FORM 1

609778

AUSTRALIA

THE PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I/We, INSTITUT FRANCAIS DU PETROLE and ELF FRANCE

of 4, avenue de Bois Preau 92502 Rueil Malmaison, France and 137, rue de l'Universite 75007 Paris, France, respectively

hereby apply for the grant of a standard patent for an invention entitled:

NITROGEN-CONTAINING ADDITIVES AS AGENTS FOR DECREASING THE CLOUD POINT OF HYDROCARBON MIDDLE DISTILLATES AND COMPOSITIONS OF HYDROCARBON MIDDLE DISTILLATES CONTAINING THESE ADDITIVES.

which is described in the accompanying complete specification.

This application is made under the provisions of Section 51 as a divisional of Australian Patent Application No. 91347/82 by INSTITUT FRANCAIS DU PETROLE and ELF FRANCE

My/Our address for service is care of CLEMENT HACK & CO., Patent Attorneys, of 601 St. Kilda Road, Melbourne, in the State of Victoria, 3004, Australia.

FEE STAMP TO VALUE OF $280 ATTACHED
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DATED this 15th day of February 19 88

LODGED AT SUB-OFFICE
24 FEB 1988
Melbourne

INSTITUT FRANCAIS DU PETROLE and ELF FRANCE

CLEMENT HACK & CO.

TO: The Commissioner of Patents

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 15 · 2 · 91

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Forms 7 and 8

AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

Name(s) of Applicant(s)

In support of the application made by INSTITUT FRANCAIS DU PETROLE & ELF FRANCE

Title

for a patent for an invention entitled NITROGEN-CONTAINING ADDITIVES USABLE AS AGENTS FOR DECREASING THE CLOUD POINT OF HYDROCARBON MIDDLE DISTILLATES AND COMPOSITIONS OF HYDROCARBON MIDDLE DISTILLATES CONTAINING THESE ADDITIVES

Name(s) and address(es) of person(s) making declaration

I/We, Jean COLAS DES FRANCS : 4, avenue de Bois Préau 92502 RUEIL MALMAISON FRANCE
Anne POLGAR - Tour Elf - 2 Place de la Coupole La Défense 6 - 92400 COURBEVOIE-FRANCE
do solemnly and sincerely declare as follows:-

1. ~~I am/we are the applicant(s) for the patent, or~~ am/are authorised by the abovementioned applicant to make this declaration on its behalf.

2. ~~The basic application(s) as defined by Section 141~~ of the Act was/were made in the following country or countries on the following date(s) by the following applicant(s) namely:-

Country, filing date and name of Applicant(s) for the or each basic application

in _____ on _____ 19_____
by _____
in _____ on _____ 19_____
by _____

3. The said basic application(s) was/were the first application(s) made in a Convention country in respect ~~of the invention the subject of the application~~.

Name(s) and address(es) of the or each actual inventor

4. The actual inventor(~~s~~) of the said invention ~~is~~/are Paul MALDONADO 20, rue Centrale 69360 Saint Symphorien D'ozon, France; Robert LEGER rue Pieree Semard 5 residence Cazardes 69520 Grigny France; Choua COHEN 111, avenue Barthelemy Buyer 69005 Lyon France; Bernard SILLION 13 rue des Erables 78150 Rocquencourt, France.

See reverse side of this form for guidance in completing this part

5. The facts upon which the applicant(s) ~~is~~/are entitled to make this application are as follows:-
The said applicants are the assignees of the actual inventors.

(a) DECLARED at RUEIL MALMAISON this 6th day of April 1988

(b) DECLARED at: COURBEVOIE this 13th day of April 1988

(a) Head of Patent Department (b) Anne POLGAR

J. COLAS DES FRANCS Ingénieur en Propriété Industrielle

This form may be completed and filed after the filing

(12) PATENT ABRIDGMENT (11) Document No. AU-B-12145/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 609778

(54) Title
NITROGEN-CONTAINING ADDITIVES AS AGENTS FOR DECREASING THE CLOUD POINT OF HYDROCARBON MIDDLE DISTILLATES AND COMPOSITIONS OF HYDROCARBON MIDDLE DISTILLATES CONTAINING THESE ADDITIVES

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(56) Prior Art Documents
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(57) Claim

1. Oil middle distillate composition, characterized as comprising a major proportion of oil middle distillate and a minor proportion, sufficient to decrease the cloud point of said distillate, of an additive consisting of a material having an average molecular weight of 300 to 10,000 and resulting from the reaction of at least one aliphatic dicarboxylic compound selected from the maleic and alkylmaleic anhydrides, the alkenylsuccinic anhydrides having 10 to 30 carbon atoms in the alkenyl radical, polyalkenylsuccinic anhydrides, the corresponding dicarboxylic acids and lower alkyl diesters, with at least one compound having a primary amine function, complying with one of the general formulas:

$$R - Z\left[(CH_2)_n - NH\right]_m - H \qquad (I)$$

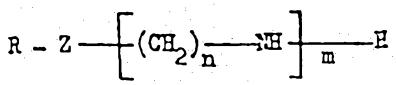
and

$$HO - CH_2 - R^5 - NH_2 \qquad (II)$$

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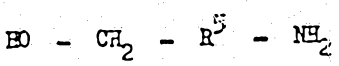
wherein R represents a monovalent saturated aliphatic radical of 1 to 30 carbon atoms, Z is selected from the -NR'- groups, wherein R' is a hydrogen atom or a monovalent saturated aliphatic radical containing 1 to 30 carbon atoms, and the oxygen atom -O-, n is an integer from 2 to 4, m is zero or an integer from 1 to 4 when Z is -NH- or an integer from 1 to 4 in all other cases; and R^5 represents a divalent saturated aliphatic radical having 1 to 18 carbon atoms; said compound having a primary amine function being used in a proportion of 0.9 to 1.2 mole per mole of said dicarboxylic compound and said reaction being effected at a temperature of 120 to 200°C for a sufficient time to form the theoretical amount of volatile products consisting of water and/or alcohol, which are eliminated.

