

1.154.966



# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Fuel Composition with a Depressed Pour Point

- 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:—
- 10 This invention relates to a fuel composition with a depressed pour point.
- Dependent on the base material selected and the processing method followed, certain fuels, particularly petroleum fuels, may contain wax.
- 15 This wax will separate out if the fuel becomes cooled down to below a certain temperature. Upon further cooling the wax continues to separate out until the wax/oil mixture eventually no longer flows. The lowest temperature observed during a standard laboratory test, at which the waxy mixture still flows, is called the pour point.
- The pour point of a fuel is of great practical importance. In order to avoid difficulties when employing the fuels in practice, the pour point of the fuel should lie below the minimum temperature at which this fuel is stored, transported and used.
- 25 It may be assumed that problems relating to the pour points of petroleum products will, in the future, play a more important part, particularly in Europe where increasingly large quantities of waxy crude oils such as those originating from Africa will have to be processed.
- 35 According to their method of preparation, petroleum fuels are classified as residual fuels and distillate fuels. Residual fuels contain a certain percentage of residual components. The amount of residual components contained in the fuel may vary between wide limits, but is mostly from 20 to 80 per cent by weight of the total fuel quantity. The residual components may have been obtained as, among others, a residue in the distillation of crude oil under either atmospheric pressure (long residue) or reduced pressure (short residue). They may also be residues obtained by thermal or catalytic cracking processes. As the residual products mostly are of too high a viscosity, they are blended with distillate oils, such as gas oils and flashed distillates.
- From their boiling ranges, distillate fuels can be roughly classified as gasolines, kerosines and gas oils. A special grade of distillate fuels is constituted by the so-called flashed distillates. These are prepared as follows. At atmospheric pressure a crude oil is distilled to a bottom temperature of about 350° C. The residue thus obtained (long residue) is subsequently, by flashing under substantially reduced pressure, separated into a flashed distillate and a residue (short residue). During the flash distillation the pre-heated feed is passed continuously into a flash chamber where evaporation takes place under constant equilibrium conditions. Gaseous and liquid products are continuously discharged. In flashing, fractionating does not play any significant part. The temperature at which the flashing is carried out is limited by possible cracking and coke formation. These side reactions will start playing a part if the temperature rises far above 400° C. In flashing, a considerably reduced pressure is applied in order to obtain from a given residue (long residue) a high yield of flashed distillate. As a result of the distillation technique employed the flashed distillates contain higher waxes which normally are found only in residues. In general the melting points of these waxes lie above 35° C., while their boiling points lie above 350° C. Owing to the presence of these higher waxes, which generally are not found in the usual distillate fuels such as gas oils, the flashed distillates show a close relationship to

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the residual fuels, in particular as regards their characteristics at low temperatures.

The application of fuels which contain waxes of the above type covers a wide range in which, dependent on the specific application, the fuel has to meet special requirements. These requirements have been laid down in a number of specifications of which the most important ones concern the pour point and the viscosity. These wax-containing fuels are employed, for instance, as fuel oil for heating purposes and as a fuel for low-speed diesel engines. In these applications the pour point is highly significant.

In the past, many compounds have been proposed which, after having been added to a wax-containing petroleum product, were expected to depress the pour point. Although favourable results were obtained by using a number of these compounds in lubricating oils and in some gas oils, it has been found that they are inactive in fuels containing the aforementioned higher waxes. In some instances, by making use of these compounds in high concentrations, a slight depression of the pour point could be obtained, yet the resulting effect proved inadequate considering the pour point requirements which such fuels have to meet in actual practice. In general it can be said that a compound may be classed as a pour point depressant only if it is capable of depressing a pour point by at least 6° C. when applied in a concentration not exceeding 0.2 per cent by weight.

Until now it has proved impossible in practice to depress in an economically justified manner the pour point of fuels containing the aforementioned higher waxes, by adding particular substances. In order to meet the specifications it was until now essential, when preparing such fuels, to reduce the wax content of the fuel by either admixing low-wax components or by dewaxing.

It has now been found, in accordance with the present invention, that the pour point of wax-containing fuels having at least 3 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C. can be depressed in a simple way by adding one or more polymers described in more detail below.

The suitable polymers for the present invention may be regarded as having been obtained by polymerization of monoolefinically unsaturated compounds which at least partly consist of at least one monoolefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms. By "monoolefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms" is meant an aliphatic compound which contains the group  $>C=Q<$  as well as the group  $CH_3-(CH_2)_n-CH_2-$ , in which  $n \geq 16$ . For convenience, the terms

"long hydrocarbon chains" and "long hydrocarbon side chains" are used below to refer to unbranched saturated hydrocarbon chains and hydrocarbon side chains, respectively, of at least 18 carbon atoms.

Although the invention generally relates to fuels having at least 3 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C., it is particularly of importance for depressing the pour point of such fuels which at least partly consist of residual components and/or components obtained as a flashed distillate in the flashing of an atmospheric distillation residue (long residue) of a crude oil.

In addition to the waxes with a melting point above 35° C. and a boiling point above 350° C., the fuels may also contain other waxes. Dependent on the blending ratio and the nature of the components of which the fuel is made up, the total wax content may vary between wide limits. The invention is of importance especially for depressing the pour point of wax-containing fuels which contain at least 6 per cent by weight of those waxes of which the melting point lies above 35° C. and the boiling point above 350° C.

