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(54) **Polyesters as flow improvers for hydrocarbons.**

(57) A polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 to 50% by weight of polyoxyalkylene groups of molecular weight from 100 to 5000 is used to improve the cold flow properties of liquid hydrocarbon especially distillate fuels and has improved interaction with other additives.

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Polyesters as Flow Improvers for Hydrocarbons

Mineral oils containing wax therein have the characteristic of becoming less fluid as the temperature of the oil decreases. This loss of fluidity is generally due to increase in viscosity and/or the crystallisation of the wax into plate-like crystals which eventually form a spongy mass entrapping the oil therein.

It has long been known that various compositions act as wax crystal modifiers and pour depressants when blended with waxy mineral oils. These compositions modify the size and shape of wax crystals and reduce the adhesive forces between the wax and oil in such a manner as to permit the oil to remain fluid at a lower temperature.

Various pour point depressants have been described in the literature and several of these are in commercial use. For example, U.S. Pat. No. 3,048,479 teaches the use of copolymers of ethylene and C_3-C_5 vinyl esters, e.g. vinyl acetate as pour depressants for fuels, specifically heating oils, diesel and jet fuels. Hydrocarbon polymeric pour depressants based on ethylene and higher alpha-olefins, e.g. propylene, are also known. U.S. Patent 3,961,916 teaches the use of a mixture of copolymers, one of which is a wax crystal nucleator and the other a growth arrestor to control the size of the wax crystals.

Similarly United Kingdom Patent 1263152 suggests that the size of the wax crystals may be controlled by using a copolymer having a lower degree of side chain branching.

It has also been proposed in for example United States Patent 1469016 that the copolymers of di-n-alkyl fumarates and vinyl acetate which have previously been used as pour point depressants for lubricating oils may be used as co-additives with ethylene/vinyl acetate copolymers in the treatment of distillate fuels with high final boiling points to improve their low temperature flow properties. According to United Kingdom Patent 1469016 these polymers may be C_6 to C_{18} alkyl esters of unsaturated C_4 to C_8 dicarboxylic acids particularly lauryl fumarate; lauryl-hexadecyl fumarate. Typically the materials used are mixed esters with an average of about 12 carbon atoms (Polymer A).

Our European Patent Applications 85301047, 85301048, 85301675 and 85301676 suggest that the effectiveness of these type of materials may be improved if the copolymers containing very specific alkyl groups such as specific di-n-alkyl fumarate/vinyl acetate copolymers. For example, polymers in which the average number of carbon atoms in the alkyl groups in the copolymer must be from 12 to 14 and that it must contain no more than 10 wt.% of copolymer in which the alkyl groups contains more than 14 carbon atoms and preferably no more than 20 wt.% of copolymer in which the alkyl group contains fewer than 12 carbon atoms have been found to be particularly effective in certain fuels and polymers with specific longer alkyl groups particularly effective in other fuels.

Our European Patent Application 0061895 A_2 describes the use of polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof containing at least two C_{10} to C_{30} linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular weight 100 to 5000 the alkyl group in the polyoxyalkylene glycol containing from 1 to 4 carbon atoms as additives for distillate fuels.

It has also been shown that in many instances using mixtures of two types of additive will give a synergistic improvement in cold temperature flow properties especially in distillate fuels. Mixing can however lead to problems of additive interaction sometimes leading to a reduction in their effectiveness which can cause serious problems for the refiner who may frequently wish to mix large quantities of fuels from different sources and containing different additives for storage purposes an aim of the present invention is to reduce this problem.

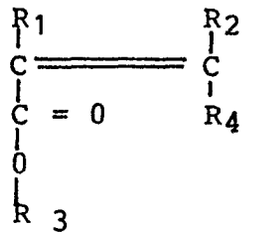
We have now found that polyoxyalkylene glycol groups may be incorporated into an unsaturated ester copolymer to provide an effective low temperature flow improver for hydrocarbons especially distillate fuels although they may be used in heavy fuels, residual fuels, crude oils and as pour depressants in lubricating oils. The unsaturated ester copolymer into which the polyoxyalkylene group is incorporated may be the types previously proposed as flow improvers for middle distillate fuels. We have also found that when these copolymers are used in distillate fuels the problem of adverse interaction with other additives such as ethylene vinyl acetate copolymers may be reduced.

The present invention therefore provides the use for improving the flow properties of liquid hyrocabon fuel oil of an additive comprising a polymer or copolymer of an ethylenically unsaturated ester of weight average molecular weight from 1000 to 200,000 containing from 0.1% to 50% by weight of polyoxyalkylene groups of molecular weight from 100 to 5000.

The polymers of the present invention are preferably used as additives for distillate fuels they are preferably used in an amount from 0.0001 to 5 wt.% based on the weight of the distillate petroleum fuel oil and the present invention also includes distillate fuel containing such an additive.

The polymers used in the present invention preferably have a weight average molecular weight in the range of 1000 to 100,000, preferably 20,000 to 70,000 as measured, for example, by Gel Permeation Chromatography, calibrated against polystyrene molecular weight standards.

The unsaturated esters of the present invention may be derived from ethylenically unsatured mono, di or polycarboxylic acids or mixtures thereof and may be obtained from unsaturated esters or mixtures thereof with other ethylenically unsaturated monomers such as ethylene, propylene or butene. Examples of dicarboxylic acid esters useful for preparing the polymer can be represented by the general formula:



wherein R_1 and R_2 are hydrogen or a C_1 to C_4 alkyl group, e.g., methyl, R_3 is a C_8 to C_{18} average, the average preferred depending upon the use to which the polymer is to be put. R_3 may be a mixture of a broad range of alkyl groups such as those used in U.K. patent 1469016 for use as a lubricating oil pour depressant or the specific monomer range of our European Patent Applications 85301047, 85301048, 85301675 and 85301676 for use as distillate additives where they can not only improve low temperature flow and filterability but also lower the cloud point of the fuel and R_4 is $COOR_3$, hydrogen or a C_1 to C_4 alkyl group. Where these types of unsaturated esters are used as raw materials for the production of the polymers of the present invention the polyoxyalkylene group may be incorporated into the molecule during the esterification of the carboxylic acid to produce the ester described above. For example the polyethylene glycol may be mixed with the alcohol R_3OH in the appropriate ratio and used to esterify for example Fumaric acid. The esters of the above formula may be homopolymerised or copolymerised with other ethylenically unsaturated monomers such as short chain unsaturated esters for example vinyl esters such as vinyl acetate, vinyl propionate and vinyl butyrate and alkyl acrylates and alkyl methacrylates.