13. An additive, useful, in particular, to decrease the cloud point of middle distillates, characterized as having a molecular weight of 300 to 10,000 and resulting from the reaction, with at least one aliphatic dicarboxylic compound selected from the maleic and allylmaleic anhydrides, the alkenylsuccinic and polyalkenylsuccinic anhydrides, the corresponding di-carboxylic acids and light alkyl diesters, of at least one compound having a primary amine function, complying with one of the general formulas:



(I)

and



(II)

wherein R represents a monovalent saturated aliphatic radical of 1 to 30 carbon atoms, Z is selected from - NR' - groups, wherein R' is a hydrogen atom or a monovalent saturated aliphatic radical containing 1 to 30 carbon atoms, and the oxygen atom - O -, n is an integer from 2 to 4, m is zero or an integer from 1 to 4 ; and R^5 represents a divalent saturated aliphatic radical having 1 to 18 carbon atoms.

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Form 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

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Accepted:
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Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled: NITROGEN-CONTAINING ADDITIVES AS AGENTS FOR DECREASING THE CLOUD POINT OF HYDROCARBON MIDDLE DISTILLATES AND COMPOSITIONS OF HYDROCARBON MIDDLE DISTILLATES CONTAINING THESE ADDITIVES.

The following statement is a full description of this invention, including the best method of performing it known to me:—

PF/CP1F/2/80

The invention relates to new nitrogen additives which can be used as agents for decreasing the cloud point of hydrocarbon middle distillates (fues oils, gas oils), as well as to compositions of middle distillates containing said additives.

The oil distillates concerned by the invention are middle distillates (fuel oils, gas oils) whose distillation range (standard ASTM D 86-87) is between 150°C and 450°C. Gas oils which are more particularly concerned distill between an initial temperature from 160°C to 190°C and a final temperature from 350°C to 390°C.

A great number of products sold on the market have the purpose to improve the limit filtrability temperature and the pour point of oil cuts of high paraffin content, for example :

- polymers based on long chain olefins,
- copolymers based on alpha-olefins,
- ethylene-vinyl acetate copolymers,
- N-acylaminoethylesters of acid-containing polymers, or
- halocarbon compounds.

These products act on the kinetic of crystallization phenomena and change the crystal size, thus allowing the use of the suspension at a lower temperature without plugging of the pipes and the filters. The above products do not modify the temperature at which the first paraffin crystals appear. As a matter of fact, it has been considered, up to now, that this temperature was dependent on the molecular weight and the composition of the paraffins and on the nature of the solvent.

A decrease of the cloud point of middle distillates (particularly gas oils) by means of an additive would be highly beneficial to the refiners, since it would allow without changing the distillation diagram, to comply with the standards which are presently subject to an increasing severity.

It has now been discovered that contain chemicals, whose definition is given hereinafter, when added to middle distillates, have the property to make the first paraffin crystals appear at a lower temperature than that observed in the absence of these additives. This property is the more unobvious as it is still maintained after several cycles of heating and cooling and operates according to a mechanism which has not yet been explained.

This class of chemical compounds also has an action on other properties of middle distillates (particularly gas oils), by modifying the behavior of the medium which contains the precipitated paraffins.

Thus, the compounds proposed in this invention have a substantial affect on the limit filterability temperature and the pour point.

When paraffin crystals have formed by cooling, their normal tendency is to assemble by gravity at the bottom. This phenomenon, generally called settling, results in the plugging of ducts and filters and is detrimental to a safe use of middle distillates, particularly gas oils. The chemicals proposed in the invention can decrease substantially the settling rate of the paraffins formed by cooling of gas oils and other middle distillates.

Finally, the proposed products for having the above mentioned properties, also confer to the gas oils and middle distillates, to which they are added, anti-corrosion properties with respect to metal surfaces.

As a general rule, the additives of the invention can be defined as products having an average molecular weight of about 300 to 10 000, obtained by condensation of at least one compound comprising a primary amine function, complying with one of the following general formulas (I) and (II) :

$$R - Z - \left[(CH_2)_n - NH \right]_m - H \qquad (I)$$

and

$$HO - CH_2 - R^5 - NH_2 \qquad (II)$$

with at least one dicarboxylic compound as hereinafter defined.

In formula (I), R is generally a monovalent saturated aliphatic radical comprising from 1 to 30 carbon atoms ; Z can be, depending on the case, an oxygen atom or a divalent group of the type - NR' -, R' being either a hydrogen atom or a monovalent aliphatic radical ; n is an integer from 2 to 4 and m may be zero or an integer from 1 to 4.

The compounds of the above formula (I) may consist of primary amines of the formula $R^1 - NH_2$ (in that case, in formula (I), Z represents a - NH - group and the value of m is zero).

The radical R^1 is preferably linear and comprises from 12 to 30, particularly from 16 to 25 carbon atoms.

Specific examples of these amines are : dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine and docosylamine, hexadecylamine and octadecylamine being preferred.

The compounds of the formula (I) may also consist of polyamines obtained from saturated aliphatic amines of the formula :

$$R^1 - NH - \left[(CH_2)_n - NH \right]_m - H$$

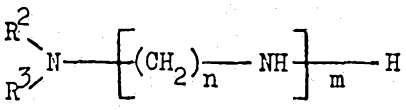
corresponding to the general formula (I) wherein Z is a - NH - group ; m may have a value from 1 to 4 and n a value from 2 to 4, preferably 3.

Preferably, the radical R^1 is linear and comprises from 12 to 30 and particularly from 16 to 25 carbon atoms.

Specific compounds are : N-dodecyl 1,3-diamino propane, N-tetradecyl 1,3-diamino propane, N-hexadecyl 1,3-diamino propane, N-octadecyl 1,3-diamino propane, N-eicosyl 1,3-diamino propane, N-docosyl 1,3-diamino propane, N-hexadecyldipropylene triamine, N-octadecyl dipropylene triamine, N-eicosyldipropylene triamine and N-docosyl dipropylene triamine. There are more advantageously used

N-docosyl-, N-eicosyl-, N-octadecyl-, N-hexadecyl- or N-dodecyl 1,3-diamino propane, as well as N-hexadecyl- and N-octadecyl- dipropylene - triamine.