For a practical application of the present invention, it is preferred to have present at least one said polymer with at least one unbranched saturated hydrocarbon side chain in which the number of carbon atoms amounts to a maximum of 30, and in particular amounts to a maximum of 26.

The polymers which are applicable as pour point depressants according to the present invention may consist of main chains that are built up from carbon atoms, which main chains carry long hydrocarbon side chains. These long hydrocarbon side chains may be attached either directly or indirectly to the main chains. In the first instance 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 there are one or more other atoms, such as carbon, oxygen, sulphur, nitrogen and/or phosphorus atoms, between the first carbon atoms of the long hydrocarbon side chain and the carbon atom of the main chain to which the side chain is attached. Polymers are preferred in which the long hydrocarbon side chains are attached to the main chain either directly or indirectly via one or more oxygen and/or carbon atoms.

In principle, the preparation of such polymers may be carried out in two ways. In the first place these polymers can be prepared by polymerization of monoolefinically unsaturated compounds which at least partly consist of at least one monoolefinically unsaturated aliphatic compound having a long hydrocarbon chain. In the second place these polymers can be

prepared by introducing as an after-treatment at least one long hydrocarbon chain as a side chain into a product obtained by polymerization of at least one monoolefinically unsaturated compound having no long hydrocarbon chain.

The polymers suitable for use as pour point depressants in accordance with the present invention may be either homopolymers or copolymers.

If the preparation is carried out by direct polymerization, i.e. without after-treatment, the material to be polymerized should always contain monoolefinically unsaturated aliphatic compounds with a long hydrocarbon chain. When homopolymers are prepared in this manner, one specific monoolefinically unsaturated aliphatic monomer with a long hydrocarbon chain is used as starting material. When copolymers are prepared in this manner, as starting material there is used a monomer mixture which, in addition to one specific monoolefinically unsaturated aliphatic monomer with a long hydrocarbon chain, contains one or more other monomers which may or may not have long hydrocarbon chains.

If the preparation is carried out by indirect polymerization, i.e. with after-treatment, the material to be polymerized need not contain monoolefinically unsaturated aliphatic compounds with long hydrocarbon chains. When homopolymers are prepared in this manner, as starting material is used one specific aliphatic monomer from which a polymer can be prepared that is suitable for the desired after-treatment. When copolymers are prepared in this manner, as starting material is used a monomer mixture which, in addition to one specific monomer from which a polymer can be prepared that is suitable for the desired after-treatment, contains one or more other monomers which may or may not contribute to the suitability of the polymer for the desired after-treatment, and which may or may not have long hydrocarbon chains.

In some instances it may be of importance that the polymers, in addition to their function as pour point depressants, have a certain dispersant effect. This can be realized, for example, by incorporating during the preparation process one or more polar monomers in the starting material, as a result of which polymers are formed which contain polar groups, such as hydroxyl, carboxyl, acid-anhydride or nitrogen-containing groups. If the preparation of the polymers is carried out by polymerization followed by an after-treatment, care should be taken that in the after-treatment at least part of the polar groups originally present in the polymer are maintained as such.

The molecular weight of the polymers that are suitable as pour point depressants according to the invention may vary widely. For

practical applications it is preferable to choose polymers whose average molecular weight (number of average  $M_n$ ) lies between  $10^3$  and  $10^6$ , and particularly between  $4 \cdot 10^3$  and  $10^5$ .

Dependent on the nature of the wax with melting point above  $35^\circ \text{C}$ . and boiling point above  $350^\circ \text{C}$ . that is present in the fuel it may be preferable to incorporate in the fuel one or more polymers according to the invention in which the long hydrocarbon chains differ in chain length by a number of carbon atoms.

As examples of monoolefinically unsaturated aliphatic compounds which have long hydrocarbon chains and which can be used for the preparation of polymers according to the invention there may be mentioned vinyl and allyl esters of saturated aliphatic monocarboxylic acids, such as vinyl and allyl esters of arachidic acid and behenic acid; alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids, such as *n*-octadecyl acrylate and *n*-eicosyl methacrylate; alkyl amides of monoolefinically unsaturated aliphatic monocarboxylic acids, such as *n*-eicosyl acrylamide and *n*-docosylmethacrylamide; dialkyl esters of monoolefinically unsaturated aliphatic dicarboxylic acids, such as di-*n*-octadecyl maleate and di-*n*-tetracosyl fumarate; dialkyl amides of monoolefinically unsaturated aliphatic dicarboxylic acids, such as di-*n*-eicosyl maleic diamide and di-*n*-docosyl fumaric diamide; imides of monoolefinically unsaturated aliphatic dicarboxylic acids, such as *n*-octadecyl maleic imide and *n*-eicosylmaleic imide; alkylvinyl ethers, such as *n*-docosylvinyl ether and *n*-tetracosylvinyl ether; and mono-olefins such as octacosene-1 and docosene-1.