Typical copolymers of the type described above may be obtained by the copolymerisation of a dicarboxylic acid mono or di- ester monomers such as dialkyl fumarates with various amounts, e.g., 5 to 70 mole %, of other unsaturated esters or olefins. Such other esters include short chain alkyl esters having the formula:

$$\begin{matrix} H & & R^1 \\ C & = & C \\ R'' & & R''' \end{matrix}$$

where R^1 is hydrogen or a C_1 to C_4 alkyl group, R"' is -COOR"" or -OOCR"" where R"" is a C_1 to C_5 alkyl group branched or unbranched, and R"' is R" or hydrogen. Examples of these short chain esters are methacrylates, acrylates, fumarates and maleates the vinyl esters such as vinyl acetate and vinyl propionate being preferred. More specific examples include methyl methacrylate, isopropenyl acetate and isobutyl acrylate.

Our preferred copolymers of this type contain from 40 to 60 mole % containing the polyoxyalkylene moiety fumarate and 60 to 40 mole % of vinyl acetate.

These ester polymers are generally prepared by polymerising the ester monomers in a solution of hydrocarbon solvent such as heptane, benzene, cyclohexane, or white oil, at a temperature generally in the range of from 20°C to 150°C. and usually promoted with a peroxide or azo type catalyst such as benzoyl peroxide azodiisobutyonitrile under a blanket of an inert gas such as nitrogen or carbon dioxide in order to exclude oxygen.

An alternative method for incorporating the polyoxyalkylene group into the ester copolymers of the present invention is to copolymerise the above described ethylenically unsaturated esters with an ethylenically unsaturated ester for the formula

$$R - COO\ R'$$

Where R is an ethylenically unsaturated hydrocarbyl group and R' is a polyoxyalkylene group. Examples of such esters include polyethylene glycol mono or di-oleate, polyethylene glycol mono or di-cinamate, polyethylene glycol acrylates etc. For example di-hexadecyl fumarate, vinyl acetate and the di ester of oleic acid and polyoxyethylene glycol of molecular weight 600 may be copolymerised to give a copolymer of the invention

Alternatively the polyoxyalkylene group may be incorporated into the ester polymer by producing polymers containing free acid groups and then esterifying with the polyoxyalkylene alcohol or glycol. For example copolymers of maleic anhydride with other unsaturated materials such as vinyl esters, dialkyl fumarates styrene or olefines may be esterified with the polyoxyalkylene alcohol or glycol. The polyoxyalkylene alcohol used may itself be a mono-alcohol the other end of the group being etherified or esterified so as to introduce a further desirable group in the polymer chain. The polyoxyalkylene alcohol or glycol may be mixed with other alcohols especially the straight chain alkyl alcohols when the products are to be used as additives for distillate fuels.

Examples of the polyoxyalkylene alcohols that may be used include esters, ethers or ester/ethers of the general formula

R-O-(A)-O-H

Where R is Hydrogen, -Alkyl, -Alkyl -C-, -Alkyl-O-C-$(CH_2)_n$-C-

A is the polyoxyalkylene segment in which the alkylene group has 1 to 4 carbon atoms such as polyoxymethylene, polyoxyethylene or polyoxytrimethylene. It is preferred that the polyoxyalkylene segment itself has a molecular weight of about 100 to 5000.

Examples of suitable alcohols and glycols especially when the materials are to be used as additives for distillate fuels are the substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000 preferably about 200 to 2,000. The monoesters of these glycols may be used and esters of fatty acids containing about 1-30 preferably 2 to 30 carbon atoms are preferred and it is preferred to use a C_{18}-C_{24} fatty acid, especially behenic acid or mixtures of stearic and behenic acids. These esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols, for example the mono methyl ether of a PEG may be used or a polyethoxylated fatty alcohol such as the commercially available "Brij" materials.

A particularly preferred compound for use as a distillate fuel flow improver especially in narrow boiling distillates is a copolymer of vinyl acetate with an equimolar amount of a fumarate ester prepared by esterifying fumaric acid with a mixture of from at least 95 mole % of a mixture of C_{12}/C_{14} straight chain alcohols and up to 5 mole % of polyethylene glycol of molecular weight 600.

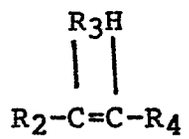
Alternatively an ester polymer or copolymer containing free carboxylic acid or hydroxy groups may be reacted with ethylene or propylene oxide to produce the materials of this invention.

The compounds of the present invention may be used as additives to improve the low temperature properties of hydrocarbon fuels such as crude oils, residual fuels and distillate fuels where they lower the pour point, control wax crystal size to improve low temperature filterability and can in some instances lower the cloud point of the fuel. By distillate fuels we mean those fuels generally used for diesel vehicles and heating oils especially domestic heating oils generally boiling in the range 120°C to 500°C more particularly 160°C to 400°C. In addition when used in some distillate fuels they have less of a tendency for adverse interaction with other distillate additives than with similar additives which do not contain the polyoxyalkylene group. The compounds may be used on their own but we have found that in distillate fuels they are particularly effective when used in combination with other additives previously proposed for improving the cold flow properties of distillate fuels generally.