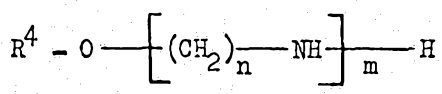
The compounds of formula (I) may also consist of polyamines of the formula :



wherein R^2 and R^3, identical or different, are each an alkyl radical with 1 to 24 and preferably 8 to 22 carbon atoms, R^2 and R^3 preferably comprising together from 16 to 32 carbon atoms ; n has a value from 2 to 4 and m a value from 1 to 4.

Specific compounds are : N, N-diethyl 1,2-diamino ethane, N, N-diisopropyl 1,2-diamino ethane, N, N-dibutyl 1,2-diamino ethane, N, N-diethyl 1,4-diamino butane, N, N-dimethyl 1,3-diamino propane, N, N-diethyl 1,3-diamino propane, N, N-dioctyl 1,3-diamino propane, N, N-didecyl 1,3-diamino propane, N, N-didodecyl 1,3-diamino propane, N, N-ditetradecyl 1,3-diamino propane, N, N-dihexadecyl 1,3-diamino propane, N, N-dioctadecyl 1,3-diamino propane, N, N-didodecyldipropylenetriamine, N, N-ditetradecyldipropylene triamine, N, N-dihexadecyldipropylene triamine and N, N-dioctadecyldipropylenetriamine.

Finally the compounds of formula (I) contemplated in this invention may consist of ether-amines, more particularly those complying with the formula :



corresponding to the general formula (I) wherein Z is an oxygen atom ; the radical R^4 comprises 1 to 24, preferably 8 to 22 carbon atoms, m is an integer from 1 to 4 and n an integer from 1 to 4, preferably 2 or 3.

Specific compounds of the ether-amine type are : 2-methoxy ethylamine, 3-methoxy propylamine, 4-methoxy butylamine, 3-ethoxy

propylamine, 3-octyloxy propylamine, 3-decyloxy propylamine, 3-hexadecyloxy propylamine, 3-eicosyloxy propylamine, 3-docosyloxy propylamine, N-(3-octyloxy propyl) 1,3-diamino propane, N-(3-decyloxy propyl) 1,3-diamino propane, 3-(2,4,6-trimethyl decyl) oxy propylamine and N- 3-(2,4,6-trimethyl decyl) oxy propyl 1,3-diamino propane.

The compound with a primary amine function which is used for preparing additives conforming to the invention may also consist of an aminoalcohol of formula (II) :

$$HO - CH_2 - R^5 - NH_2 \qquad (II)$$

wherein R^5 is a divalent saturated aliphatic radical, linear or branched, preferably linear, comprising 1 to 18 and preferably 10 to 18 carbon atoms.

Specific examples are : monoethanolamine, 1-amino 3-propanol, 1-amino 4-butanol, 1-amino 5-pentanol, 1-amino 6-hexanol, 1-amino 7-heptanol, 1-amino 8-octanol, 1-amino 10-decanol, 1-amino 11-undecanol, 1-amino 13-tridecanol, 1-amino 14-tetradecanol, 1-amino 16-hexadecanol, 2-amino 2-methyl 1-propanol, 2-amino 1-butanol and 2-amino 1-pentanol.

It must be understood that, without departing from the invention, it is possible to operate with one or more compounds of formula (I) and/or one or more compounds of formula (II).

The dicarboxylic compounds on which is effected the condensation of a compound of formula (I) or a compound of formula (II) such as described hereinbefore are more particularly selected from the anhydrides of aliphatic, preferably unsaturated, α, β - dicarboxylic acids, such as, for example, maleic anhydride, alkylmaleic anhydrides, for example methylmaleic (or citraconic) anhydride, or from the alkenyl-succinic anhydrides, for example those obtained by reacting at least one α -olefin, preferably linear, (having, for example, 10 to 30 carbon atoms) with maleic anhydride. Specific examples are n-octadecenyl succinic anhydride or dodecenyl succinic anhydride. It is obviously possible to use mixtures of two (or more) of these compounds.

It is also possible, according to the invention, to use polyalkenyl-succinic anhydrides, for example polyisobutenyl-succinic anhydrides, whose molecular weight is selected between 500 and 2000 and preferentially between 1000 and 1700. The manufacture of anhydrides of this type is well known in the prior art. For example, the anhydrides may be manufactured by the reaction of aligomers or polymers (possibly hydrogenated) of olefins with maleic anhydride.

The above mentioned anhydrides may be replaced by the corresponding dicarboxylic acids, or by the light alkyl diesters thereof (such as, for example, methyl, ethyl, propyl and butyl esters).