As examples of monoolefinically unsaturated compounds which have no long hydrocarbon chains and with which the compounds that do have such long hydrocarbon chains can be copolymerized there may be mentioned vinyl and allyl esters of saturated monocarboxylic acids, such as vinyl and allyl esters of acetic acid and palmitic acid; alkyl esters of monoolefinically unsaturated monocarboxylic acids, such as methyl methacrylate and isobutyl acrylate; dialkyl esters of monoolefinically unsaturated dicarboxylic acids, such as diethyl maleate and dioctyl fumarate; alkylvinyl ethers, such as octylvinyl ether and laurylvinyl ether; and mono-olefins, such as ethylene and butene-1.

As examples of monoolefinically unsaturated compounds which have no long hydrocarbon chains but in which there are polar groups there may be mentioned monomers containing carboxyl groups, such as acrylic acid and maleic acid; monomers containing carboxylic anhydride groups such as maleic anhydride; monomers containing hydroxyl groups such as  $\beta$ -hydroxyethyl methacrylate and monomers with nitrogen-containing groups, such as

- acrylonitrile, acrylamide, vinylpyridine, N-vinylpyrrolidone, N-vinylsuccinimide and p-aminostyrene.
- As examples of polymers obtained by direct polymerization of monoolefinically unsaturated compounds of which at least a part consists of monoolefinically unsaturated aliphatic compounds with a long hydrocarbon chain there may be mentioned copolymers of vinyl esters of saturated monocarboxylic acids among themselves;
- copolymers of vinyl esters of saturated monocarboxylic acids among themselves;
- copolymers of vinyl esters of saturated monocarboxylic acids with mono-olefins;
- copolymers of allyl esters of saturated monocarboxylic acids among themselves;
- homopolymers of alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids;
- copolymers of alkyl esters of monoolefinically unsaturated monocarboxylic acids among themselves;
- copolymers of alkyl esters of monoolefinically unsaturated monocarboxylic acids with dialkyl esters of monoolefinically unsaturated dicarboxylic acids or with mono-olefins;
- homopolymers of dialkyl esters of monoolefinically unsaturated aliphatic dicarboxylic acids, copolymers of dialkyl esters of monoolefinically unsaturated dicarboxylic acids with mono-olefins;
- homopolymers of alkylvinyl ethers;
- copolymers of alkylvinyl ethers among themselves;
- copolymers of mono-olefins among themselves;
- copolymers of monoolefinically unsaturated monocarboxylic acids with alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids;
- copolymers of anhydrides of monoolefinically unsaturated dicarboxylic acids with olefins;
- copolymers of hydroxyalkyl esters of monoolefinically unsaturated monocarboxylic acids with alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids;
- copolymers of monoolefinically unsaturated amides or monoolefinically unsaturated heterocyclic compounds with alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids.
- If the polymers are copolymers, they may be built up of two or more different monomers. As examples of terpolymers there may be mentioned terpolymers obtained by copolymerization of a vinyl ester of a saturated monocarboxylic acid with a dialkyl ester of a monoolefinically unsaturated dicarboxylic acid, and a mono-olefin or an alkyl ester of a monoolefinically unsaturated monocarboxylic acid.
- As examples of polymers with long hydrocarbon chains obtained by after-treatment of the polymerization product of monoolefinically unsaturated compounds that have no long hydrocarbon chains there may be mentioned reaction products of copolymers of monoolefinically unsaturated monocarboxylic acids, dicarboxylic acids or anhydrides thereof and mono-olefins, vinyl esters of saturated monocarboxylic acids or dialkyl esters of monoolefinically unsaturated dicarboxylic acids, with an aliphatic alcohol with a long hydrocarbon chain;
- reaction products of homopolymers of monoolefinically unsaturated aliphatic alcohols, with an aliphatic carboxylic acid or aliphatic carboxylic acid chloride with a long hydrocarbon chain; reaction products of homopolymers of alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids or copolymers of alkyl esters of monoolefinically unsaturated monocarboxylic acids among themselves or with mono-olefins, with an aliphatic amine with a long hydrocarbon chain;
- reaction products of homopolymers of monoolefinically unsaturated aliphatic aldehydes (or) alkylvinyl ketones with an aliphatic amine with a long hydrocarbon chain;
- reaction products of copolymers of anhydrides of monoolefinically unsaturated dicarboxylic acids and mono-olefins or other monoolefinically unsaturated compounds, with an aliphatic amine with a long hydrocarbon chain.
- In general it will be sufficient to incorporate a single polymer in the wax-containing fuels. If desired, two or more polymers may be applied.
- Although any polymers which may be regarded as having been obtained by the polymerization of monoolefinically unsaturated compounds of which at least a part consists of monoolefinically unsaturated aliphatic compounds with an unbranched saturated hydrocarbon chain of at least 18 carbon atoms may be used, the polymers mentioned below are preferred:
- (a) Polymers obtained by polymerization of one or more alkyl esters of monounsaturated aliphatic monocarboxylic acids, which esters, at least partly, have a long hydrocarbon chain in the part of the molecule derived from the alcohol; in particular, these polymers are a homopolymer of n-octadecyl acrylate, a homopolymer of n-icosyl acrylate, a homopolymer of n-icosyl methacrylate, a homopolymer of n-docosyl methacrylate, a copolymer of n-icosyl methacrylate with n-docosyl methacrylate, and a terpolymer of methyl methacrylate with n-icosyl methacrylate and n-docosyl methacrylate.
- (b) Homopolymers of an alkylvinyl ether having a long hydrocarbon chain; in particular a homopolymer of n-octadecylvinyl ether, and a homopolymer of n-icosylvinyl ether.
- (c) Copolymers of monoolefinically unsaturated monocarboxylic acids or hydroxy

alkyl esters of monoolefinically unsaturated monocarboxylic acids with alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids, which esters have a long hydrocarbon chain in the part of the molecule derived from the alcohol; in particular, these copolymers are a copolymer of methacrylic acid with *n*-eicosyl methacrylate, and a copolymer of  $\beta$ -hydroxyethyl methacrylate with *n*-eicosyl methacrylate.

