

**BIFUNCTIONAL ADDITIVES FOR LIQUID HYDROCARBONS**  
**OBTAINED BY GRAFTING STARTING WITH COPOLYMERS OF**  
**ETHYLENE AND/OR PROPYLENE AND VINYL ESTER**

5           **TECHNICAL FIELD**

The present invention relates to the synthesis and the use of novel copolymers based on ethylene and/or propylene and vinyl ester(s) modified by grafting, effective for improving both the resistance to cold and the lubricity of liquid hydrocarbons, in particular middle distillates originating from the distillation of petroleum and crude  
10 oils, in particular those with a low sulphur content.

**PRIOR ART**

For a long time, the oil industry has been developing additives which promote the filterability of motor fuels at low temperatures: they are copolymers of ethylene and vinyl acetate and/or vinyl propionate (EVA or EVP), called CFPP (cold filter  
15 plugging point) additives. Their role is to modify the crystallization and more particularly to limit the size of the paraffin crystals formed at low temperature, for example lower than 5°C, with a view to passing through the filters arranged inside internal combustion engines or in heating installations. This type of additives, widely known to a person skilled in the art, is very often added to the middle distillates of  
20 standard type, and in particular those used as Diesel fuels or as heating fuels. Additional quantities of these additives can be added to the motor fuels sold in service stations in particular to meet very cold weather specifications.

Other types of additives such as copolymers of ethylene, vinyl acetate and branched vinyl ester such as vinyl neodecanoates (VeoVA) having a role on the CFPP  
25 have been described, in particular in US 2004 /0226216.

In order to improve the resistance to cold, i.e. both the CFPP and the pour point of the distillates, additives can be added to these CFPP (EVA or EVP) additives which act either alone or in combination with these additives on the pour point of the distillates. The prior art copiously describes such combinations of additives  
30 improving both the cold filter plugging point and the pour point of the hydrocarbon distillates of standard type at low temperatures.

Thus, US 3,275,427 describes a middle distillate of distillation cut comprised between 177 and 400°C containing an additive constituted by 90 to 10% by weight of a copolymer of ethylene comprising from 10 to 30% by weight of vinyl acetate units of molecular weight comprised between 1,000 and 3,000 and from 10 to 90% by weight of a lauryl polyacrylate and/or lauryl polymethacrylate with a molecular mass by weight varying from 760 to 100,000. It should be noted that these polyacrylates improve the filterability temperature determined according to the standard NF EN116 without damaging the pour point temperature determined by the standard NF 60105.

For the transport of the crude oils and heavy distillates by pipe, the authors of the patent US 3,726,653 were confronted with the problem of the improvement of pouring in particular at the low temperatures at which these products could solidify in the pipes. In order to improve these properties in hydrocarbon compositions containing paraffins 5 to 20% by weight of which have a boiling point greater than 350°C and a softening point greater than 35°C, the inventors propose to add to these compositions from 10 ppm to 2% by weight of a mixture of a polymer of an olefinic ester of carboxylic acids with 3 to 5 carbon atoms with an alcohol with 14 to 30 carbon atoms and with a molecular mass by weight varying from 1,000 to 1,000,000, with a copolymer of ethylene and vinyl acetate comprising from 1 to 40, preferably from 14 to 24 vinyl acetate units of average molecular weight of 20,000 to 60,000. The molar ratio of the olefinic ester polymer to the copolymer of ethylene and vinyl acetate varies from 0.1:1 to 10:1.

In order to control the size of the paraffin crystals present at levels of at least 3% in middle distillates having a boiling point comprised between 120°C and 480°C, US 4,153,422 proposes adding to these middle distillates from 10 ppm to 1% by weight of a mixture of a homopolymer of an olefinic ester of acrylic or methacrylic acid comprising an alkyl chain with 14 to 16 carbon atoms and with a molecular mass by weight varying from 1,000 to 200,000, with an ethylene and vinyl acetate copolymer with an average numerical molecular weight lower than 4,000. The molar ratio of olefinic ester homopolymer to copolymer of ethylene and vinyl acetate varies from 0.1:1 to 20:1.

In addition to the resistance to cold properties, the liquid hydrocarbons, in particular the diesel fuels, aviation fuels and motor fuels or fuel oils for domestic

applications (DFO) must have lubrication abilities for the protection of pumps, injection systems and/or all moving parts with which these products come into contact, for example in an internal combustion engine. With the wish to use purer and purer products which are less and less polluting, the oil refining industry is led to propose motor fuels or fuel oils with a sulphur content which is more and more reduced: since 1<sup>st</sup> January 2005 the sulphur level authorized in motor fuels within the European Union has been limited to 50 ppm and it must be less than 10 ppm starting from 1<sup>st</sup> January 2009. Now, as the sulphur compounds are eliminated, a loss of the lubricity of these motor fuels is observed. Below a certain level of sulphur-containing products, there is even an appreciable appearance of wear phenomena and even the breakage of moving parts in pumps and/or injection systems is noticed.

It is therefore necessary to compensate for the lubricating effect of the sulphur-containing compounds by the least possible polluting, and if possible non-polluting, compounds but having a lubricity sufficient to limit the risks of wear.

In order to resolve this problem, several types of additives have already been proposed. Thus primarily anti-wear additives, proven in the field of lubricants, of the unsaturated fatty acid ester and fatty acid dimer, aliphatic amine, fatty acid and diethanolamine ester and long-chain aliphatic monocarboxylic acid type as described in patents US 2,527,889, US 4,185,594, US 4,204,481, US 4,208,190, US 4,248,182 are added to the gas oils. Most of these additives have a sufficient lubricity, but at excessively high concentrations, which is very detrimental financially. Moreover, the additives containing dimer acids, like those containing trimer acids, cannot be used in motor fuels supplying vehicles in which the fuel can be in contact with the lubrication oil, as the chemical reaction of these acids forms deposits which are sometimes insoluble in the oil, and more importantly are incompatible with the detergents usually used.

Patent US 4,609,376 recommends the use of anti-wear additives obtained from mono- and poly-carboxylic acid esters and polyhydroxylated alcohols in motor fuels containing alcohols in their composition.

US 2,686,713 recommends the introduction of tall oil up to 60 ppm into diesel fuels in order to prevent the formation of rust on the metal surfaces in contact with these motor fuels.