The additives of the present invention may be used with the polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, containing at least two C_{10} to C_{30} linear saturated alkyl groups and a polyoxyalkylene glycol of molecular weight 100 to 5,000 preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form the subject of European Patent Publication 0061895 A2. Examples of suitable coadditives of this typeare the reaction product of glycols generally the substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) with fatty acids containing

about 10-30 preferably 18 to 24 carbon atoms, especially behenic acid or mixtures of stearic and behenic acids, the esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols. Esters obtained by reacting fatty acids with polyalkoxylated amines or ammonia may also be used.

The polymers and copolymers of this invention when used as fuel additives especially distillate fuels may also be used with the ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers which may be copolymerized with ethylene, include unsaturated mono and diesters of the general formula:



wherein R_3 is hydrogen or methyl; R_2 is a $-OOCR_5$ group wherein R_5 is hydrogen or a C_1 to C_{28}, more usually C_1 to C_{17} and preferably a C_1 to C_8, straight or branched chain alkyl group; or R_2 is a $-COOR_5$ group wherein R_5 is as previously described but is not hydrogen and R_4 is hydrogen or $-COOR_5$ as previously defined. The monomer, when R_2 and R_4 are hydrogen and R_2 is $-OOCR_5$, includes vinyl alcohol esters of C_1 to C_{29}, more usually C_1 to C_{18}, monocarboxylic acid, and preferably C_2 to C_5 monocarboxylic acid. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl isobutyrate, vinyl acetate being the preferred vinyl ester. We prefer that the copolymers contain from 20 to 40 wt.% of the vinyl ester more preferably from 25 to 35 wt.% vinyl ester. They may also be mixtures of two copolymers such as those described in United States Patent 3961916.

It is preferred that these copolymers have a number average molecular weight as measured by vapor phase osmometry (VPO) of 1000 to 6000 preferably 1000 to 4000.

Our polymers and copolymers may also be used in distillate fuels in combination with polar compounds, either ionic or nonionic, which have the capability in fuels of acting as wax crystal growth inhibitors. Polar nitrogen containing compounds have been found to be especially effective when used in combination with the glycol esters, ethers or ester/ethers and such three component mixtures are within the present invention. These polar compounds are generally the C_{20}-C_{300} preferably C_{20}-C_{100} amine salts and/or amides formed by reaction of at least one molar proportion of hydrocarbyl substituted amines with a molar proportion of hydrocarbyl acid having 1-4 carboxylic acid groups or their anhydrides; ester/amides may also be used. These nitrogen compounds are described in U.S. Patent 4,211,534. Suitable amines are usually long chain C_{12}-C_{40} primary, secondary, tertiary or quaternary amines of mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally containing about 20 to 300 total carbon atoms. The nitrogen compound should also have at least one straight chain C_8-C_{40} alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, hydrogenated tallow amine and the like. Examples of secondary amines include dioctadecyl amine, methyl-behenyl amine and the like. Amine mixtures are also suitable and many amines derived from natural materials are mixtures. The preferred

amine is a secondary hydrogenated tallow amine of the formula HNR_1R_2 wherein R_1 and R_2 are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C_{14}, 31% C_{16}, 59% C_{18}.

Examples of suitable carboxylic acids for preparing these nitrogen compounds (and their anhydrides) include cyclohexane dicarboxylic acid, cyclohexene dicarboxylic acid, cyclopentane dicarboxylic acid, dialpha-naphthyl acetic acid, naphthalene dicarboxylic acid and the like. Generally these acids will have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, terephthalic acid, and ortho-phthalic acid. Ortho-phthalic acid or its anhydride is the particularly preferred embodiment.

It is preferred that the nitrogen containing compound have at least one straight chain alkyl segment extending from the compound containing 8-40, preferably 8-24 carbon atoms. Also at least one ammonium salt, amine salt or amide linkage is required to be present in the molecule. The particularly preferred amine compound is that amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of di-hydrogenated tallow amine. Another preferred embodiment is the diamide formed by dehydrating this amide-amine salt.

Other amine derivatives which may be used as co-additives are oil soluble amine carboxylic acid salts and/or amides e.g. trioctylamine myristate or behenate. Reaction products of polyamines with fatty carboxylic acids such as the product of reacting tetraethylene pentamine with stearic or behenic acid may be used as may fatty amides themselves.

The copolymers may be used in combination with one or more additives of the type described above.

The relative proportions of additives used in the preferred mixtures of the invention are from 0.5 to 20 parts by weight of the ester polymer containing the polyoxyalkylene group to 1 part of the other additives. The total amount of additive used will depend upon the particular fuel but generally we use from 0.0001% to 5% by weight of the fuel.

The additive systems of the present invention may conveniently be supplied as concentrates in oil for incorporation into the bulk fuel. These concentrates may also contain other additives as required. These concentrates preferably contain from 3 to 75 wt %, more preferably 3 to 60 wt %, most preferably 10 to 50 wt.% of additive preferably. Such concentrates are also within the scope of the present invention.

The present invention is illustrated by the following Examples in which the effectiveness of the additives of the present invention as pour point depressants and filterability improvers in distillate fuels were compared with other similar additives in the Cold Filter Plugging Point Test (CFPPT) which is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-185. This test is designed to correlate with the cold flow of a middle distillate fuel in automatic diesels.

In brief, a 40 ml sample of the oil to be tested is cooled in a bath which is maintained at about -34°C to give non-linear cooling at about 1°C/min. Periodically (at each one degree Centrigrade drop in temperature starting from at

least 2°C above the cloud point) the cooled oil is tested for its ability to flow through a fine screen in a prescribed time period using a test device which is a pipette to whose lower end is attached an inverted funnel which is positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area defined by a 12 millimetre diameter. The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the sceen up into the pipette to a mark indicating 20 ml of oil. After each successful passage the oil is returned immediately to the CFPP tube. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds. This temperature is reported as the CFPP temperature. The difference between the CFPP of an additive free fuel and of the same fuel containing additive is reported as the CFPP depression by the additive. A more effective additive flow improver gives a greater CFPP depression at the same concentration of additive.