(d) Copolymers of mono-olefins with dialkyl esters of monoolefinically unsaturated aliphatic dicarboxylic acids, which esters have long hydrocarbon chains in the parts of the molecule derived from the alcohol; in particular a copolymer of ethylene with di-*n*-octadecyl maleate.

(e) Copolymers of mono-olefins with anhydrides of monoolefinically unsaturated aliphatic dicarboxylic acids, which copolymers have been after-treated with a primary alkylamine having a long hydrocarbon chain; in particular a copolymer of ethylene with maleic anhydride, which copolymer has been after-treated with *n*-octadecylamine.

(f) Copolymers of vinyl esters of saturated monocarboxylic acids, which esters, at least partly, have a long hydrocarbon chain in the part of the molecule derived from the acid; in particular a copolymer of vinyl esters of hydrogenated rapeseed oil fatty acids.

The concentration in which the polymers can be applied may vary between wide limits, dependent on the nature, structure and molecular weight of the polymer to be used, the nature and quantity of the waxes present in the fuel and the pour-point depressing effect desired. In some cases a quantity as small as 0.001 per cent by weight calculated on the fuel composition will be sufficient for obtaining the desired pour point. In most cases a quantity of 2.0 per cent by weight is amply sufficient. It is preferable to incorporate in the fuel 0.01 to 0.5 per cent by weight of the polymers.

The present fuel compositions may, in addition to the polymers with a pour-point depressing effect, contain small quantities of other compounds which are generally added to fuels of this type. Examples of such compounds are, among others, anti-oxidants, anti-corrosion additives, metal deactivators and additives for preventing filter clogging and emulsion formation.

The invention is illustrated by the following examples.

Thirteen polymers and two mixtures of polymers according to the invention were used in different concentrations in the following eleven fuels.

At least 75%w (per cent by weight) of the waxes present in the fuels A—K had a melting point above 35° C. and a boiling point above 350° C.

#### Fuel A.

A residual fuel with a maximum pour point of 32° C. and a kinematic viscosity of 35 cS at 50° C., consisting of 49%w of a residue obtained in the atmospheric distillation of a West African crude oil and 51 per cent by weight of a hydrocarbon oil distillate. This fuel contained 10%w of wax.

#### Fuel B.

A residual fuel with a maximum pour point of 8° C. and a kinematic viscosity of 103 cS at 50° C., consisting of 84%w of a residue obtained in the atmospheric distillation of a Middle East crude oil, and 16%w of a hydrocarbon oil distillate. This fuel contained 6%w of wax.

#### Fuel C.

A residual fuel with a maximum pour point of 26° C. and a kinematic viscosity of 14 cS at 50° C., consisting of 60%w of a residue obtained in the atmospheric distillation of a North African crude oil, and 40%w of a hydrocarbon oil distillate. This fuel contained 10.5%w of wax.

#### Fuel D.

A distillate fuel with a pour point of 38° C. and a kinematic viscosity of 25 cS at 50° C., obtained as a flashed distillate in flashing an atmospheric residue of a North African crude oil. This fuel contained 13%w of wax.

#### Fuel E.

A residual fuel with a maximum pour point of 29° C., a kinematic viscosity of 144 cS at 60° C. and a wax content of 7.4%w, consisting of a residue obtained in the atmospheric distillation of a West African crude oil.

#### Fuel F.

A residual fuel with a maximum pour point of 26° C., a kinematic viscosity of 95 cS at 60° C. and a wax content of 10.4%w, consisting of a residue obtained in the atmospheric distillation of a Middle East crude oil.

#### Fuel G.

A residual fuel with a maximum pour point of 26° C., a kinematic viscosity of 36 cS at 100° C. and a wax content of 12.5%w, consisting of 82%w of a residue obtained in the vacuum distillation of a North African crude oil, and 18%w of a heavy gas oil obtained in a catalytic cracking process.

#### Fuel H.

A residual fuel with a maximum pour point of 32° C. and a kinematic viscosity of 38 cS at 60° C. and a wax content of 14.2%w, consisting of a residue obtained in the atmospheric distillation of a North African crude oil.

**Fuel I.**

5 A residual fuel with a maximum pour point of 38° C., a kinematic viscosity of 46 cS at 50° C. and a wax content of 18.5%w, consisting of a residue obtained in the atmospheric distillation of a West African crude oil.

**Fuel J.**

10 A residual fuel with a maximum pour point of 32° C., a kinematic viscosity of 48 cS at 50° C. and a wax content of 14.7%w, consisting of a residue obtained in the atmospheric distillation of a Middle East crude oil.

