil composition as claimed in claim 1 or claim 2, in which the polymer contains unbranched saturated aliphatic hydrocarbon side chains of the formula  $-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_3$  in which  $n$  is at least 12.

- 25 4. A crude oil composition as claimed in any one of the preceding claims, in which the polymer contains aliphatic hydrocarbon side chains with at least 16 and at most 30 carbon atoms.

- 30 5. A crude oil composition as claimed in claim 4, in which the polymer contains aliphatic hydrocarbon side chains with at least 18 and at most 26 carbon atoms.

- 35 6. A crude oil composition as claimed in any one of the preceding claims, in which the aliphatic hydrocarbon side chains in the polymer are attached indirectly to the main chain via one or more oxygen and/or carbon atoms.

- 40 7. A crude oil composition as claimed in any one of the preceding claims, in which the polymer has been obtained by polymerization of an olefinically unsaturated compound or compounds, that compound or at least one of those compounds containing, in addition to a polymerizable  $>\text{C}=\text{C}<$  group, an aliphatic hydrocarbon chain with at least 14 carbon atoms.

- 45 8. A crude oil composition as claimed in any one of the preceding claims, in which the number average molecular weight of the polymer is in the range between 1,000 and 1,000,000, as determined by the osmometric method.

- 50 9. A crude oil composition as claimed in claim 8, in which the number average molecular weight of the polymer is in the range between 4,000 and 100,000.

- 55 10. A crude oil composition as claimed in any one of the preceding claims, in which the

polymer contains aliphatic hydrocarbon side chains with at least 14 carbon atoms, which chains differ in length by a number of carbon atoms.

11. A crude oil composition as claimed in any one of the preceding claims, in which the polymer is a homo- or copolymer of alkyl ester or esters of unsaturated carboxylic acid or acids. 70

12. A crude oil composition as claimed in claim 11, in which the polymer is a homo- or copolymer of alkyl ester or esters of unsaturated monocarboxylic acid or acids. 75

13. A crude oil composition as claimed in claim 12, in which the polymer is a homo- or copolymer of alkyl acrylate or alkyl acrylates. 80

14. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-tetradecyl acrylate. 85

15. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-hexadecyl acrylate.

16. A crude oil composition as claimed in claim 13 in which the polymer is a copolymer of alkyl acrylates with 18 to 26 carbon atoms in the alkyl group. 90

17. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-octadecyl acrylate. 95

18. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-eicosyl acrylate.

19. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a homo- or copolymer of alkyl vinyl ether or ethers. 100

20. A crude oil composition as claimed in claim 19, in which the polymer is a homopolymer of *n*-octadecyl vinyl ether. 105

21. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a copolymer of a mono-olefin and a dialkyl ester of an unsaturated dicarboxylic acid with at least 14 carbon atoms in the alkyl groups. 110

22. A crude oil composition as claimed in claim 21, in which the polymer is a copolymer of ethylene and di-*n*-octadecyl maleate.

23. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a homo- or copolymer of vinyl ester or esters of saturated monocarboxylic acid or acids. 115

24. A crude oil composition as claimed in claim 23, in which the polymer is a copolymer of vinyl esters of hydrogenated rape-seed oil fatty acids. 120

25. A crude oil composition as claimed in any one of the preceding claims, in which the polymer is present in an amount of from 0.001 to 2.0 %w. 125

26. A crude oil composition as claimed in claim 25, in which the polymer is present in an amount of from 0.002 to 0.2 %w. 130

It was found that the rate of discharge of the doped oil from the tanker was 15% higher than that of the undoped oil.

- 5 After discharge of the undoped oil stored on arrival in West Europe in unheated floating-roof tanks a solid wax-oil mixture remained behind on the tank wall. This was not the case with the doped oil.