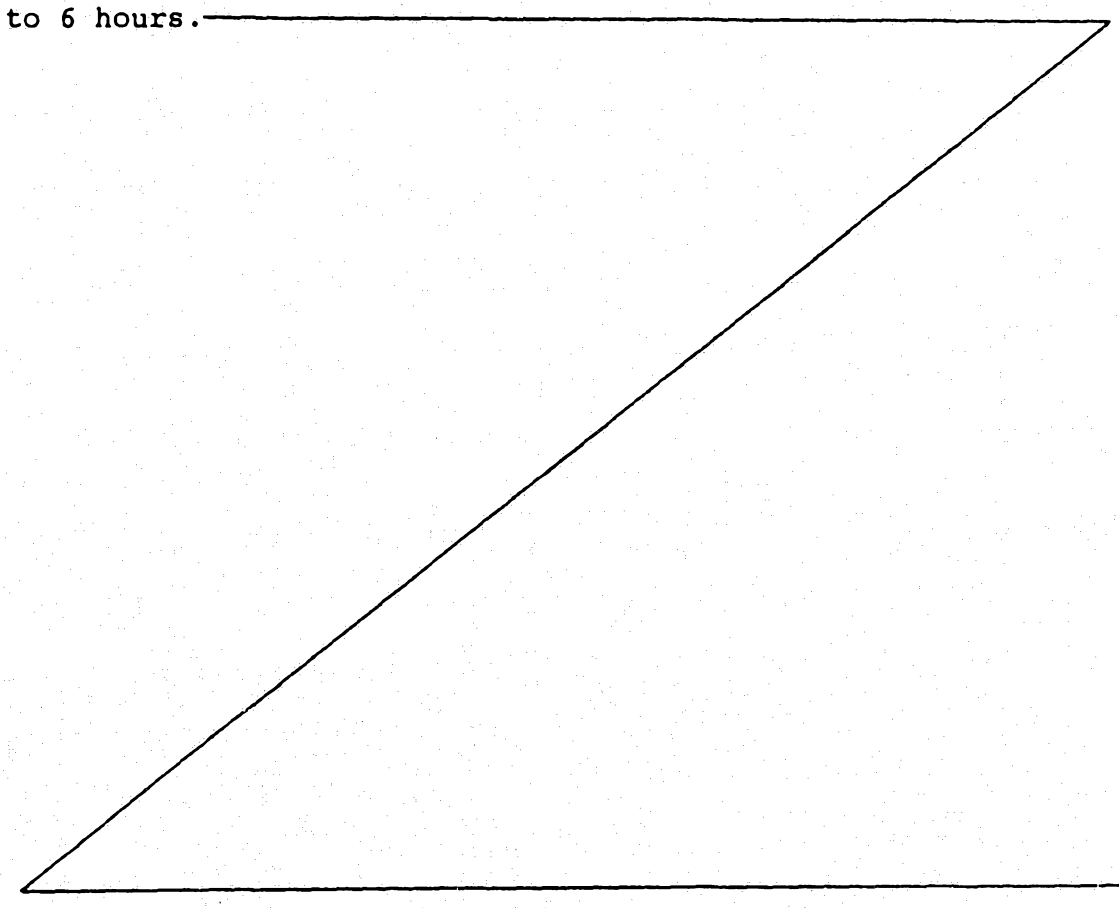
The compounds with a primary amine function of the formulas (I) and (II) are commonly used in a proportion of 1.02 to 1.2 mole, preferably 1.05 to 1.1 mole, per mole of the dicarboxylic compound. The compound with a primary amine function (I) or (II) may also be used in slight defect, down to 0.9 mole per mole of the dicarboxylic compound. The proportion is thus generally from 0.9 to 1.2 mole/mole.

The condensation of the compounds of formula (I) and/or (II) on the dicarboxylic compounds (for example dicarboxylic acids, esters or preferably anhydrides) may be effected without solvent; but preferably with a solvent, consisting more particularly of an aromatic or naphteno-aromatic hydrocarbon having a boiling point of for example, from 70 to 250°C: toluene, xylenes, diisopropylbenzene or an oil cut having the appropriate distillation range.

The additive compositions of the invention can be prepared, in practice, as follows: the compound of

formula (I) and/or (II) is introduced progressively into a reactor containing the dicarboxylic compound, while maintaining the temperature between 30 and 80°C. The temperature is then raised to 120-200°C while eliminating the resultant volatile products (water or alcohols), either stripping with a stream of inert gas or by azeotropic distillation with the selected solvent; the content of dry substance is, for example from 40 to 70%, more often about 60%.

The reaction time, after addition of the reactants is, for example, from 1 to 8 hours, preferably 3 to 6 hours.



The additives contemplated in this invention are particularly efficient for improving the cloud point of oil middle distillates (particularly gas oils), thus decreasing the temperature at which appear the first crystals of paraffin contained therein.

Although the action of these additives on the temperature at which the paraffin crystals appear in the middle distillates has not yet been clearly elucidated, a positive improvement of the cloud point of the middle distillates treated with these additives is observed, when the latter are added in a proportion of, for example, from 20 to 2000 g per ton of middle distillate. The preferred concentrations range from 100 to 2000 g/t. The decrease of the cloud point may reach, for example, 5°C, sometimes more.

It is also remarkable that the additives of the invention, which improve efficiently the cloud point of middle distillates, have also the properties of inhibiting the settling of n-paraffins contained in middle distillates, at rest, of improving the limit filterability temperature and the pour temperature and of inhibiting the corrosion of metal surfaces in contact with these distillates.

Thus, in the range of additive concentrations from 20 to 2000 g per ton, it is possible to observe a decrease the filterability temperature of, for example, up to 12°C, a decrease of the pour point of up to 20°C, a decrease of the proportion of settled paraffins and a clear anticorrosion effect particularly on ferrous metals.

The middle distillate compositions according to the invention may be prepared by directly admixing additives to the middle distillate.

It is however often advantageous to introduce them in the form of "mother-solutions" previously prepared in the above-mentioned solvents.

The "mother-solutions" can contain, for example, from 20 to 60 % by weight of additive.

The following examples illustrate the invention and must not be considered as limitative thereof in any respect.

- EXAMPLE 1

2,700 g of a polyamine of the trade (containing, in admixture, about 27 % of palmityl 1,3 propane diamine and 70 % of stearyl 1,3 propane diamine, with a 370 g equivalent of primary amine) and 2,700 g of xylene are introduced into a 20 liter reactor provided with an efficient stirrer ; the amine is dissolved at 50°C ; after cooling to 30°C, a solution of 699 g of maleic anhydride in 1,050 g of xylene is added, while maintaining the inner temperature at 40°C. The addition lasts one hours ; heating at xylene reflux is then performed for 3 hours, the inner temperature being 144°C ; 157 g of water, corresponding to 128 g of reaction water and 29 g of water contained in the amine, are removed by distillation ; once the reaction is complete, 500 g of xylene are distilled to obtain a 50 % b.w. solution of additive I in xylene.

Additive I has been analyzed after evaporation of the solvent. Its molecular weight, by number, measured by tonometry, amounts to 1800. The thin layer infra-red spectrum shows the presence of imide bands at 1700 and 1780 cm^{-1}, secondary amide bands at 1635 and 1560 cm^{-1} and a secondary amine band at 3300 cm^{-1}.