**Fuel K.**

15 A residual fuel with a maximum pour point of 35° C., a kinematic viscosity of 175 cS at 50° C. and a wax content of 14.2%w consisting of a residue obtained in the thermal cracking of a residue obtained in the atmospheric distillation of a North African crude oil.

20 The pour point of the various fuels was determined as follows.

**I. Pour point for fuels of type D.**

25 The fuel is heated to 46° C., without being stirred, in a test tube and is then cooled down. From 44° C. on, after every 3° C. drop in temperature, the test tube is carefully held at a slant. The temperature at which the test tube can be held horizontal for 5 seconds without the waxy mass starting to flow is called the solid point. The lowest temperature read off before the solid point is obtained, in

other words, the lowest temperature at which the waxy mixture still flows, is the pour point. The pour point is obtained by adding 3° C. to the temperature of the solid point. 35

**II. Maximum pour point for fuels of types A, B, C, E, F, G, H, I, J and K.**

The fuel is heated to 104° C. while being stirred, is then poured into a test tube and is cooled down to -20° C. Subsequently, the sample is heated to 46° C. without being stirred, and the pour point is further determined in the same way as mentioned under I for fuels of type D. The pour point thus determined is called the maximum pour point in this specification. 40 45

The results of the experiments are stated in the table below, which indicates by how many degrees Centigrade the pour point or maximum pour point is depressed after addition of the various polymers. 50

Table I shows the depression of the pour point of fuels A—D, obtained by incorporating therein polymers according to the invention. 55

For comparison, moreover, seven polymers of a related type but having no unbranched saturated hydrocarbon side chains of at least 18 carbon atoms were incorporated in these four fuels. The figures of Table I show that the pour point of the fuels is not depressed by these polymers. 60

Table II shows the influence on the pour point of fuels E—K of 4 polymers and 2 polymer mixtures according to the invention. 65

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TABLE

| Type of fuel                                                                                                               | Depression of the |      |      |      |      |      |      |      |      |      |
|----------------------------------------------------------------------------------------------------------------------------|-------------------|------|------|------|------|------|------|------|------|------|
| type of polymer<br>concentration of the polymer, %w.                                                                       | A                 |      |      |      |      | B    |      |      |      |      |
|                                                                                                                            | 0.20              | 0.08 | 0.04 | 0.02 | 0.01 | 0.20 | 0.08 | 0.04 | 0.02 | 0.01 |
| n-C <sub>20</sub> methacrylate homopolymer, M <sub>n</sub> = 30,000                                                        | 42                | 42   | 33   | 15   | 9    | 15   | 15   | 15   | 15   | 6    |
| n-C <sub>20</sub> /n-C <sub>22</sub> methacrylate copolymer, molar ratio 1:1, M <sub>n</sub> = 30,000                      | 36                | 33   | 27   | 27   | 12   | 18   | 18   | 18   | 18   | 9    |
| n-C <sub>22</sub> methacrylate homopolymer, M <sub>n</sub> = 30,000                                                        | 27                | 27   | 24   | 18   | 6    | 9    | 9    | 9    | 9    | 6    |
| C <sub>1</sub> /n-C <sub>20</sub> /n-C <sub>22</sub> methacrylate copolymer, molar ratio 2:1:1, M <sub>w</sub> = 1,200,000 | 45                | 36   | 18   | 6    |      | 18   | 18   | 9    |      |      |
| β-hydroxy ethyl/n-C <sub>20</sub> methacrylate copolymer, molar ratio 3:10                                                 | 42                | 36   | 27   |      |      | 18   | 18   | 18   |      |      |
| methacrylic acid/n-C <sub>20</sub> methacrylate copolymer, molar ratio 3:10                                                | 42                | 39   | 27   |      |      | 18   | 18   | 18   |      |      |
| n-C <sub>18</sub> acrylate homopolymer, M <sub>n</sub> = 23,900                                                            |                   | 45   |      | 21   | 12   |      | 21   |      | 21   | 12   |
| n-C <sub>20</sub> acrylate homopolymer, M <sub>n</sub> = 23,700                                                            |                   | 24   |      | 18   | 12   |      | 15   |      | 9    | 9    |
| n-C <sub>18</sub> vinyl ether homopolymer, M <sub>n</sub> = 2150                                                           |                   | 33   |      |      |      |      | 12   |      | 6    |      |
| n-C <sub>20</sub> vinyl ether homopolymer, M <sub>n</sub> = 7600                                                           |                   | 27   |      | 9    |      |      | 12   |      | 6    |      |
| ethylene/di-n-C <sub>18</sub> maleate copolymer molar ratio 1:1, M <sub>n</sub> = 10,000                                   |                   | 30   |      | 21   |      |      | 27   |      | 24   |      |
| ethylene/n-C <sub>18</sub> maleinic acidimide copolymer, molar ratio 1:1 M <sub>n</sub> = 10,000                           |                   | 15   |      |      |      |      | 21   |      |      |      |

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18

I

pour point °C.