Another route chosen is the introduction of vegetable oil esters or the vegetable oils themselves into these motor fuels to improve their lubricity or their anti-friction qualities. These include the esters derived from rapeseed, flax, soya, sunflower oils or the oils themselves (see patents EP 635 558 and EP 605 857). One of the major  
 5 drawbacks of these esters is their low lubricity at a concentration of less than 0.5% by weight in motor fuels.

In order to improve the lubricity of the gas oils, WO 95/33805 recommends the introduction of a resistance to cold additive constituted by nitrogen-containing additives comprising one or more N-R<sub>13</sub> groups in which R<sub>13</sub> comprises 12 to 24  
 10 carbon atoms, is linear, slightly branched or alicyclic and aromatic, the nitrogen group being able to be linked by CO or CO<sub>2</sub> and to form carboxylates of amines or amides.

US 3,667,152 describes the use of tall oil acid (or TOFA, abbreviation of tall oil fatty acid) as an anti-wear additive.

EP 915 944 describes anti-friction additives for improving the lubricant  
 15 properties of diesel fuels with a low sulphur content, constituted by at least one saturated or unsaturated, C12-C24 monocarboxylic aliphatic hydrocarbon, and at least one polycyclic hydrocarbon compound chosen from the group constituted by resin acids, their derivatives (amine carboxylates, esters and nitriles). These anti-friction additives can be used in liquid hydrocarbons in the presence of other additives, such  
 20 as detergents, pro-cetane additives, demulsifiers, anti-corrosion additives, additives which improve resistance to cold, odour modifiers, and also known anti-friction additives.

WO 94/00536 describes compositions improving the low temperature properties of fuel oils comprising

- 25 a) terpolymers of ethylene - 2 different unsaturated esters and/or
- b) mixtures of 2 different copolymers [ethylene- 1 unsaturated ester or an acrylate] in which the longest ester alkyl chains are C6 to C13 alkyl chains.

EP 1116780 describes multifunctional additives which improve the cold properties and lubricity of motor fuels. These additives contain two different  
 30 compounds A) 5-95% of an oil-soluble amphiphilic compound and B) 5-95% of a terpolymer of ethylene - C2-C4 vinyl ester - C8-C15 neocarboxylic vinyl ester (i.e.

which contains a tertiary C). The lubricant properties are provided by the amphiphilic compound.

US 5,254,652 describes terpolymers of ethylene - vinyl acetate - C9 or C10 neoalkanoate vinyl ester which improve the flow properties of motor fuels at low  
5 temperatures.

A need exists to improve not only the resistance to cold (filterability temperature and pour point) but also the lubricity of the motor fuels based on liquid hydrocarbons, in particular low-sulphur or sulphur-free motor fuels.

### SUMMARY OF THE INVENTION

10 The present invention, subject of the present application, relates to copolymers which can advantageously be used as bifunctional additives which improve both the resistance to cold and the lubricity of the liquid motor fuels in which they are incorporated.

Thus the first purpose of the invention relates to the use of these copolymers as  
15 additives for motor fuel bases, preferably of distillate type for diesel fuels or for domestic fuel oils (DFO).

The invention therefore relates to the use as a bifunctional lubricity and resistance to cold additive for liquid hydrocarbon compositions of at least one copolymer comprising:

- 20 • units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_{n1}$ - and/or propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_{n2}$  with  $n1 + n2 = n$  ranging from 98 to 643, preferably ranging from 124 to 515;  $n1$  being advantageously equal to  $n$ ;
- 25 • units derived from vinyl esters of formula B: -  $(\text{CH}_2\text{-CHOO-CR}_1)_{m-x}$ - in which  $\text{R}_1$  represents a  $\text{C}_1\text{-C}_{15}$  linear or branched alkyl group, preferably methyl, propyl, and/or a C5 to C15 branched alkyl group, in which the branching is situated at any point of the alkyl radical, preferably in position 2 or 3 of the alkyl chain; preferably vinyl esters are chosen from the comonomers among C5-C15
- 30 comonomers, preferably chosen from the pivalate, isopentanoate, isohexanoate, isononanoate, isodecanoate and/or isotridecanoate, and advantageously 2-ethyl hexanoate, neoalkanoates, in particular the neononanoate, neodecanoate and/or

neoundecanoate; with m ranging from 2 to 105, preferably ranging from 16 to 71 and x ranging from 0.2 to 105, preferably ranging from 1.6 to 71;

- units of formula C: - (CH<sub>2</sub>-CHOH)<sub>x1</sub> - in which x1 ranges from 0 to 0.30x, preferably x1 = 0;
- units of formula D: - (CH<sub>2</sub>-CHOO-CR<sub>2</sub>)<sub>x2</sub> - in which x2 ranges from 0.70x to x, preferably x2 = x, and R<sub>2</sub> represents a C<sub>8</sub>-C<sub>24</sub> saturated or unsaturated, linear or branched, alkyl or alkenyl group, preferably C<sub>14</sub>-C<sub>20</sub> or also C<sub>14</sub> to C<sub>18</sub>

with  $x = x_1 + x_2$

Preferably, the percentage in moles of units A and/or A' in the copolymer ranges from 79 to 99% in moles, preferably 86.7 to 90.7% in moles; the percentage in moles of units B in the polymer ranges from 0 to 19% in moles, preferably 4.6 to 12% in moles; the percentage in moles of units C in the polymer is close to 0 to 6.3% in moles and advantageously equal to 0% in moles; the percentage in moles of units D in the polymer is from 0.1 to 21% in moles, preferably from 0.1 to 10% in moles, more preferably from 0.93 to 8.6% in moles.

Preferably, said at least one copolymer is in the form of a concentrated solution in a hydrocarbon distillate, preferably at a concentration of more than 50% by weight, preferably more than 70% by weight or preferably more than 80% by weight, preferably 60 to 80% by weight.

According to a preferred embodiment, the hydrocarbon liquid composition is a hydrocarbon distillate containing from 0 to 5,000 ppm of sulphur, and contains 10 to 5,000 ppm of said at least one copolymer, optionally in a mixture with other additives such as detergents, dispersants, demulsifiers, anti-foam agents, biocides, reodorants, cetane improvers, anti-corrosion agents, friction modifiers, lubricity, combustion, cloud point, pour point improvers, anti-sedimentation agents and conductivity improvers, resistance to cold additives, lubricants.