Additives II to VII have the same bands as additive I. Their molecular weights range between 1500 and 3000.

The activity of additive I is determined with two gas oil cuts of Aramco origin, whose characteristics are given in Table I below :

TABLE I

	DISTILLATION ASTM		% DISTILLED	VOLUMIC MASS AT
	IP °C	FP °C	AT 350°C	15°C IN (Kg/l)
Gas oil No. 1	181	382	89	0.846
Gas oil No. 2	186	385	87	0.847

The effect of additive I on the decrease of the cloud point of each of the two gas oil cuts, in relation with the additive concentration, determined according to standard NF T 60105, is shown Table II below.

TABLE II

ADDITIVE CONCENTRATION (% b.w.)	CLOUD POINT (°C) GAS OIL No. 1	CLOUD POINT (°C) GAS OIL No. 2
0	+ 2	+ 6
0.01	+ 1	+ 5
0.05	0	+ 4
0.1	- 1	+ 2
0.15	- 1	+ 2
0.2	- 2	+ 1

- EXAMPLE 2

Additives differing mainly by the starting amine are used in an amount of 0.1 % b.w. in the two gas oil cuts of example 1, the method of manufacture being the same as in example 1.

Additive I : product used in example 1 ;

Additive II : product obtained by condensing N-stearyl-dipropylene triamine on maleic anhydride ;

Additive III : product obtained by condensing stearyl amine on maleic anhydride.

The results are given in Table III below :

TABLE III

CLOUD POINT (°C)	GAS OIL No. 1	GAS OIL No. 2
Additive-free	+ 2	+ 6
+ 0.1 % additive I	- 1	+ 2
+ 0.1 % additive II	0	+ 3
+ 0.1 % additive III	+ 1	+ 5

It is found that the effect of decreasing the cloud point is maximum in the case of additive I, wherein the starting amine is a mixture of two N-alkyl 1,3 propane diamines.

- EXAMPLE 3

Additives differing essentially by the length of the alkyl chain of the starting amine are used in this example, in an amount of 0.1 % b.w. in the same two gas oils as above.

There are thus used :

Additive I : product used in example 1

Additive IV : product obtained by condensing N-behenyl 1,3 propane diamine on maleic anhydride (behenyl = C_{22})

Additive V : product obtained by condensing N-lauryl 1,3 propane diamine on maleic anhydride (lauryl = C_{12})

The results of the determinations of the cloud point are given in Table IV below

TABLE IV

CLOUD POINT (°C)	GAS OIL No. 1	GAS OIL No. 2
Additive-free	+ 2	+ 6
+ 0.1 % additive I	- 1	+ 2
+ 0.1 % additive IV	- 1	+ 2
+ 0.1 % additive V	+ 1	+ 5

It can be observed that the additive obtained from a diamine with an alkyl chain of 12 carbon atoms has a lower efficiency than the additives obtained from a diamine with a longer chain of 16, 18 or 22 carbon atoms.

- EXAMPLE 4

Additives differing essentially by the nature of the starting dicarboxylic compound are used in this example, in a proportion of 0.1 b.w. in the same two gas oils as above.

There are thus used :

Additive I : product used in example 1, obtained from maleic anhydride.

Additive VI : product obtained by condensing N-stearyl 1,3 propane diamine on methylmaleic (citraconic) anhydride.

Additive VII : product obtained by condensing N-stearyl 1,3 propane diamine on n-octadecenyl succinic anhydride.

The determined cloud points are shown in Table V below :

TABLE V

CLOUD POINT (°C)	GAS OIL No. 1	GAS OIL No. 2
Additive-free	+ 2	+ 6
+ 0.1 % additive I	- 1	+ 2
+ 0.1 % additive VI	0	+ 3
+ 0.1 % additive VII	0	+ 3

- EXAMPLE 5

The inhibiting effect of an additive conforming to the invention on the settling of n-paraffins crystallizing in a gas oil cut maintained at rest at low temperature is determined in this example.

The additive is additive I already used above.

Two 100 cc test tubes are filled with the already used gas oil No. 2 (distillation range : IP = 186°C, FP = 385°C).

No additive is introduced into the first test tube.

0.1 % b.w. of additive is introduced into the second test tube.

The two test tubes are closed hermetically, then left at rest in a cold room at - 10°C for one week.

After one week, the settling rate of the settled paraffins expressed as the volume of the upper limpid phase, is reported in the following Table :

TABLE VI

TEST TUBE No. 1 ADDITIVE-FREE GAS OIL	TEST TUBE No. 2 GAS OIL + ADDITIVE I
50 % vol	15 % vol

All the precipitated paraffins are thus present in 50 % by volume of the additive-free gas oil, which makes the lower portion more difficult to use as the result of the plugging of the pumps, filters and pipes.

As concerns the additive-containing gas oil, the upper limpid phase amounts to only 15 %. The paraffins are thus in 85 % of the total volume. They are in a state of better dispersion and can be transported more easily.

- EXAMPLE 6

The effect of an additive conforming to the invention is tested, in this example, on the limit filterability temperature (LFT) of the two gas oil cuts described above.

The LFT values are determined according to standard NF M 07 - 042.

TABLE VII

CONCENTRATION OF ADDITIVE I (% b.w.)	TLF GAS OIL No. 1	TLF GAS OIL No. 2
0	0°C	+ 3°C
0.15	- 8°C	- 5°C
0.20	- 9°C	- 9°C

- E X A M P L E 7

The anti-corrosion effect of additive I of example 1 is tested in this example.

Product I has been used in the two gas oils No. 1 and No. 2, as hereinbefore described, at a concentration of 0.01 % by weight.

The corrosion test consists of determining the rate of corrosion, by synthetic sea water, of cylindrical test pieces of polished steel or iron, according to the ASTM standard D 665 modified in the following manner :

The temperature is 32.2°C ; the test time is 20 hours.

The additive-free gas oils No. 1 and No. 2 cause 100 % of the surface of the test pieces to rust ; the two gas oils containing 0.01 % b.w. of additive do not cause any rusting of the test pieces.