| C    |      |      |      |      | D    |      |      |      |      |       |        |       |
|------|------|------|------|------|------|------|------|------|------|-------|--------|-------|
| 0.20 | 0.08 | 0.04 | 0.02 | 0.01 | 0.20 | 0.08 | 0.04 | 0.02 | 0.01 | 0.005 | 0.0025 | 0.001 |
| 12   | 12   | 6    |      |      | 27   | 27   | 24   | 21   | 18   | 15    | 12     | 6     |
| 18   | 18   | 9    |      |      | 24   | 24   | 24   | 18   | 18   | 15    | 12     | 9     |
| 33   | 30   | 27   | 18   | 6    | 21   | 21   | 18   | 18   | 18   | 15    | 9      | 6     |
| 6    |      |      |      |      | 36   | 27   | 21   |      |      |       |        |       |
| 12   | 9    |      |      |      | 30   | 27   | 21   |      |      |       |        |       |
| 12   | 6    |      |      |      | 30   | 30   | 21   |      |      |       |        |       |
|      | 15   |      |      |      |      | 27   |      | 21   | 12   |       |        |       |
|      | 33   |      | 24   |      |      | 18   |      | 15   | 12   |       |        |       |
|      | 12   |      |      |      |      | 24   |      | 12   |      |       |        |       |
|      | 18   |      | 9    |      |      | 15   |      | 15   |      |       |        |       |
|      | 15   |      |      |      |      | 24   |      | 18   |      |       |        |       |
|      |      |      |      |      |      | 12   |      | 6    |      |       |        |       |

TABLE

| Type of fuel                                                                                                                          | Depression of the |      |      |      |      |      |      |      |      |      |
|---------------------------------------------------------------------------------------------------------------------------------------|-------------------|------|------|------|------|------|------|------|------|------|
| type of polymer<br>concentration of the polymer, %w.                                                                                  | A                 |      |      |      |      | B    |      |      |      |      |
|                                                                                                                                       | 0.20              | 0.08 | 0.04 | 0.02 | 0.01 | 0.20 | 0.08 | 0.04 | 0.02 | 0.01 |
| copolymer of vinyl esters of hydrogenated rapeseed oil fatty acids (30% C <sub>18</sub> ; 35% C <sub>20</sub> ; 35% C <sub>22</sub> ) |                   | 36   |      | 21   |      |      | 24   |      | 24   |      |
| n-C <sub>16</sub> methacrylate homopolymer                                                                                            | 0                 | 0    |      |      |      | 0    | 0    |      |      |      |
| n-C <sub>16</sub> acrylate homopolymer, M <sub>n</sub> = 24,900                                                                       | 3                 | 0    |      |      |      |      |      |      |      |      |
| n-C <sub>16</sub> vinyl ether homopolymer                                                                                             | 0                 | 0    |      |      |      |      |      |      |      |      |
| n-C <sub>12</sub> /n-C <sub>14</sub> /n-C <sub>16</sub> methacrylate copolymer                                                        | 0                 | 0    |      |      |      | 0    | 0    |      |      |      |
| β-hydroxyethyl/n-C <sub>12</sub> /n-C <sub>14</sub> /n-C <sub>16</sub> methacrylate copolymer                                         | 0                 | 0    |      |      |      |      |      |      |      |      |
| methacrylic acid/n-C <sub>12</sub> /n-C <sub>14</sub> /n-C <sub>16</sub> methacrylate copolymer                                       | 0                 | 0    |      |      |      |      |      |      |      |      |
| oleyl-vinyl ether                                                                                                                     | 0                 | 0    |      |      |      | 0    | 0    |      |      |      |

I (continued)

pour point °C

| C    |      |      |      |      | D     |      |      |      |      |       |        |       |
|------|------|------|------|------|-------|------|------|------|------|-------|--------|-------|
| 0.20 | 0.08 | 0.04 | 0.02 | 0.01 | 0.20  | 0.08 | 0.04 | 0.02 | 0.01 | 0.005 | 0.0025 | 0.001 |
| 12   |      |      |      |      | 27 15 |      |      |      |      |       |        |       |
| 0    | 0    |      |      |      | 0     | 0    |      |      |      |       |        |       |
| 3    | 0    |      |      |      | 3     | 0    |      |      |      |       |        |       |
| 0    |      |      |      |      | 0     | 0    |      |      |      |       |        |       |
|      |      |      |      |      | 0     | 0    |      |      |      |       |        |       |
|      |      |      |      |      | 0     | 0    |      |      |      |       |        |       |
| 0    | 0    |      |      |      | 0     | 0    |      |      |      |       |        |       |