According to a preferred embodiment, the distillate comprises at least one hydrocarbon cut originating from the group constituted by the distillates with a boiling point comprised between 150 and 450°C, an initial crystallization temperature ICT greater than or equal to -20°C, preferably greater than or equal to

-15°C, preferably comprised between -15°C and + 10°C, comprising distillates from direct distillation, distillates from vacuum distillation, hydrotreated distillates, distillates originating from catalytic cracking and/or hydrocracking of vacuum distillates, distillates resulting from ARDS type conversion and/or visbreaking processes, distillates originating from the upgrading of Fischer Tropsch cuts, distillates resulting from the BTL conversion of vegetable and/or animal biomass, taken alone or in a mixture, and esters of vegetable and animal oils or their mixtures.

Preferably, the distillate comprises a C9 to C40 n-paraffin content comprised between 1 and 40% by mass.

Preferably, said copolymer, as a distillate additive for Diesel fuel comprises from 0 to 500 ppm of sulphur.

Preferably, said copolymer as a distillate additive for heating fuel oil comprises from 0 to 5,000 ppm of sulphur.

According to a preferred embodiment, said copolymer is intended as a distillate additive for heavy fuel oil.

The second purpose is to provide a process for the preparation of these novel polymers via an esterification process of the vinyl ester units which have been hydrolyzed previously either in part or in total.

The third purpose of the present invention relates to the novel copolymers of ethylene and/or propylene and vinyl ester(s) as mentioned above which are chemically modified by grafting branchings essentially derived from fatty acid(s) in particular for their use in motor fuel bases as bifunctional additives.

These motor fuel bases are in general rich in paraffins, weakly aromatic and as a result have a low solvent power. The addition of the copolymers according to the present invention therefore applies not only to the distillates originating from the direct distillation of hydrocarbons originating from crude oils with a very high paraffin content but also to the hydrocarbons originating from the heaviest cuts of refining operations i.e. cracking, hydrocracking and catalytic cracking processes and visbreaking processes or also the synthetic distillates originating from the conversion of gas and/or coal such as those originating from the Fischer Tropsch process, but also those resulting from the treatment of vegetable and/or animal biomass, such as in

particular NexBTL and the distillates containing esters of vegetable and/or animal oils, taken alone or in a mixture.

The present invention relates to copolymers comprising:

a) units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_{n1}$ - and/or propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_{n2}$  with  $n1 + n2 = n$  ranging from 98 to 643, preferably ranging from 124 to 515;  $n1$  being advantageously equal to  $n$ ;

b) units of formula B: -  $(\text{CH}_2\text{-CHOO-CR}_1)_{m-x}$ - in which  $R_1$  represents a  $C_1$ - $C_{15}$  linear or branched alkyl group, preferably methyl, ethyl, and/or a  $C_5$  to  $C_{15}$  branched alkyl group, in which the branching is situated at any point of the alkyl radical, preferably in position 2 or 3 of the alkyl chain; among the preferred  $C_5$ - $C_{15}$  vinyl comonomers, there can be mentioned the pivalate, isopentanoate, isohexanoate, isononanoate, isodecanoate and/or isotridecanoate, and advantageously 2-ethyl hexanoate, neoalkanoates, in particular the neononanoate, neodecanoate and/or neoundecanoate; with  $m$  ranging from 2 to 105, preferably ranging from 16 to 71 and  $x$  ranging from 0.2 to 105, preferably ranging from 1.6 to 71;

c) units of formula C: -  $(\text{CH}_2\text{-CHOH})_{x1}$ - in which  $x1$  ranges from 0 to  $0.30x$ , preferably  $x1 = 0$ ;

d) units of formula D: -  $(\text{CH}_2\text{-CHOO-CR}_2)_{x2}$ - in which  $x2$  ranges from  $0.70x$  to  $x$ , preferably  $x2 = x$ , and  $R_2$  represents a  $C_8$ - $C_{24}$  saturated or unsaturated, linear or branched alkyl group and preferably  $C_{14}$ - $C_{20}$  or also  $C_{14}$  to  $C_{18}$ ;

with  $x = x1 + x2$

Advantageously, the percentage in moles of units A and/or A' in the copolymer can represent from 79 to 99% in moles, preferably 86.7 to 90.7% in moles;

the percentage in moles of units B can represent from 0 to 19% in moles, preferably 4.6 to 12% in moles;

the percentage in moles of units C can represent from 0 to 6.3% in moles, preferably the percentage in moles of units C is close to, or even equal to 0% in moles;

the percentage in moles of units D can represent from 0.1 to 21% in moles, preferably 0.93 to 8.6% in moles.

The present invention also relates to the process for the preparation of the copolymers according to the invention as defined previously; this process comprises the following stages:

1) providing a starting copolymer of ethylene and/or propylene and vinyl ester(s) comprising:

a) units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_{n1}$ - and/or propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_{n2}$  with  $n1 + n2 = n$  and

b) units of formula B: -  $(\text{CH}_2\text{-CHOCOR}_1)_m$ - in which  $R_1$  is chosen from the  $\text{C}_1\text{-C}_{15}$  linear or branched alkyl groups, alone or in a mixture, and preferably comprises the methyl group and/or the ethyl group and/or a C5 to C15 branched alkyl groups, as defined previously;

$n$  and  $m$  being as defined previously;

2) hydrolysis reaction, at least partial, of the alkyl esters present in units B, then

3) esterification reaction, at least partial, and preferably total, of these hydrolyzed sites by at least one fatty acid of formula  $\text{R}_2\text{COOH}$ ,  $\text{R}_2$  being as defined previously and/or at least one fatty acid derivative such as an acid anhydride, acid halide, preferably acid chloride; the esterification level is preferably greater than 50%, advantageously greater than 80%, and particularly advantageously equal to 100%.

Another process for the preparation of copolymers consists in carrying out a transesterification of a copolymer as defined in 1) with an alcohol of type  $\text{R}_2\text{CH}_2\text{OH}$ ; a transesterification process is for example described in WO 94/00536.