- E X A M P L E 8

In this example, the effect of additive I, according to the invention, on the pour point of gas oil cuts is tested. The pour points are determined according to the French standard NFT 60105 ;

The additive is tested in an amount of 0.1 % by weight. The results are given in Table VIII below.

TABLE VIII

GAS OIL	DISTILLATION ASTM		% DISTILLED AT 350°	VOLUMIC MASS kg/l AT 15°C	POUR POINT	
	IP°C	FP°C			WITHOUT ADDITIVE	WITH ADDITIVE
No. 1	181	382	89	0.846	- 6°C	- 9°C
No. 2	186	385	87	0.847	- 3°C	- 9°C
No. 3	201	366	93	0.833	- 3°C	- 15°C
No. 4	186	386	89	0.833	- 3°C	- 21°C

- EXAMPLE 9

A solution consisting of 294 g (3 moles) of maleic anhydride dissolved in 500 g of xylene is introduced into a 3 liter reactor provided with a Dean and Stark water-separation system and an efficient stirrer. While maintaining the temperature of the solution between 30 and 40°C, a solution of 1230 g (3 moles) of N,N-didodecyl 1,3-diamino propane in 1000 g of xylene is added thereto in 1.5 h. The whole is heated for 3 hours at xylene reflux, during time 55 g of water discharged from the reaction medium are collected. The reaction product constitutes additive VIII which is present as a solution is xylene at a concentration very close to 50 % b.w.

- EXAMPLE 10

Although operating as in example 9, 532 g (2 moles) of dodecenylsuccinic anhydride are condensed on 820 g (2 moles) of N,N-didodecyl 1,3-diamino propane. The condensation product constitutes additive IX whose concentration in xylene is so adjusted as to attain 50 % b.w.

- EXAMPLE 11

In this example, use is made of a polyisobutenyl-succinic anhydride with a weight of 1200, corresponding to 0.90 anhydride group per 1000 g. According to the operating mode of example 9, 1200 g (1 mole) of this polyisobutenyl-succinic anhydride are condensed on a mixture of products consisting of 289 g (0.5 mole) of N,N dioctadecyl 1,3-diamino propane and 40.8 g (0.4 mole) of N,N.dimethyl 1,3-diamino propane as a solution in xylene. The reaction product constitutes additive X ; its xylene concentration is adjusted to 50 % b.w.

The effect of the so-obtained additives VIII, IX and X has been tested on the cloud point (determined according to standard NF T 60 - 105), the limit filterability temperature (determined according to standard NF M 07 - 042) and the pour point (determined according to standard NF T 60 - 105) of the two gas oils No. 1 and No. 2, the concentration of the additive being 0.1 % b.w. in each case.

The results are given in Table IX below :

TABLE IX

ADDITIVES	CLOUD POINT (°C)		T.L.F. (°C)		POUR POINT (°C)	
	G_1	G_2	G_1	G_2	G_1	G_2
0.1 % VIII	- 1	+ 3	- 4	0	- 9	- 9
0.1 % IX	- 2	+ 2	- 5	- 3	- 12	- 9
0.1 % X	- 3	+ .1	- 7	- 5	- 12	- 9
Without	+ 2	+ 6	0	+ 3	- 6	- 3

- EXAMPLE 12

294 g (3 moles) of maleic anhydride dissolved in 500 g of

xylene are introduced into a stirred 3 l reactor, and the temperature is decreased to 30°C. A solution of 797 g (3.1 moles) of 3-(2,4,6-trimethyl decyl) oxy propylamine in 324 g of xylene is added, while maintaining the temperature below 40°C. The addition lasts one hour, and heating is then performed for 3 hours at xylene reflux. The inner temperature is 144°C. 67 g of water are removed by distillation, corresponding to 54 g of reaction water and 13 g of water contained in the amine ; after completion of the reaction, 200 g of dilution xylene are added to obtain a 50 % b.w. solution of additive XI in xylene.

Additive XI has been analyzed after evaporation of the solvent. Its molecular weight by number, determined by tonometry, is 500. The thin layer infra-red spectrum shows imide bands at 1700 and 1780 cm^{-1}, secondary amide bands at 1635 and 1560 cm^{-1} and an ether band at 1100 cm^{-1}.

The additives XII to XVI, whose manufacture is described in the following examples, show the same I.R. absorption bands as those of additive XI ; their molecular weights are between 600 and 3000.

- EXAMPLES 13 and 14

The method of manufacture is the same as in example 12, with similar molar ratios, but the amine compounds differ.

- EXAMPLE 13

Additive XII is obtained by condensing maleic anhydride on N- 3-(2,4,6-trimethyl decyl) oxy propyl 1,3-diaminopropane.

- EXAMPLE 14

Additive XIII is obtained from the condensation product of maleic anhydride on a mixture comprising, by mole, 55 % of ethanolamine and 45 % of a N-alkyl propylenediamine cut of the trade, whose alkyl chains consist of about 27 % of C_{16} chain and 72 % of C_{18} chain (equivalent molecular weight : 370 per primary amine

function).

- EXAMPLES 15 to 17

These examples are conducted according to the operating mode of example 12, the molar ratios of the reactants being the same as in example 12.

- EXAMPLE 15

3-(2,4,6- trimethyl decyl) oxy propylamine is condensed on a polyisobutenyl succinic anhydride whose weight is about 1000 and which has 0.675 anhydride function per 1000 g, thus producing additive XIV.

- EXAMPLE 16

3-(2,4,6-trimethyl decyl) oxy propylamine is condensed on an alkenyl succinic anhydride obtained by reacting equimolecular proportions of maleic anhydride and of a cut of linear α-olefins containing approximately 49 % of C_{20} olefin, 42 % of C_{22} olefin and 9 % of C_{24} olefin.

The result of this condensation is additive XV.

- EXAMPLE 17

Ethanolamine is condensed on the alkenylsuccinic anhydride of example 16, the molar ratio of the ethanolamine to the anhydride content of the alkenylsuccinic anhydride being 1/1. Additive XVI is obtained.