TABLE II

| Type of fuel                                                                                                                                                                                                                      | Depression of the pour point in °C. |      |           |           |           |           |      |      |      |  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|------|-----------|-----------|-----------|-----------|------|------|------|--|
| type of polymer<br>concentration of the polymer<br>%w                                                                                                                                                                             | E                                   | F    | G         | H         | I         | J         | K    |      |      |  |
|                                                                                                                                                                                                                                   | 0.08 0.04                           | 0.08 | 0.08 0.04 | 0.08 0.04 | 0.08 0.04 | 0.08 0.04 | 0.08 | 0.04 | 0.08 |  |
| n-C <sub>18</sub> acrylate homopolymer<br>(M <sub>n</sub> = 23,900)                                                                                                                                                               | 27 24                               | 12   | 6         | 9 6       |           | 12        |      |      |      |  |
| Mixture of 25%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 24,900), 50%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 23,900) and 25%w n-C <sub>20</sub> acrylate homopolymer (M <sub>n</sub> = 23,700) | 27 24                               | 12   | 12 12     | 15        | 9         | 15 9      |      |      |      |  |
| n-C <sub>20</sub> acrylate homopolymer, M <sub>n</sub> = 23,700                                                                                                                                                                   | 33 30                               | 9    | 9 6       | 21 9      | 9 6       | 30 15     | 12   |      |      |  |
| ethylene/di-n-C <sub>18</sub> maleate copolymer, mol ratio 1:1, (M <sub>n</sub> = 10,000)                                                                                                                                         | 33 30                               |      |           | 6         | 9 6       | 9         |      |      |      |  |
| n-C <sub>22</sub> methacrylate homopolymer, M <sub>n</sub> = 30,000                                                                                                                                                               |                                     |      |           | 15 9      | 9 9       | 18 6      | 6    |      |      |  |
| mixture of 50%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 23,900) and 50% n-C <sub>20</sub> acrylate homopolymer (M <sub>n</sub> = 23,700)                                                                         |                                     |      |           | 15        | 12 6      | 15 6      | 6    |      |      |  |

## WHAT WE CLAIM IS:—

1. A fuel composition with a depressed pour point, comprising a wax-containing fuel having at least 3 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C., and one or more polymers which may be regarded as having been obtained by polymerization of mono-olefinically unsaturated compounds which at least partly consist of at least one mono-olefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

2. A fuel composition as claimed in claim 1, in which the fuel at least partly consists of residual components.

3. A fuel composition as claimed in claim 1 or claim 2, in which the fuel at least partly consists of components obtained as a flashed distillate in the flashing of an atmospheric distillation residue of a crude-oil.

4. A fuel composition as claimed in any one

5. A fuel composition with a depressed pour point, comprising a wax-containing fuel having at least 3 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C., and one or more polymers which may be regarded as having been obtained by polymerization of mono-olefinically unsaturated compounds which at least partly consist of at least one mono-olefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

10. A fuel composition as claimed in any one

TABLE II

| Type of fuel                                                                                                                                                                                                                      | Depression of the pour point in °C. |      |           |           |           |           |      |  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|------|-----------|-----------|-----------|-----------|------|--|
|                                                                                                                                                                                                                                   | E                                   | F    | G         | H         | I         | J         | K    |  |
| type of polymer                                                                                                                                                                                                                   | 0.08 0.04                           | 0.08 | 0.08 0.04 | 0.08 0.04 | 0.08 0.04 | 0.08 0.04 | 0.08 |  |
| concentration of the polymer %w                                                                                                                                                                                                   |                                     |      |           |           |           |           |      |  |
| n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 23,900)                                                                                                                                                                  | 27 24                               | 12   | 6         | 9 6       |           | 12        |      |  |
| Mixture of 25%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 24,900), 50%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 23,900) and 25%w n-C <sub>20</sub> acrylate homopolymer (M <sub>n</sub> = 23,700) | 27 24                               | 12   | 12 12     | 15        | 9         | 15 9      |      |  |
| n-C <sub>20</sub> acrylate homopolymer, M <sub>n</sub> = 23,700                                                                                                                                                                   | 33 30                               | 9    | 9 6       | 21 9      | 9 6       | 30 15     | 12   |  |
| ethylene/di-n-C <sub>18</sub> maleate copolymer, mol ratio 1:1, (M <sub>n</sub> = 10,000)                                                                                                                                         | 33 30                               |      |           | 6         | 9 6       | 9         |      |  |
| n-C <sub>22</sub> methacrylate homopolymer, M <sub>n</sub> = 30,000                                                                                                                                                               |                                     |      |           | 15 9      | 9 9       | 18 6      | 6    |  |
| mixture of 50%w n-C <sub>18</sub> acrylate homopolymer (M <sub>n</sub> = 23,900) and 50% n-C <sub>20</sub> acrylate homopolymer (M <sub>n</sub> = 23,700)                                                                         |                                     |      |           | 15        | 12 6      | 15 6      | 6    |  |

## WHAT WE CLAIM IS:—

1. A fuel composition with a depressed pour point, comprising a wax-containing fuel having at least 3 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C., and one or more polymers which may be regarded as having been obtained by polymerization of mono-olefinically unsaturated compounds which at least partly consist of at least one mono-olefinically unsaturated aliphatic compound

having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

2. A fuel composition as claimed in claim 1, in which the fuel at least partly consists of residual components.

3. A fuel composition as claimed in claim 1 or claim 2, in which the fuel at least partly consists of components obtained as a flashed distillate in the flashing of an atmospheric distillation residue of a crude oil.

4. A fuel composition as claimed in any one



of claims 1 to 3, in which the fuel contains at least 6 per cent by weight of waxes with a melting point above 35° C. and a boiling point above 350° C.

5 5. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having at least one unbranched saturated hydrocarbon side chain with a maximum of 30 carbon atoms.

10 6. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having at least one unbranched saturated hydrocarbon side chain with a maximum of 26 carbon atoms.