The starting copolymers used in stage 1) are random copolymers comprising:

a) units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_n$ - and/or from propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_n$  with  $n1 + n2 = n$

b) units of formula B: -  $(\text{CH}_2\text{-CHOCOR}_1)_m$ - in which  $R_1$  is chosen from  $\text{C}_1\text{-C}_{15}$  linear or branched alkyl group,

$n$  and  $m$  being as defined previously

The copolymers according to the invention have an average numerical molar weight  $\overline{Mn}$  measured by polystyrene standard calibration GPC, comprised in general between 4,500 and 20,000 g.mol<sup>-1</sup>.

5 The copolymer obtained at the end of stage 2) is obtained by a stage of partial or total hydrolysis of the ester groups of the starting copolymer of ethylene and/or propylene and vinyl ester(s) described above.

10 In general, the hydrolysis rate can represent from 10 to 100% of the hydrolysable sites (units B). The hydrolysis can be direct or obtained by transesterification in an acid or basic medium preferably by basic methanolysis; the conversion rate of the vinyl ester groups to vinyl alcohol groups is controlled by the volume of methanolic soda solution introduced (in the case of transesterification in a basic medium). Thus, by varying the hydrolysis rate of stage a) of the process, the number of esters grafted on the final copolymer is therefore varied.

15 The hydrolysis stage 2) is followed by at least one esterification of the vinyl alcohol groups formed in the previous stage by one or more fatty acids (stage 3) preferably converted to acid chlorides, for example using oxalyl chloride, in order to improve the esterification yield.

20 Within the meaning of the present invention, by fatty acid is meant an aliphatic carboxylic acid deriving from, or contained in, animal and/or vegetable fats, oils or waxes. The natural fatty acids have a saturated or unsaturated, linear, branched and/or cyclic carbon-containing chain with 4 to 28 carbon atoms (generally an even number); preferably, the fatty acids are chosen from the acids having a C<sub>8</sub> to C<sub>24</sub> non-cyclic hydrocarbon chain, alone or in a mixture, such as stearic acid, oleic acid, linoleic acid, palmitic acid and/or linolenic acid, and are advantageously chosen from  
25 the fatty acids having at least one unsaturation.

The scope of the invention would not be exceeded if the esterification stage was implemented using fatty acids derived from tall oil, which are better known by the abbreviation TOFA (tall oil fatty acids). These TOFAs are in general obtained by distillation of the tall oil, which is a by-product of the production of pine wood pulp  
30 by the sulphate process; they comprise a major quantity of fatty acids as defined above as well as a minor quantity of resin acids, such as abietic, dihydroabietic,

tetrahydroabietic, dehydroabietic, neoabietic, pimaric, levopimaric, and/or parastrinic acids, etc. The grafted copolymers obtained can also contain ester functions of resin acids formed from the resin acids present in the mixture of acids used.

At the end of stage 3) (esterification of the copolymer originating from stage 2)), a grafted copolymer is obtained which is partially or preferably totally esterified.

The copolymers according to the invention can be advantageously used as obtained at the end of stage 3) as additives for liquid hydrocarbons, motor fuels and fuel oils.

The copolymers according to the invention have good solubility in the hydrocarbons of middle distillate type, greater than that of the copolymers of ethylene and/or propylene and vinyl ester(s) of the prior art, such as EVA or EVP. This allows a significant improvement in the filterability characteristics of the motor fuels or other fuels with additives or the blocking tendency characteristics (standard IP 387) of the motor fuels and other fuels with additives. It is noted that the solubility of the copolymers according to the invention is improved with respect to that of the copolymers of EVA and/ EVP when the FBT (Filter Blocking Tendency) values are measured; in practice, this better solubility of the compositions of hydrocarbons supplemented with the copolymers according to the invention allows blocking of the filters (of diameter in general equal to 1.6  $\mu\text{m}$ ) to be avoided.

The improvement in solubility of the copolymers according to the invention allows hydrocarbons with additives to be obtained which retain their initial filterability characteristics at ambient temperature and remain perfectly filterable in filtration systems that can be encountered for example in the fuel systems of engines and heating installations.

In addition, the lower viscosity of the copolymers in comparison to EVA and/or EVP makes it possible to achieve concentrated solutions of copolymer(s) according to the invention in the hydrocarbons with a reduced level of aromatic solvent without detriment to the pumpability and use of these solutions (constraints of viscosity and of rheological behaviour in the pumping or injection systems).

The copolymers according to the invention can also be used in the form of a concentrated solution in a solvent, in general in a hydrocarbon distillate, preferably at a concentration of more than 50% by weight, preferably more than 70% by weight, or

advantageously at a concentration greater than or equal to 80%; concentrated solutions in a solvent, in general in a hydrocarbon distillate which are also preferred comprise 60 to 80% by weight of copolymer(s) according to the invention.

5        These copolymers according to the invention or preferably their concentrated solutions as defined above are in particular used as bifunctional additives: both as filterability additives, i.e. additives making it possible to lower the cold filter plugging point (CFPP) of compositions based on liquid hydrocarbons and as additives which improve the lubricity or anti-friction additives for these compositions based on liquid hydrocarbons.

10        The compositions of liquid hydrocarbons in general originate from oil refining operations, in particular from the direct distillation of hydrocarbons but can also originate from thermal cracking, hydrocracking and/or catalytic cracking processes and visbreaking processes. They are preferably middle distillates that can be used as diesel fuels, domestic heating fuel oils (DFO), kerosene, heavy fuel oils.

15        With increasing demand for motor fuels, in particular diesel, refiners are looking to introduce cuts from sources other than petroleum which are more difficult to use in these fuels as they can lead to poorer resistance to cold behaviour in the latter, by increasing their cold filter plugging point and flow temperature. Among these novel sources of distillates, there can in particular be mentioned:

- 20        - the heaviest cuts originating from the cracking and visbreaking processes, with a high concentration of heavy paraffins, comprising more than 18 carbon atoms,  
      - the synthetic distillates originating from the conversion of gas such as those originating from the Fischer Tropsch process,  
      - the synthetic distillates resulting from the treatment of biomass of vegetable  
25        and/or animal origin, such as in particular NexBTL,  
      - and the oils and/or esters of vegetable or animal oils.