Example 1

The fuels used in thes Example were:

Fuel	Untreated CFPP °C	ASTM-D-86 Distillation°C Initial Boiling Point	20%	90%	Final Boiling Point
A	-5	182	220	354	385
B	-5	196	253	340	363
C	-3	222	275	336	360

The additives used were

Additive 1 a copolymer of a mixed C_{12}/C_{14} fumarate ester obtained by reaction of 50:50 molar mixture of normal C_{12} and C_{14} alcohols with fumaric acid and solution copolymerisation with vinyl acetate in 1 to 1 mole ratio at 60°C using azo diisobutyonitrile as catalyst.

Additive 2 the dihebenate ester of polyethylene qly col of molecular weight 600.

Additive 3 the dibehenate ester of polyethylene glycol of molecular weight 400.

Additive 4 was the same as Additive 1 except that 2.5 mole % of a polyethylene qlycol of 600 averaqe molecular weight was included in the C_{12}/C_{14} alcohol mixture used to esterify the fumaric acid and the polymerisation was carried out at 80°C.

Additive 5 was the same as Additive 4 except 2.5 mole % of the monomethyl ether of polyethylene qlycol of 750 molecular weiqht was used in place of the polyethylene qlycol of 600 molecular weiqht.

The CFPP depressions obtained in the fuels when treated with these additives and mixtures thereof were as follows:

Fuel	Additive	Amount ppm	CFPP Lowering
A	1	120	0°C
	4	120	8°C
B	1:3	200:60	2°C
	4:3	200:60	7°C
C	1:3	400:100	2°C
	4:3	400:100	8°C

In each instance showing a greater reduction in the CFPP temperature when the polyoxyalkylene segment is present in the molecule.

Example 2

The Additives of Example 1 were tested in the following fuels.

Fuel	Untreated CFPP °C	ASTM-D-96 Distillation °C Initial Boiling Point	20%	90%	Final Boiling Point
D	-4	256	287	326	343
E	-3	222	275	336	360
F	-5	238	281	331	352
G	-5	182	220	354	385
H	0	196	236	344	366
I	-3	201	249	318	340

And the amount of additive (a 2:1 by weight mixture of Additives 1 or 5 with Additive 3) required to reach the target CFPP was measured with the following results

	Target CFPP °C	Additive Mixture: 1 and 3 Amount Required to Reach Target CFPP	Additive Mixture: 5 and 3 Amount Required to Reach Target CFPP
D	-9	1100	800
F	-9	900	500
E	-9	700	300
I	-6	>1500	800

Example 3

The CFPP depressions obtained using 2:1 mixtures of Additives 1, 4 or 5 with 3 were found to be as follows

Fuel	PPM of Additive	CFPP Depression Additive Mixture		
		1 and 3	5 and 3	4 and 3
G	100	8	12	-
H	400	6	12	-
E	400	4	8	8
F	600	3	6	5
D	800	2	5	4
I	1500	2	6	6

Example 4

Additives of the present invention were used in fuel G together with an ethylene vinyl acetate (EVA) copolymer according to United Kingdom Patent 1263152 containing 36 wt % vinyl acetate and having a number average molecular weight of 2000 as measured by Vapor Phase Osmometry.

The other additives used were

Additive 1 of Example 1.

Additive 6 was the same as Additive 1 except that 5 mole % of a poly-ethylene glycol of 600 molecular weight dioleate was added to the C_{12}/C_{14} alcohol mixture used to esterify the fumaric acid.

Additive 7 was the same as Additive 1 except that the dialkyl fumarate was obtained from the following mixture of alcohols

45 moles $n\text{-}C_{12}$ alcohol
45 moles $n\text{-}C_{14}$ alcohol
10 moles $n\text{-}C_{16}$ $(CH_2\text{-}CH_2O)_{220}\text{-}OH$

Additive 8 was the same as Additive 6 except that 2 mole % of the polyethylene glycol of 600 molecular weight was used.

The CFPP values obtained were as follows:

PPM EVA Copolymer	Other Additive Number	PPM	CFPP °C
None	-	-	-6
100	-	-	-6
200	-	-	-8
0	1	200	-7
0	6	200	-5
0	7	200	-9
0	8	200	-10
100	1	100	-7
100	6	100	-16
100	7	100	-16
100	8	100	-14

Example 5

The effect of the amount of additive used on the CFPP values for Fuels E, F, G and I was determined using the following Additive Mixtures

Code	Mixture	
X	2:1	Mole Ratio of Additive 1 and Additive 3
Y	2:1	Mole Ratio of Additive 5 and Additive 3

The results are shown in the graphs Figures 1 to 4 Figures 3 and 4 also including results obtained using the same treat rate of the EVA copolymer used in Example 4 alone .

Example 6

The compounds of the present invention were tested as pour depressants in a solvent neutral lubricating oil. The polymers were prepared by the process described above from an equimolar amount of the fumarate ester prepared from the following mixture of alcohols.

C_{12}	20 Parts
C_{13}	30 Parts
C_{14}	30 Parts
C_{15}	20 Parts

and vinyl acetate (Additive 9) and a similar polymer in which the alcohol mixture contains 2.5 mole% of the polyethylene glyucol of 750 molecular weight used in Additive 5 (Additive 10).

The pour points were measured according to the ASTM D 97 method with the following results.

Treat Rate	0	0.1 wt.% Polymer		0.2 wt.% Polymer	
Additive	-	9	10	9	10
Pour Point °C	-6	-9	-15	-15	-21

Example 7

Additive 9 was the same as Additive 1 except that a commercial alcohol mixture sold as Dobanol 25 was used instead of the mixture of C_{12} and C_{14} alcohols. Dobanol 25 is a mixture of

20 wt.% C_{12} alcohols
30 wt.% C_{13} alcohols
30 wt.% C_{14} alcohols
20 wt.% C_{15} alcohols

80 wt.% of which are normal alcohols and 20 wt.% with a methyl branch at the 1 position.