WHAT WE CLAIM IS:—

- 10 1. A crude oil composition comprising a waxy crude oil and a polymer containing aliphatic hydrocarbon side chains with at least 14 carbon atoms, which polymer may be taken to have been obtained by polymerization of
- 15 olefinically unsaturated compounds.
2. A crude oil composition as claimed in claim 1, in which the polymer may be taken to have been obtained by polymerization of olefinically unsaturated compounds which consist
- 20 at least partly of olefinically unsaturated aliphatic compounds containing a saturated hydrocarbon chain with at least 14 carbon atoms.
3. A crude oil composition as claimed in claim 1 or claim 2, in which the polymer contains unbranched saturated aliphatic hydrocarbon side chains of the formula
- 25  $\text{—CH}_2\text{—(CH}_2\text{)}_n\text{—CH}_3$  in which  $n$  is at least 12.
4. A crude oil composition as claimed in any one of the preceding claims, in which the polymer contains aliphatic hydrocarbon side chains with at least 16 and at most 30 carbon atoms.
- 35 5. A crude oil composition as claimed in claim 4, in which the polymer contains aliphatic hydrocarbon side chains with at least 18 and at most 26 carbon atoms.
6. A crude oil composition as claimed in any one of the preceding claims, in which the aliphatic hydrocarbon side chains in the polymer are attached indirectly to the main chain
- 40 via one or more oxygen and/or carbon atoms.
7. A crude oil composition as claimed in any one of the preceding claims, in which the polymer has been obtained by polymerization of an olefinically unsaturated compound or compounds, that compound or at least one of those
- 45 compounds containing, in addition to a polymerizable  $\text{>C=C<}$  group, an aliphatic hydrocarbon chain with at least 14 carbon atoms.
8. A crude oil composition as claimed in any one of the preceding claims, in which the number average molecular weight of the polymer is in the range between 1,000 and 1,000,000, as determined by the osmometric method.
- 55 9. A crude oil composition as claimed in claim 8, in which the number average molecular weight of the polymer is in the range between 4,000 and 100,000.
10. A crude oil composition as claimed in
- 60 any one of the preceding claims, in which the
- 65

polymer contains aliphatic hydrocarbon side chains with at least 14 carbon atoms, which chains differ in length by a number of carbon atoms.

11. A crude oil composition as claimed in any one of the preceding claims, in which the polymer is a homo- or copolymer of alkyl ester or esters of unsaturated carboxylic acid or acids. 70
12. A crude oil composition as claimed in claim 11, in which the polymer is a homo- or copolymer of alkyl ester or esters of unsaturated monocarboxylic acid or acids. 75
13. A crude oil composition as claimed in claim 12, in which the polymer is a homo- or copolymer of alkyl acrylate or alkyl acrylates. 80
14. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-tetradecyl acrylate. 85
15. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-hexadecyl acrylate.
16. A crude oil composition as claimed in claim 13 in which the polymer is a copolymer of alkyl acrylates with 18 to 26 carbon atoms in the alkyl group. 90
17. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-octadecyl acrylate. 95
18. A crude oil composition as claimed in claim 13, in which the polymer is a homopolymer of *n*-eicosyl acrylate.
19. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a homo- or copolymer of alkyl vinyl ether or ethers. 100
20. A crude oil composition as claimed in claim 19, in which the polymer is a homopolymer of *n*-octadecyl vinyl ether. 105
21. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a copolymer of a mono-olefin and a dialkyl ester of an unsaturated dicarboxylic acid with at least 14 carbon atoms in the alkyl groups. 110
22. A crude oil composition as claimed in claim 21, in which the polymer is a copolymer of ethylene and di-*n*-octadecyl maleate.
23. A crude oil composition as claimed in any one of claims 1 to 10, in which the polymer is a homo- or copolymer of vinyl ester or esters of saturated monocarboxylic acid or acids. 115
24. A crude oil composition as claimed in claim 23, in which the polymer is a copolymer of vinyl esters of hydrogenated rape-seed oil fatty acids. 120
25. A crude oil composition as claimed in any one of the preceding claims, in which the polymer is present in an amount of from 0.001 to 2.0 %w. 125
26. A crude oil composition as claimed in claim 25, in which the polymer is present in an amount of from 0.002 to 0.2 %w. 130



27. A crude oil composition as claimed in any one of the preceding claims, which has been prepared by incorporating the polymer in the waxy crude oil at or near the place of production of the crude oil.
28. A crude oil composition as claimed in any one of the preceding claims, in which the waxy crude oil is a mixture of waxy crude oils or a mixture of one or more waxy crude oils and one or more non-waxy crude oils.
29. A crude oil composition as claimed in claim 1 and substantially as described.

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