      These novel motor fuel bases can be used alone or in a mixture with standard petroleum middle distillates defined above as motor fuel base and/or domestic fuel oil base; they generally comprise long paraffinic chains greater than or equal to 16  
30        carbon atoms.

      The liquid hydrocarbon compositions according to the invention comprise a major proportion of liquid hydrocarbons, preferably of middle distillate type, with a

sulphur content preferably lower than 5,000 ppm, preferably lower than 500 ppm, and more preferably lower than 50 ppm, and a minor proportion comprising at least one copolymer according to the invention.

5 Preferably, in the distillates according to the invention, the major proportion is constituted by the distillates with a boiling point comprised between 150 and 450°C, initial crystallization temperature ICT greater than or equal to -20°C, preferably greater than or equal to -15°C, preferably comprised between -15 °C and +10 °C, and comprises distillates from direct distillation, distillates from vacuum distillation, hydrotreated distillates, distillates originating from catalytic cracking and/or  
10 hydrocracking of vacuum distillates, distillates resulting from ARDS (atmospheric residue desulphuration) type conversion and/or visbreaking processes, distillates originating from the upgrading of Fischer Tropsch cuts, distillates resulting from the BTL (biomass to liquid) conversion of vegetable and/or animal biomass, taken alone or in combination, and esters of vegetable and animal oils or their mixtures.

15 According to a preferred embodiment of the invention, the distillates according to the invention have a C9 to C40 n-paraffin content comprised between 1 and 40% by mass.

According to another subject, the invention relates to a Diesel fuel comprising from 0 to 500 ppm of sulphur and comprising at least one distillate according to the  
20 invention.

According to another subject, the invention relates to a heating fuel oil comprising from 0 to 5,000 ppm of sulphur and comprising at least one distillate according to the invention. According to another subject, the invention relates to a heavy fuel oil comprising at least one distillate according to the invention.

25 According to a preferred embodiment of the invention, the hydrocarbon compositions contain from 10 to 5,000 ppm by weight, preferably from 10 to 1,000 ppm of at least one copolymer according to the invention.

Apart from the bifunctional additive or additives according to the invention, the hydrocarbon compositions can also contain one or more others which are different,  
30 chosen from the detergents, anti-corrosion agents, dispersants, demulsifiers, anti-foam agents, biocides, reodorants, procetane additives, friction modifiers, combustion-promoting agents (catalytic combustion and soot promoters), agents

improving the cloud point, pour point, cold filter plugging point, anti-sedimentation agents, anti-wear agents and/or conductivity modifying agents, or even one or more other additives which improve the pour point, the cold filter plugging point, and the lubricity.

5           Among these additives, there can be mentioned particularly:

a) procetane additives, in particular (but not limitatively) chosen from alkyl nitrates, preferably 2-ethyl hexyl nitrate, aroyl peroxides, preferably benzyl peroxide, and alkyl peroxides, preferably ter-butyl peroxide;

10           b) anti-foam additives, in particular (but not limitatively) chosen from polysiloxanes, oxyalkylated polysiloxanes, and amides of fatty acids originating from vegetable or animal oils. Examples of such additives are given in EP 861 882, EP 663 000, EP 736 590;

15           c) detergent and/or anti-corrosion additives, in particular (but not limitatively) chosen from the group constituted by amines, succinimides, alkenylsuccinimides, polyalkylamines, polyalkyl polyamines and polyetheramines. Examples of such additives are given in EP 938 535;

20           d) lubricity additive or anti-wear agent, in particular (but not limitatively) chosen from the group constituted by fatty acids and their ester or amide derivatives, in particular glycerol monooleate, and derivatives of mono- and polycyclic carboxylic acids. Examples of such additives are given in the following documents: EP 680 506, EP 860 494, WO 98/04656, EP 915 944, FR 2 772 783, FR 2 772 784;

25           e) cloud point additives, in particular (but not limitatively) chosen from the group constituted by terpolymers of long chain olefin/(meth)acrylic ester /maleimide, and polymers of fumaric/maleic acid esters. Examples of such additives are given in EP 71 513, EP 100 248, FR 2 528 051, FR 2 528 051, FR 2 528 423, EP 1 12 195, EP 1 727 58, EP 271 385, EP 291 367;

30           f) anti-sedimentation or dispersant additives, in particular (but not limitatively) chosen from the group constituted by copolymers of (meth)acrylic acid/alkyl (meth)acrylate amidified by a polyamine, polyamine alkenylsuccinimides, derivatives of phthalic acid and a double chain fatty amine; alkyl phenol resins. Examples of such additives are given in EP 261 959, EP 593 331, EP 674 689, EP 327 423, EP 512 889, EP 832 172, US 2005/0223631; US 5 998 530; WO 93/14178.

g) multifunctional cold operability additives chosen from the group constituted by the polymers based on olefin and alkenyl nitrate as described in EP 573 490.

h) resistance to cold additives such as copolymers of alpha olefin and vinyl ester(s) such as EVA, EVP, copolymers of ethylene, vinyl acetate and branched vinyl ester such as vinyl neodecanoates (VEOVA) described in particular in US 2004/0226216;

i) lubricants such as fatty acids, TOFAs, their derivatives such as esters, in particular.

These other additives are in general added in a quantity ranging from 10 to 1,000 ppm (each).

The bifunctional additives according to the invention can be added to the hydrocarbon compositions within the refinery, and/or be incorporated downstream of the refinery, optionally in a mixture with other additives, in the form of a package of additives.

#### 15      Example of the preparation of the grafted polymers:

Starting with the same copolymer of ethylene and vinyl acetate EVA containing 28% by weight of vinyl acetate (denoted EVA 28), i.e. 11.2% in moles, of average numerical molar weight = 5,000 g.mol<sup>-1</sup> measured by polystyrene standard GPC, 4 types of different grafts (units D) denoted D1 to D4 were grafted, according to the preparation process according to the invention.

D1 is a TOFA (mixture of acids derived from tall oil, containing from 2 to 3% by weight of resin acids and a mixture of C8 to C24, but mostly C18, fatty acids; its concentration of saturated and/or unsaturated C14 - C18 fatty acids can vary from 80 to 90%). The copolymer grafted with D1 can also comprise resin acid ester functions formed from the resin acids present in the mixture of acids derived from tall oil.