Additive 10 was the same as Additive 9 except that a mixture of 1.975 moles of Dobanol 25 and 0.025 moles of polyethylene glycol of molecular weight 750 were used.

These Additives were tested as 4:1 ratio mixtures of Additive with Additive 3 in
Fuel D and
Fuel J which has an untreated CFPP of -5°C and the following ASTM D-96 distillation.

Initial Boiling Point	202°C
20%	272
90%	329
Final Boiling Point	344

with the following results

Total Treat Rate	500 PPM		800 PPM		1200 PPM	
Additive	9:3	10:3	9:3	10:3	9:3	10:3
CFPP in Fuel D					-6	-9
CFPP in Fuel J	-8	-10	-9	-11		

Example 8

Additives were tested in Fuel K which had a cloud point of +5°C and the following ASTM D-96 distillation

Initial Boiling Point	203°C
20%	261
90%	322
Final Boiling Point	349°C

and the appearance of the fuel recorded at -5°C after cooling at 1°C per hour.

1000 ppm of the additives were used as 4:1 mixtures and the results were as follows:

Additive	Appearance
Additive 1 : Additive 2	solid
Additive 5 : Additive 2	fluid
Additive 1 : Additive 3	solid
Additive 5 : Additive 3	fluid

Example 9

Additive 11 was the same as Additive 1 except that 10- mole % of the C_{12}/C_{14} alcohol was replaced by the monomethyl ether of polyethylene glycol of molecular weight 750.

The Additives were tested in a blend of 50 wt.% of Fuel L have an untreated CFPP of -2°C and ASTM-D-96 distillation of

Initial Boiling Point	198°C
20%	256
90%	343
Final Boiling Point	367

and 50 wt.% of a Fuel D containing 200 ppm of an ethylene vinyl acetate copolymer of 32 wt.% vinyl acetate to give a CFPP of -9°C. The amount of additive required to give the blend a CFPP of -9°C was determined to be as follows

Additives Used	1:11 : 3	1:3
Ratio	1:1:1	2:1
	Amounts Required	
	600	> 1200

The tests were repeated using as the fuel a mixture of 50 wt.% of Fuel J and 50 wt.% of Fuel M containing 200 ppm of the ethylene vinyl acetate copolymer.

Fuel M had an untreated CFPP of -4°C and an ASTM D-96 distillation of

Initial Boiling Point	186°C
20%	254
90%	331
Final Boiling Point	355

The amount of additive required to give a CFPP of -9°C was found to be as follows

Additives Used	1:11 : 3	1 : 3
Ratio	1 :1 : 1	2 : 1
	Amount Required	
	600	1200

CLAIMS

1 The use for improving the flow properties of liquid hydrocarbons of a polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 5 to 50% by weight of polyoxyalkylene groups of molecular weight from 100 to 5000.

2 The use according to Claim 1 in which the ethylenically unsaturated ester is a fumarate ester.

3 The use according to Claim 2 in which the polyoxyalkylene group is present by esterifying the fumaric acid with an alcohol mixture containing a polyoxyalkylene alcohol or glycol.

4 The use according to Claim 2 or Claim 3 in which the fumarate ester is copolymerised with another ethylenically unsaturated ester.

5 The use according to Claim 4 in which the other ethylenically unsaturated ester is vinyl acetate.

6 The use according to Claim 1 in which the polymer or copolymer is prepared by copolymerising an unsaturated ester of formula

R COO R'

where R is an ethylenically unsaturated hydrocarbon group and R' is a polyoxyalkylene group with another ethylenically unsaturated monomer.

7 The use according to Claim 6 in which the other ethylenically unsaturated monomer is a vinyl ester.

8 The use according to Claim 1 in which the polymer or copolymer is prepared by esterifying a polymer containing free carboxylic acid groups with a polyoxyalkylene alcohol or glycol.

9 The use according to Claim 8 in which the polyoxyalkylene alcohol or glycol is used in admixture with other alcohols.

10 The use according to any of the preceding claims in combination with one or more of the additives selected from the group consisting of

(i) ethylene unsaturated ester copolymer flow improvers

(ii) polyoxyalkylene ester ethers, ester/ethers and mixtures thereof

(iii) ionic or nonionic polar compounds

11 The use according to any of the preceding claims in which the hydrocarbon fuel is a distillate petroleum fuel.

12 A distillate petroleum fuel containing from 0.0001 to 5 wt.% based on the weight of the distillate petroleum fuel oil of polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 to 50 wt.% of polyoxyalkylene groups of molecular weight from 100 to 5000.

13 A distillate petroleum fuel according to Claim 12 in which the ethylenically unsaturated ester is a fumarate ester.

14 A distillate petroleum fuel according to Claim 13 in which the polyoxyalkylene group is present by esterifying the fumaric acid with an alcohol mixture containing a polyoxyalkylene alcohol or glycol.

15 A distillate petroleum fuel according to Claim 13 or Claim 14 in which the fumarate ester is copolymerised with another ethylenically unsaturated ester.

16 A distillate petroleum fuel according to Claim 15 in which the other ethylenically unsaturated ester is vinyl acetate.

17 An additive concentrate comprising an oil solution containing from 3 to 75 wt.% based on the weight of the concentrate of polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 to 50 wt.% of polyoxyalkylene groups of molecular weight from 100 to 5000 optionally together with other additives.

CLAIMS FOR AUSTRIA

1 A process for improving the flow properties of liquid hydrocarbons comprising adding thereto a polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 5 to 50% by weight of polyoxyalkylene groups of molecular weight from 100 to 5000.

2 A process according to Claim 1 in which the ethylenically unsaturated ester is a fumarate ester.

3 A process according to Claim 2 in which the polyoxyalkylene group is present by esterifying the fumaric acid with an alcohol mixture containing a polyoxyalkylene alcohol or glycol.