In the above examples, the additives are obtained as a solution in xylene whose concentration is adjusted, so as to obtain 50 % b.w. solutions of additive in xylene.

The activity of these additive compositions is tested by incorporating them, in a proportion of 0.1 % b.w. of additive with

respect to the gas oil, to the two gas oils cuts of ARAMCO origin, designated as G_1 and G_2, whose properties have been given above.

Three determinations have been performed on each of the so-formed compositions :

- cloud point according to standard NF T 60 - 105
- limit filterability temperature (LFT) according to standard NF M 07 - 042
- pour point according to method NF T 60 - 105.

The results of these determinations are given in Table X below :

TABLE X

ADDITIVES	CLOUD POINT (°C)		TLF (°C)		POUR POINT (°C)	
	G_1	G_2	G_1	G_2	G_1	G_2
Without	+2	+6	0	+3	-6	-3
0.1 % XI	-1	+3	-6	-2	-9	-6
0.1 % XII	-1	+3	-3	0	-12	-9
0.1 % XIII	-2	+3	-7	-5	-12	-9
0.1 % XIV	-1	+3	-3	0	-9	-9
0.1 % XV	-3	+2	-8	-4	-24	-21
0.1 % XVI	-2	+2	-8	-5	-21	-18

- EXAMPLE 18

The inhibiting effect of an additive according to the invention on the settling of n-paraffins crystallizing in a gas oil cut maintained at rest at low temperature is tested in this example.

Two 100 cc test tubes are filled with the previously used gas oil No. 2 (distillation range IP = 186°C, FP = 385°C).

No additive is introduced into the first test tube.

0.1 % b.w. of additive XI is introduced into the second test tube. The two test tubes are hermetically closed and left at rest in a cold room at -10°C for one week.

After one week, the settling rate of the settled paraffins, expressed as the volume of the limpid upper phase, is noted in the following Table :

TABLE XI

TEST TUBE No. 1	TEST TUBE No. 2
ADDITIVE - FREE GAS OIL	GAS OIL + ADDITIVE XI
50 % vol.	15 % vol.

All the precipitated paraffins are present in 50 % of the volume of the additive - free gas oil, which makes the lower portion thereof more difficult to use, as a result of the pumps, filters and pipes plugging.

There is only 15 % of limpid upper phase in the additive-containing gas oil. The paraffins are contained in 85 % of the total volume. They are better dispersed and can be transported more easily.

- EXAMPLE 19

The anti-corrosion effect of additive XI of example 12 is tested in this example.

Product XI has been used in the two already described gas oils G_1 and G_2 at a concentration of 0.01 % b.w.

The corrosion test consists of examining the corrosion rate of cylindrical polished steel or iron test pieces, caused by synthetic sea water, according to standard A S T M D 665 modified as follows : the temperature is 32.2°C and the test time is 20 hours.

The two additive - free gas oils G_1 and G_2 give test pieces rusted on 100 % of their surface, and the two gas oils containing 0.01 % b.w. of additive give test pieces totally free of rust.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Oil middle distillate composition, characterized as comprising a major proportion of oil middle distillate and a minor proportion, sufficient to decrease the cloud point of said distillate, of an additive consisting of a material having an average molecular weight of 300 to 10,000 and resulting from the reaction of at least one aliphatic dicarboxylic compound selected from the maleic and alkylmaleic anhydrides, the alkenylsuccinic anhydrides having 10 to 30 carbon atoms in the alkenyl radical, polyalkenylsuccinic anhydrides, the corresponding dicarboxylic acids and lower alkyl diesters, with at least one compound having a primary amine function, complying with one of the general formulas:

$$R - Z - \left[(CH_2)_n - NH \right]_m - H \qquad (I)$$

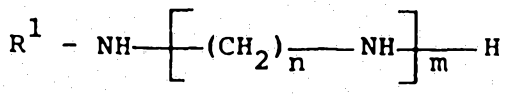
and

$$HO - CH_2 - R^5 - NH_2 \qquad (II)$$

wherein R represents a monovalent saturated aliphatic radical of 1 to 30 carbon atoms, Z is selected from the -NR'- groups, wherein R' is a hydrogen atom or a monovalent saturated aliphatic radical containing 1 to 30 carbon atoms, and the oxygen atom -O-, n is an integer from 2 to 4, m is zero or an integer from 1 to 4 when Z is -NH- or an integer from 1 to 4 in all other cases; and R^5 represents a divalent saturated aliphatic radical having 1 to 18 carbon atoms; said compound having a primary amine function being used in a proportion of 0.9 to 1.2 mole per mole of said dicarboxylic compound and said reaction being effected at a temperature of 120 to 200°C for a sufficient time to form the theoretical amount of volatile products consisting of water and/or alcohol, which are eliminated.

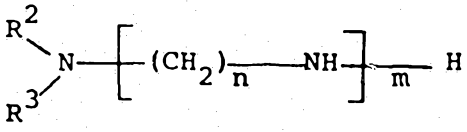
2. A composition according to claim 1, characterised in that the compound having a primary amine function (I) consists of at least one mono-amine of the formula $R^1 NH_2$ and R^1 represents a linear alkyl radical of 12 to 30 carbon atoms.

3. A composition according to claim 1, characterised in that the compound having a primary amine function (I) consists of at least one polyamine of the formula:



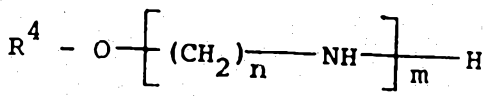
wherein R^1 represents a linear alkyl radical with 12 to 30 carbon atoms, n is an integer from 2 to 4 and m an integer from 1 to 4.

4. A composition according to claim 1, characterised in that the compound having a primary amine function (I) consists of at least one polyamine of the formula:



wherein R^2 and R^3 are each a linear alkyl radical 8 to 24 carbon atoms, R^2 and R^3 together comprising from 16 to 32 carbon atoms, n is an integer from 2 to 4 and m is an integer from 1 to 4.