15 7. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having at least one unbranched saturated hydrocarbon side chain of at least 18 carbon atoms attached directly to the main chain.

20 8. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having at least one unbranched saturated hydrocarbon side chain of at least 18 carbon atoms indirectly attached to the main chain via one or more oxygen, carbon, sulphur, nitrogen and/or phosphorus atoms.

25 9. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer that has been obtained by polymerization of monoolefinically unsaturated compounds which at least partly consist of at least one monoolefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

30 10. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer that has been obtained by introducing at least one unbranched saturated hydrocarbon chain of at least 18 carbon atoms as a side chain into a product obtained by polymerization of at least one monoolefinically unsaturated compound having no unbranched saturated hydrocarbon chain of 18 carbon or more atoms.

35 11. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having at least one unbranched saturated hydrocarbon side chain of at least 18 carbon atoms and containing at least one polar group.

40 12. A fuel composition as claimed in any one of the preceding claims, in which the average molecular weight of the said polymer or polymers lies between  $10^3$  and  $10^6$ .

45 13. A fuel composition as claimed in claim 12, in which the average molecular weight of the said polymer or polymers lies between  $4 \cdot 10^3$  and  $10^5$ .

60 14. A fuel composition as claimed in any one of the preceding claims, in which there is at least one said polymer having unbranched

saturated hydrocarbon side chains of at least 18 carbon atoms differing in chain length by a number of carbon atoms.

65 15. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by polymerization of one or more alkyl esters of monoolefinically unsaturated aliphatic monocarboxylic acids, which esters, at least partly, have an unbranched saturated hydrocarbon chain of at least 18 carbon atoms in the part of the molecule derived from the alcohol.

70 16. A fuel composition as claimed in claim 15, in which there is a homopolymer of n-octadecylacrylate.

75 17. A fuel composition as claimed in claim 15, in which there is a homopolymer of n-eicosyl acrylate.

80 18. A fuel composition as claimed in claim 15, in which there is a homopolymer of n-eicosyl methacrylate.

85 19. A fuel composition as claimed in claim 15, in which there is a homopolymer of n-docosyl methacrylate.

90 20. A fuel composition as claimed in claim 15, in which there is a copolymer of n-eicosyl methacrylate with n-docosyl methacrylate.

95 21. A fuel composition as claimed in claim 15, in which there is a terpolymer of methyl methacrylate with n-eicosyl methacrylate and n-docosyl methacrylate.

100 22. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by homopolymerization of an alkylvinyl ether having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

23. A fuel composition as claimed in claim 22, in which there is a homopolymer of n-octadecylvinyl ether.

105 24. A fuel composition as claimed in claim 22, in which there is a homopolymer of n-eicosylvinyl ether.

110 25. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by copolymerization of a monoolefinically unsaturated monocarboxylic acid with an alkyl ester of a monoolefinically unsaturated aliphatic monocarboxylic acid, which ester has an unbranched saturated hydrocarbon chain of at least 18 carbon atoms in the part of the molecule derived from the alcohol.

115 26. A fuel composition as claimed in claim 25, in which there is a copolymer of methacrylic acid with n-eicosyl methacrylate.

120 27. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by copolymerization of a hydroxy alkyl ester of a monoolefinically unsaturated monocarboxylic acid with an alkyl ester of a monoolefinically unsaturated aliphatic monocarboxylic acid, which ester has an unbranched



saturated hydrocarbon chain of at least 18 carbon atoms in the part of the molecule derived from the alcohol.

5 28. A fuel composition as claimed in claim 27, in which there is a copolymer of  $\beta$ -hydroxy ethyl methacrylate with n-eicosyl methacrylate.

10 29. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by copolymerization of a mono-olefin with a dialkyl ester of a monoolefinically unsaturated aliphatic dicarboxylic acid, which ester has unbranched saturated hydrocarbon chains of at least 18 carbon atoms in the parts of the molecule derived from the alcohol.

15 30. A fuel composition as claimed in claim 29, in which there is a copolymer of ethylene with di-n-octadecyl maleate.

20 31. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by after-treating a product obtained by copolymerization of a mono-olefin with an anhydride of a monoolefinically unsaturated aliphatic dicarboxylic acid, with a primary alkylamine having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms.

25 32. A fuel composition as claimed in claim 31, in which there is a said polymer that has been obtained by after-treatment with n-octadecylamine of a copolymer of ethylene and maleic anhydride.

33. A fuel composition as claimed in any one of the preceding claims, in which there is a said polymer that has been obtained by copolymerization of vinyl esters of saturated aliphatic monocarboxylic acids, which esters, at least partly, have an unbranched saturated hydrocarbon chain of at least 18 carbon atoms in the part of the molecule derived from the acid.

34. A fuel composition as claimed in claim 33, in which there is a copolymer of vinyl esters of hydrogenated rapeseed oil fatty acids.

35. A fuel composition as claimed in any one of the preceding claims, in which there is 0.001 to 2.0 per cent by weight of the said polymer or polymers.

36. A fuel composition as claimed in claim 35, in which there is 0.01 to 0.5 per cent by weight of the said polymer or polymers.

37. A fuel composition with a depressed pour point, substantially as described with reference to the examples, excluding the comparative examples.

38. A fuel composition as claimed in claim 1, substantially as described.

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