D2 to D4 are mixtures of saturated and unsaturated C14 to C18 fatty acids the molar composition of which in fatty acids is shown in detail in Table 1 below.

Table 1:

| Grafted acid | C <sub>14</sub> | C <sub>16</sub> | C <sub>18</sub> | C <sub>18-1</sub> | C <sub>18-2</sub> | C <sub>18-3</sub> |
|--------------|-----------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| D1           | -               | 0.6             | 1.4             | 30.8              | 41.1              | 10.7              |
| D2           |                 |                 |                 | > 86              | < 14              |                   |
| D3           | 1.8             | 16.6            | 11.6            | 24.6              | 39.3              | 6.1               |
| D4           | 1               | 45              | 5               | 38                | 11                | -                 |

The characteristics of the grafted copolymers (% in moles of units A to D are compiled in Table 2.

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Table 2:

| Polymer | Starting polymer | Type of graft | % in moles of units A (n1) | % in moles of units B (m-x) | % in moles of units C (x <sub>1</sub> ) | % in moles of units D (x <sub>2</sub> ) | % by weight of units D |
|---------|------------------|---------------|----------------------------|-----------------------------|-----------------------------------------|-----------------------------------------|------------------------|
| 1       | EVA28            | none          | 88.8 (130)                 | 11.2 (16)                   | 0 (0)                                   | 0 (0)                                   | 0                      |
| 2       | EVA28            | D1            | 88.8 (130)                 | 9.07 (13)                   | 0 (0)                                   | 2.13 (3)                                | 15                     |
| 3       | EVA28            | D1            | 88.8 (130)                 | 7.95 (11)                   | 0 (0)                                   | 3.25 (5)                                | 21.7                   |
| 4       | EVA28            | D1            | 88.8 (130)                 | 6.68 (10)                   | 0 (0)                                   | 4.52 (6)                                | 28                     |
| 5       | EVA28            | D1            | 88.8 (130)                 | 5.15 (7)                    | 0 (0)                                   | 6.05 (9)                                | 35                     |
| 7       | EVA28            | D2            | 88.8 (130)                 | 7.05 (10)                   | 0 (0)                                   | 4.15 (6)                                | 26                     |
| 8       | EVA28            | D3            | 88.8 (130)                 | 7.05 (10)                   | 0 (0)                                   | 4.15 (6)                                | 26                     |
| 9       | EVA28            | D4            | 88.8 (130)                 | 4.18 (6)                    | 0 (0)                                   | 7.02 (10)                               | 38.5                   |

The cold filter plugging points of 5 GOM middle distillates denoted “a” to “e” of EN 590 engine gas oil type, the characteristics of which are compiled in Table 3 below, with one of the copolymers 1 to 9 added at concentrations comprised between 35 and 700 ppm by weight, were measured.

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Table 3 - Characteristics of the gas oils tested

|                                      | GOM a | GOM b | GOM c | GOM d | GOM e |
|--------------------------------------|-------|-------|-------|-------|-------|
| Distillation ASTM D86                |       |       |       |       |       |
| T90-T20                              | 112.7 | 100.5 | 112   | 110   |       |
| MP-T90                               | 18.6  | 17    | 23    | 18    |       |
| T95 (°C)                             | 353.9 | 350   | 356   | 352   |       |
| Cloud point (°C) NF EN 23015         | -4    | -9    | -7    | -7    | -6    |
| CFPP (°C) EN 116                     | -5    | -9    | -6    | -7    | -7    |
| Pour point (°C) NF T 60105           | -12   | -15   | -9    | -9    | -12   |
| Paraffins (% by mass) Chromatography | 19.27 | 16.1  | 15.64 | 18.73 |       |
| ICT (°C) IP 389                      | -6    | -12.6 | -9.5  | -12   |       |
| Sulphur content (ppm) EN ISO 20846   | 39.8  | 9.2   | 48    | 35    | 9     |

The FBT (filter blocking tendency) was also measured according to the standard IP387 of a solution containing 420 ppm of copolymer 1 to 9 (solution prepared from a stock solution with 4% by mass of copolymer) as well as the lubricity measured under HFRR test conditions (High Frequency Reciprocating Rig EN ISO 12156-1 or as described in the article SAE 932692 by J.W. Hadley of the University of Liverpool) with a copolymer concentration of 210 ppm and/or 420 ppm respectively. The test involves jointly subjecting a steel sphere in contact with a stationary metal plate to a pressure corresponding to a weight of 200g and an alternating movement of 1 mm at a frequency of 50 Hz. The lubricity is expressed by the average value of the diameters of the wear scar of the sphere on the plate. A small diameter (generally less than 400  $\mu\text{m}$ ) reflects good lubricity; and conversely, a large wear diameter (greater than 400  $\mu\text{m}$ ) reflects a lubricity which is all the more insufficient, the greater the diameter.

The results are compiled in Table 4 below.

Table 4:

| Polymer | Disillate | CFPP (35 ppm) (°C) | CFPP (70 ppm) (°C) | CFPP (140 ppm) (°C) | CFPP (210 ppm) (°C) | CFPP (350 ppm) (°C) | CFPP (700 ppm) (°C) | FBT at 420 ppm | HFRR $\Delta T = 1.4$ ( $\mu\text{m}$ ) at 210 ppm | HFRR $\Delta T = 1.4$ ( $\mu\text{m}$ ) at 420 ppm |
|---------|-----------|--------------------|--------------------|---------------------|---------------------|---------------------|---------------------|----------------|----------------------------------------------------|----------------------------------------------------|
| 1       | a         |                    | -8                 | -13                 | -15                 |                     |                     | 4.4            | 556                                                |                                                    |
| 2       | a         |                    | -9                 | -16                 | -15                 |                     |                     | 1.69           | 415                                                |                                                    |
| 3       | a         |                    |                    |                     |                     |                     |                     | 1.06           |                                                    |                                                    |
| 4       | a         |                    | -13                | -15                 | -14                 |                     |                     | 1.01           | 407                                                |                                                    |
| 5       | a         |                    | -13                | -16                 | -15                 |                     |                     | 1.07           | 531                                                | 513                                                |
| 7       | a         |                    | -12                | -14                 | -14                 |                     |                     |                |                                                    |                                                    |
| 8       | a         |                    | -9                 | -10                 | -13                 |                     |                     |                |                                                    |                                                    |
| 9       | a         |                    | -8                 | -15                 | -12                 |                     |                     | 1.04           |                                                    |                                                    |
|         |           |                    |                    |                     |                     |                     |                     |                |                                                    |                                                    |
| 1       | b         |                    | -10                | -12                 | -13                 |                     |                     |                |                                                    |                                                    |
| 3       | b         |                    | -11                | -13                 | -13                 |                     |                     |                |                                                    |                                                    |
| 4       | b         |                    | -12                | -13                 | -20                 |                     |                     |                |                                                    |                                                    |
| 5       | b         |                    | -12                | -13                 | -24                 |                     |                     |                |                                                    |                                                    |
|         |           |                    |                    |                     |                     |                     |                     |                |                                                    |                                                    |
| 1       | c         |                    | -10                | -12                 | -15                 |                     |                     |                |                                                    |                                                    |
| 3       | c         |                    |                    | -15                 | -16                 |                     |                     |                |                                                    |                                                    |
| 4       | c         |                    | -15                | -18                 | -17                 |                     |                     |                |                                                    |                                                    |
| 5       | c         |                    | -16                | -19                 | -18                 |                     |                     |                |                                                    |                                                    |
|         |           |                    |                    |                     |                     |                     |                     |                |                                                    |                                                    |
| 1       | d         |                    |                    |                     |                     | -15                 | -17                 |                |                                                    |                                                    |
| 5       | d         |                    |                    |                     |                     | -18                 | -21                 |                |                                                    |                                                    |
|         |           |                    |                    |                     |                     |                     |                     |                |                                                    |                                                    |
| 1       | e         | -13                | -17                | -19                 |                     |                     |                     |                |                                                    | 549                                                |
| 3       | e         | -14                | -19                |                     |                     |                     |                     |                |                                                    | 562                                                |
| 4       | e         | -15                | -18                |                     |                     |                     |                     |                |                                                    | 395                                                |
| 5       | e         | -15                | -20                | -20                 |                     |                     |                     |                |                                                    | 570                                                |

The lubricities (HFRR WS 1.4) of the GOM middle distillate denoted “a” with variables quantities ranging from 0 to 84 ppm of D1 alone, of copolymer 2, 4 or 5 alone or of a mixture of copolymer 2, 4 or 5 and D1 added to it are compared.

The results are given in Table 5 below.

5                      TABLE 5

| Copolymer No.                                | -   | 2   | 4   | 5   | -   | 2   | -   | 4   | -   |
|----------------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| D1 alone introduced into GOM a (ppm by mass) | 0   | 0   | 0   | 0   | 34  | 34  | 60  | 60  | 84  |
| copolymer i in GOM a (ppm by mass)           | 0   | 210 | 210 | 210 | 0   | 210 | 0   | 210 | 0   |
| HFRR WS 1.4 (μm)                             | 497 | 415 | 407 | 513 | 455 | 465 | 366 | 409 | 349 |

The lubricities (WS 1.4) of the GOM middle distillate denoted “e”, which is more “severe” than GOM denoted “a”, with variable quantities ranging from 0 to 200 ppm of D1 alone, or of one of the copolymers 2 to 5 alone or of a mixture of a copolymer 2 to 5 and D1 added to it are compared. In order to avoid any change in the samples during storage and preparation operations, the grafted polymer solutions are stabilized with an antioxidant, butylated hydroxytoluene or 2,6-di-tert-butyl-4-methylphenol (BHT) at a concentration of 0.05% to 0.1% with respect to D1.

The results are compiled in Table 6 below.

Table 6:

| Copolymer No.                                    | -   | 2   | 3   | -   | 4   | 5   | 5   | -   |
|--------------------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Total quantity of free D1 in GOM e (ppm by mass) | 0   | 63  | 90  | 100 | 118 | 150 | 150 | 200 |
| D1 alone introduced into GOM e                   | No  | No  | No  | Yes | No  | No  | Yes | Yes |
| Copolymer i in GOM e                             | No  | Yes | Yes | No  | Yes | Yes | Yes | No  |
| HFRR WS 1.4 (μm)                                 | 658 | 549 | 562 | 505 | 395 | 465 | 570 | 392 |

Table 7:

|                             | D1 (ppm) | Total additives<br>(ppm by<br>mass ) | WS1.4<br>( $\mu\text{m}$ ) |
|-----------------------------|----------|--------------------------------------|----------------------------|
| GOM e + D1<br>(comparative) | 0        | 0                                    | 658                        |
|                             | 100      | 100                                  | 505                        |
|                             | 150      | 150                                  | 423                        |
|                             | 200      | 200                                  | 392                        |
|                             | 250      | 250                                  | 368                        |
| GOM e + copolymer 4 + D1    | 0        | 0                                    | 658                        |
|                             | 115      | 330                                  | 424                        |
|                             | 135      | 350                                  | 401                        |
|                             | 160      | 375                                  | 301                        |
|                             | 185      | 400                                  | 312                        |
|                             | 248      | 450                                  | 306                        |
|                             | 285      | 500                                  | 327                        |
| GOM e + copolymer 4         | 0        | 0                                    | 658                        |
|                             | 85       | 300                                  | 577                        |
|                             | 118      | 420                                  | 395                        |
|                             | 150      | 532                                  | 297                        |
|                             | 185      | 656                                  | 266                        |

CLAIMS

1. Use as bifunctional lubricity and resistance to cold additive for liquid hydrocarbon compositions of at least one copolymer comprising:

5 a) units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_{n1}$ — and/or propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_{n2}$  with  $n1 + n2 = n$  ranging from 98 to 643, preferably ranging from 124 to 515;  $n1$  being advantageously equal to  $n$ ;

b) units derived from vinyl esters of formula B: -  $(\text{CH}_2\text{-CHOO}(\text{R}_1))_{m-x}$ — in which  $\text{R}_1$  represents a  $\text{C}_1\text{-C}_{15}$  linear or branched alkyl group, preferably methyl, propyl, and/or a  $\text{C}_5$  to  $\text{C}_{15}$  branched alkyl group, in which the branching is situated at  
10 any point of the alkyl radical, preferably in position 2 or 3 of the alkyl chain; preferably vinyl esters are chosen from  $\text{C}_5\text{-C}_{15}$ -comonomers, preferably chosen from the pivalate, isopentanoate, isohexanoate, isononanoate, isodecanoate and/or isotridecanoate, and advantageously 2-ethyl hexanoate, neoalkanoates, in particular  
15 neononanoate, neodecanoate and/or neoundecanoate; with  $m$  ranging from 2 to 105, preferably ranging from 16 to 71 and  $x$  ranging from 0.2 to 105, preferably ranging from 1.6 to 71;

c) units of formula C: -  $(\text{CH}_2\text{-CHOH})_{x1}$ — in which  $x1$  ranges from 0 to  $0.30x$ , preferably  $x1 = 0$ ;