4 A process according to Claim 2 or Claim 3 in which the fumarate ester is copolymerised with another ethylenically unsaturated ester.

5 A process according to Claim 4 in which the other ethylenically unsaturated ester is vinyl acetate.

6 A process according to Claim 1 in which the polymer or copolymer is prepared by copolymerising an unsaturated ester of formula

R COO R'

where R is an ethylenically unsaturated hydrocarbon group and R' is a polyoxyalkylene group with an admixture with other alcohols.

7 A process according to Claim 6 in which the other ethylenically unsaturated monomer is a vinyl ester.

8 A process according to Claim 1 in which the polymer or copolymer is prepared by esterifying a polymer containing free carboxylic acid groups with a polyoxyalkylene alcohol or glycol.

9 A process according to Claim 8 in which the polyoxyalkylene alcohol or glycol is used in admixture with other alcohols.

10 A process according to any of the preceding claims in combination with one or more of the additives selected from the group consisting of

(i) ethylene unsaturated ester copolymer flow improvers

(ii) polyoxyalkylene ester ethers, ester/ethers and mixtures thereof

(iii) ionic or nonionic polar compounds

11 A process according to any of the preceding claims in which the polymer or copolymer is added as a concentrate comprising an oil solution containing from 3 to 75 wt.% based on the weight of the concentrate of polymer or copolymer of weight average molecular weight from 1000 to 200,000 prepared from an ethylenically unsaturated ester and containing from 0.1 to 50 wt.% of polyoxyalkylene groups of molecular 20 weight from 100 to 5000 optionally together with other additives.