5. A composition according to claim 1, characterised in that the compound having a primary amine function (I) consists of at least one ether-amine of the formula:



wherein R^4 represents an alkyl radical of 8 to 22 carbon atoms, n is an integer from 2 to 4 and m an integer from 1 to 4.

6. A composition according to claim 1, characterised in that the compound having a primary amine function (II) consists of at least one amino-alcohol of the formula:

$$HO - CH_2 - R^5 - NH_2$$

where R^5 represents a linear alkylene radical containing 10 to 18 carbon atoms.

7. A composition according to any one of claims 1 to 6, characterised in that said aliphatic dicarboxylic compound is selected from maleic anhydride, methylmaleic anhydride, n-octadecenyl and dodecenyl succinic anhydrides and polyisobutenylsuccinic anhydrides

having a molecular weight from 500 to 2000.

8. A composition according to any one of claims 1 to 7, characterised in that the reaction comprising admixing, at a temperature of 30^{o} to $80^{o}C$, said dicarboxylic compound with said compount of formula (I) or (II) and heating the resultant mixture at a temperature of 120 to $200^{o}C$ for 1 to 8 hours.

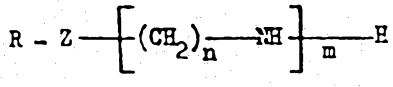
9. A composition according to any one of claims 1 to 8, characterised in that said middle distillate has a distillation range between 150 and $450^{o}C$.

10. A composition according to claim 9, characterised in that said middle distillate consists of a gas oil cut having an initial distillation range from an initial temperature of 160 to $190^{o}C$ to a final temperature of 350 to $390^{o}C$.

11. A composition according to any one of claims 1 to 10, characterised in that the proportion of said additive is from 20 to 2000 g/ton.

12. A composition according to claim 11, characterised in that the proportion of said additive is 1000 g/ton.

13. An additive, useful, in particular, to decrease the cloud point of middle distillates, characterized as having a molecular weight of 300 to 10,000 and resulting from the reaction, with at least one aliphatic dicarboxylic compound selected from the maleic and allylmaleic anhydrides, the alkenylsuccinic and polyalkenylsuccinic anhydrides, the corresponding di-carboxylic acids and light alkyl diesters, of at least one compound having a primary amine function, complying with one of the general formulas:



(I)

and



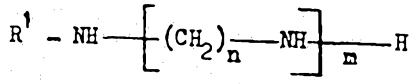
(II)

wherein R represents a monovalent saturated aliphatic radical of 1 to 30 carbon atoms, Z is selected from - NR' - groups, wherein R' is a hydrogen atom or a monovalent saturated aliphatic radical containing 1 to 30 carbon atoms, and the oxygen atom - O -, n is an integer from 2 to 4, m is zero or an integer from 1 to 4 ; and R^5 represents a

divalent saturated aliphatic radical having 1 to 18 carbon atoms.

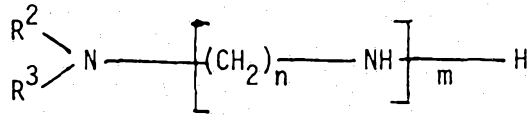
14. An additive according to claim 13, characterized in that the compound having a primary amine function (I) consists of at least one mono-amine of the formula $R^1 \quad NH_2$ where R^1 represents a linear alkyl radical of 12 to 30 carbon atoms.

15. An additive according to claim 14, characterized in that the compound having a primary amine function (I) consists of at least one polyamine of the formula



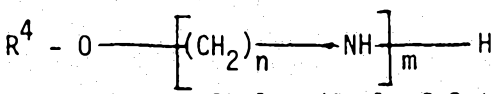
wherein R^1 represents a linear alkyl radical with 12 to 30 carbon atoms, n is an integer from 2 to 4 and m an integer from 1 to 4.

16. An additive according to claim 13, characterized in that the compound having a primary amine function (I) consists of at least one polyamine of the formula



wherein R^2 and R^3 are each a linear alkyl radical of 8 to 22 carbon atoms, R^2 and R^3 together comprising from 16 to 32 carbon atoms, n is an integer from 2 to 4 and m is an integer from 1 to 4.

17. An additive according to claim 13, characterized in that the compound having a primary amine function (I) consists of at least one ether-amine of the formula:



wherein R^4 represents an alkyl radical of 8 to 22 carbon atoms, n is an integer from 2 to 4 and m an integer from 1 to 4.

18. An additive according to claim 13, characterized in that the compound having a primary amine function (II) consists of at least one amino-alcohol of the formula :



where R^5 represents a linear alkylene radical containing 10 to 18 carbon atoms.

19. An additive according to one of claims 13 to 18, characterized in that said aliphatic dicarboxylic compound is selected from maleic anhydride, methylmaleic anhydride, n-octadecenyl and dodecenyl succinic anhydrides and the polyisobutenylsuccinic anhydrides having a molecular weight from 500 to 2000.

20. An additive according to one of claims 13 to 19, characterized in that the reaction performed to prepare it comprises admixing, at a temperature of 30 to 80°C, said dicarboxylic compound with said compound of formula (I) or (II) in substantially equimolecular proportions, and heating the resultant mixture at a temperature of 120 to 200°C for 1 to 8 hours.

21. A middle distillate composition, characterized in that it comprises a major proportion of middle distillate of distillation range from 150 to 450°C, and a minor proportion, sufficient to descrease the cloud point thereof, of at least one additive according to one of claims 1 to 8.

22. A middle distillate composition according to claim 21, characterized in that said middle distillate consists of a gas oil cut distilling between an initial temperature of 160 to 190°C and a final temperature of 350 to 390°C.

23. A middle distillate composition according to one of claims 21 and 22, characterized in that the proportion of said additive is from 20 to 2000 g/ton.

24. A middle distillate composition according to claim 23, characterized in that the proportion of said additive is about 1000 g/ton.

Dated this 15th day of February 1988

INSTITUT FRANCAIS DU PETROL and ELF FRANCE

By Their Patent Attorneys:

CLEMENT HACK & CO.

Fellows Institute of Patent
Attorneys of Australia