20 d) units of formula D: -  $(\text{CH}_2\text{-CHOO}(\text{R}_2))_{x2}$ — in which  $x2$  ranges from  $0.70x$  to  $x$ , preferably  $x2 = x$ , and  $\text{R}_2$  represents a  $\text{C}_8\text{-C}_{24}$ , linear or branched, alkyl or alkenyl group, preferably  $\text{C}_{14}\text{-C}_{20}$  or also  $\text{C}_{14}$  to  $\text{C}_{18}$

with  $x = x1 + x2$

2. Use according to claim 1, in which the percentage in moles of units A  
25 and/or A' in the copolymer ranges from 79 to 99% in moles, preferably 86.7 to 90.7% in moles; the percentage in moles of units B in the polymer ranges from 0 to 19% in moles, preferably 4.6 to 12% in moles; the % in moles of units C in the polymer is close to 0 to 6.3% in moles and advantageously equal to 0% in moles; the percentage in moles of units D in the polymer is from 0.1 to 21% in moles, preferably  
30 from 0.1 to 10% in moles, more preferably 0.93 to 8.6% in moles.

3. Use according to one of claims 1 or 2 in which said at least one copolymer is in the form of a concentrated solution in a hydrocarbon distillate,

preferably at a concentration of more than 50% by weight, preferably more than 70% by weight or preferably more than 80% by weight, preferably 60 to 80% by weight.

4. Use according to one of claims 1 to 3 in which the hydrocarbon liquid composition is a hydrocarbon distillate containing from 0 to 5,000 ppm of sulphur, and contains 10 to 5,000 ppm of said at least one copolymer, optionally in a mixture with other additives such as detergents, dispersants, demulsifiers, anti-foam agents, biocides, reodorants, cetane improvers, anti-corrosion agents, friction modifiers, lubricity, combustion, cloud point, pour point improvers, anti-sedimentation agents and conductivity improvers, resistance to cold additives, lubricants.

5. Use according to claim 4 in which the distillate comprises at least one hydrocarbon cut originating from the group constituted by the distillates with a boiling point comprised between 150 and 450°C, an initial crystallization temperature ICT greater than or equal to -20°C, preferably greater than or equal to -15°C, preferably comprised between -15°C and +10°C, comprising distillates from direct distillation, distillates from vacuum distillation, hydrotreated distillates, distillates originating from catalytic cracking and/or hydrocracking of vacuum distillates, distillates resulting from atmospheric residue desulphuration (ARDS) type conversion and/or visbreaking processes, distillates originating from the upgrading of Fischer Tropsch cuts, distillates resulting from the biomass to liquid (BTL) conversion of vegetable and/or animal biomass, taken alone or in combination, and esters of vegetable and animal oils or their mixtures.

6. Use according to claim 5 in which the distillate comprises a C9 to C40 n-paraffin content comprised between 1 and 40% by mass.

7. Use according to one of claims 1 to 6 of said copolymer, as a distillate additive for Diesel fuel comprising from 0 to 500 ppm of sulphur.

8. Use according to one of claims 1 to 5 of said copolymer as a distillate additive for heating fuel oil comprising from 0 to 5000 ppm of sulphur.

9. Use according to one of claims 1 to 5 of said copolymer as a distillate additive for heavy fuel oil.

**Abstract**

The invention relates to the synthesis and the use of copolymers based on ethylene and/or of propylene and of vinyl ester(s) modified by grafting, effective for improving both the resistance to cold and the lubricity of liquid hydrocarbons in particular the middle distillates originating from the distillation of petroleum and crude oils, in particular those with a low sulphur content and relates to a copolymer comprising:

a) units derived from ethylene of formula A -  $(\text{CH}_2\text{-CH}_2)_{n1}$ - and/or propylene of formula A' -  $((\text{CH}_3)\text{CH-CH}_2)_{n2}$  with  $n1 + n2 = n$  ranging from 98 to 643, preferably ranging from 124 to 515;  $n1$  being advantageously equal to  $n$ ;

b) units of formula B: -  $(\text{CH}_2\text{-CHOOCR}_1)_{m-x}$ - in which  $R_1$  represents a  $C_1$ - $C_{15}$  linear or branched alkyl group, preferably methyl, propyl, and/or a  $C_5$  to  $C_{15}$  branched alkyl group, in which the branching is situated at any point of the alkyl radical, preferably in position 2 or 3 of the alkyl chain; preferably chosen from the preferred  $C_5$ - $C_{15}$  vinyl comonomers, preferably chosen from the pivalate, isopentanoate, isohexanoate, isononanoate, isodecanoate and/or isotridecanoate, and advantageously 2-ethyl hexanoate, neoalkanoates, in particular neononanoate, neodecanoate and/or neoundecanoate; with  $m$  ranging from 2 to 105, preferably ranging from 16 to 71 and  $x$  ranging from 0.2 to 105, preferably ranging from 1.6 to 71;

c) units of formula C: -  $(\text{CH}_2\text{-CHOH})_{x1}$ - in which  $x1$  ranges from 0 to  $0.30x$ , preferably  $x1 = 0$ ;

d) units of formula D: -  $(\text{CH}_2\text{-CHOOCR}_2)_{x2}$ - in which  $x2$  ranges from  $0.70x$  to  $x$ , preferably  $x2 = x$ , and  $R_2$  represents a  $C_8$ - $C_{24}$  saturated or unsaturated, linear or branched, alkyl group, preferably  $C_{14}$ - $C_{20}$  or also  $C_{14}$  to  $C_{18}$

$$\text{with } x = x_1 + x_2$$