12 A process according to any of the preceding claims in which the liquid hydrocarbon is a petroleum distillate fuel.

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FIG.1

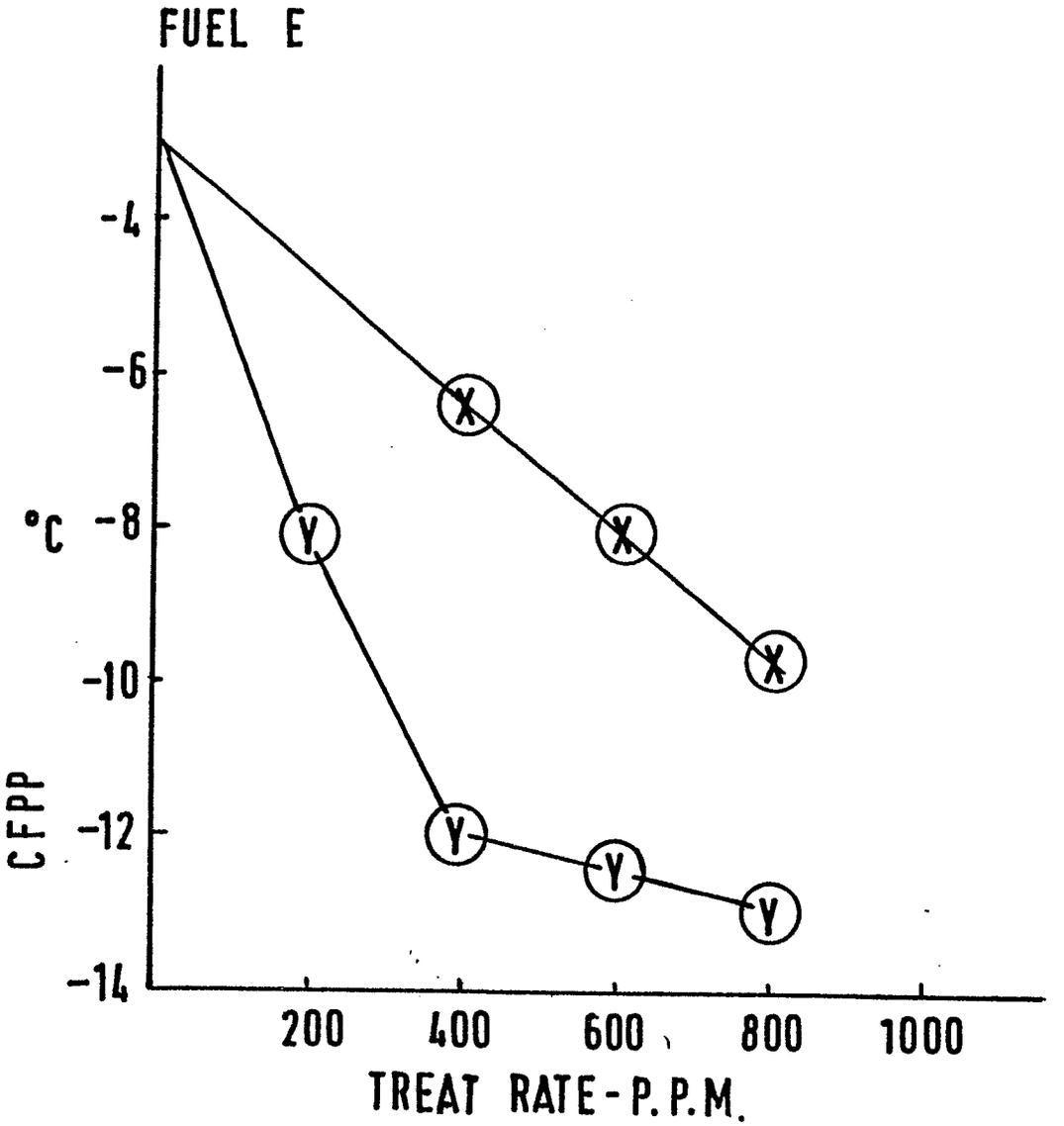

FIG.2

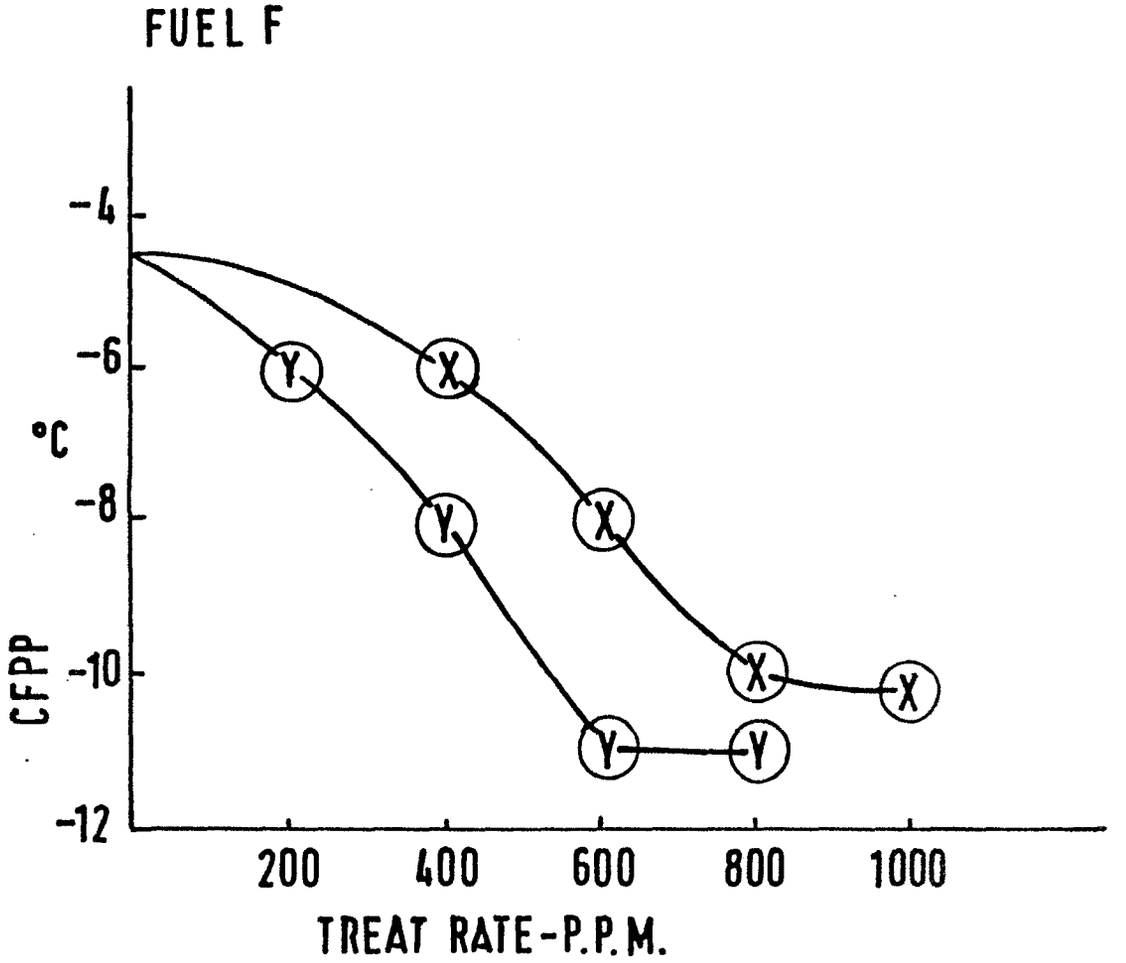

FIG.3

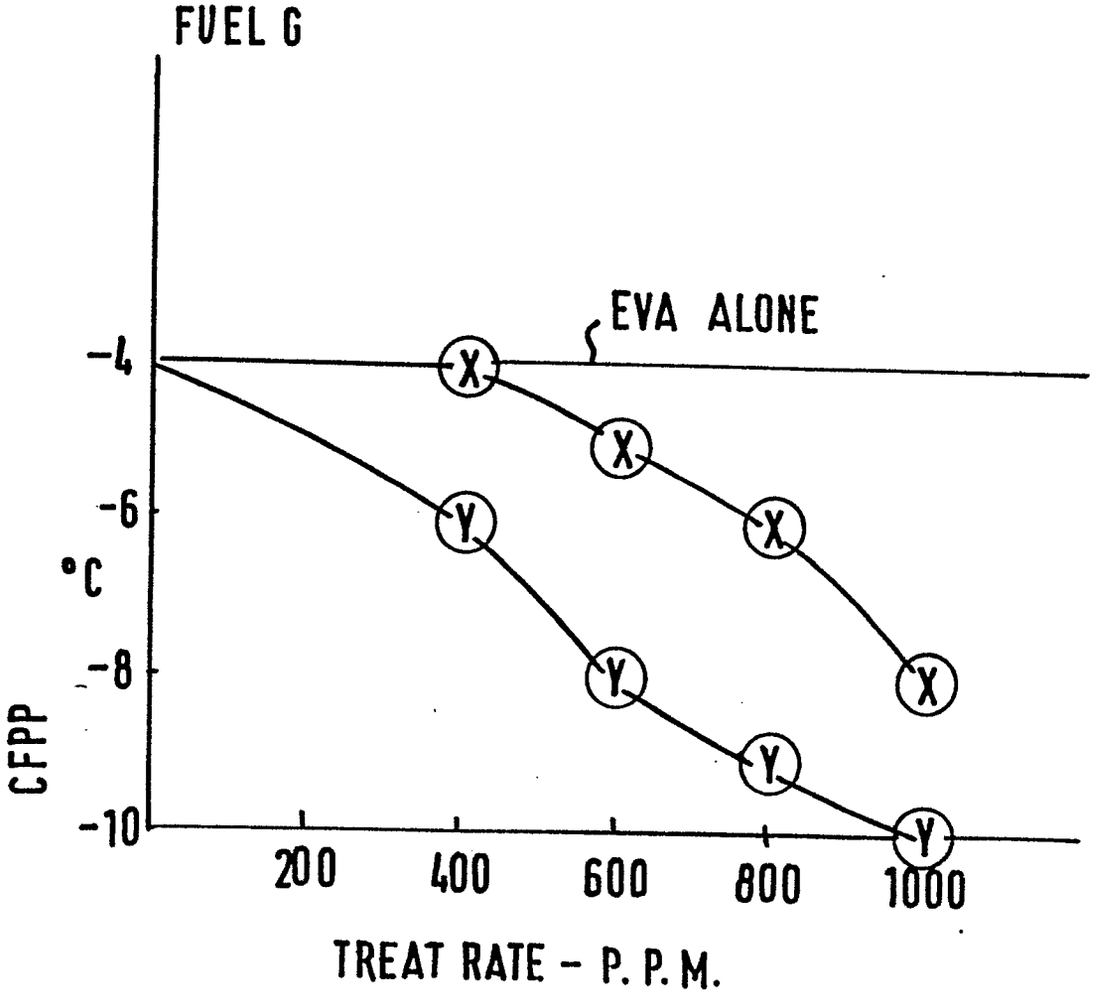
FUEL G
EVA ALONE
-4
-6
-8
-10
°C
CFPP
200
400
600
800
1000
TREAT RATE - P. P. M.

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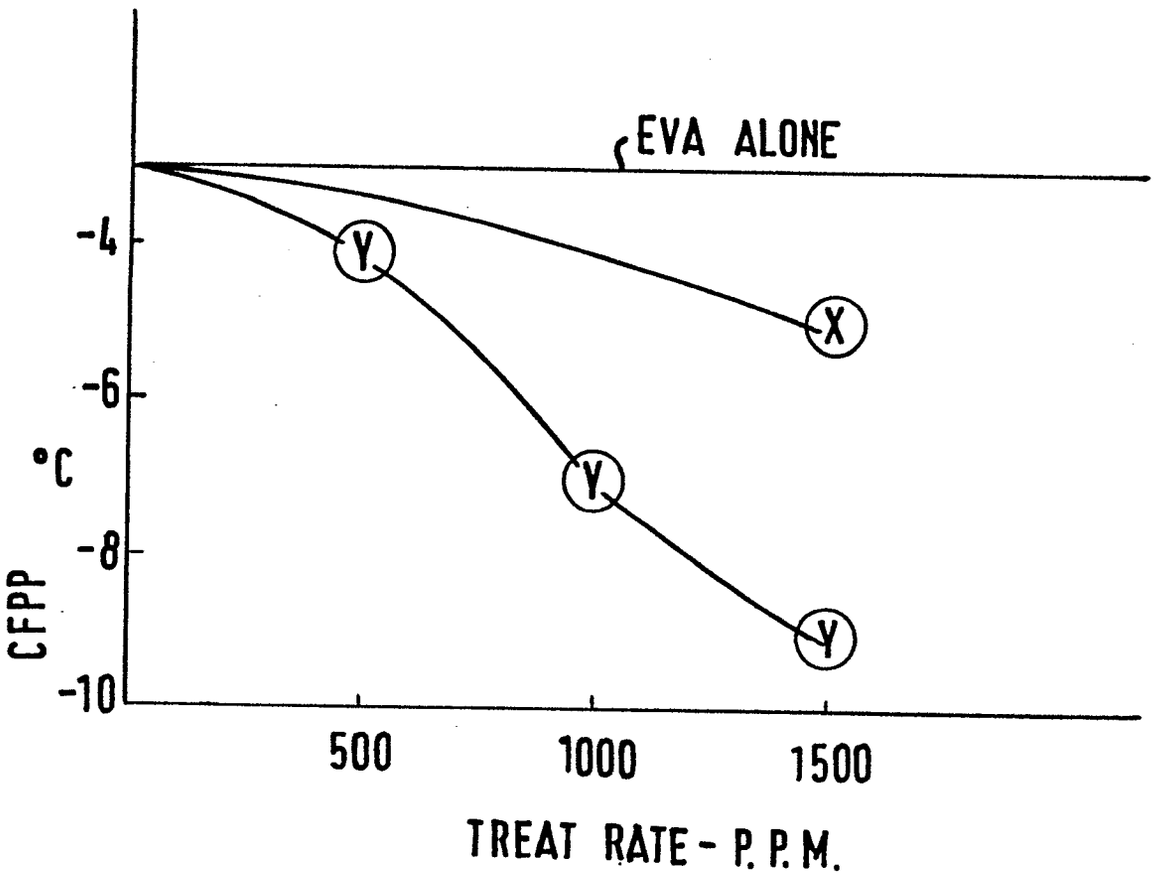
FIG.4
FUEL I



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0183447
Application number

EP 85 30 8322

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 277 157 (STEWART et al.) * Claims; column 1 - column 7, line 37; table II; example 3; column 13, lines 24-49 *	1,2,4, 6,8,11	C 10 L 1/18 C 10 L 1/14
Y		10,11, 17	
A		12,13, 15	
X	--- GB-A- 798 457 (CALIFORNIA RESEARCH CORP.) * Claims 1-7; pages 1-4; table I *	1,6,8	
A	--- US-A-4 160 459 (SWEENEY) * Abstract; claims; example II *	11-13, 17 1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 L
A		5,11-13,17	
Y	--- EP-A-0 061 895 (EXXON) * Abstract; claims 1,7,8,12-14; page 7, lines 4,5 *	10,11, 17	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-02-1986	DE LA MORINERIE B.M.

CATEGORY OF CITED DOCUMENTS

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& : member of the same patent family, corresponding document

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	---	3	
X	DE-C-1 198 561 (ROHM & HAAS CO.) * Claims 1,2; columns 1,2; column 16, lines 9-18 *	1,2,4-8,12,13,15-17	
A	---	10,11	
A	FR-A-1 146 459 (ESSO) * Whole document * ---	1-17	
A	GB-A-1 083 549 (ESSO) * Claims * --- -----	8,10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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