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(54) Fuel compositions.

(57) Cold flow properties are improved by adding in minor proportion by weight to a distillate fuel oil a polymer of a C_1 to C_{17} alkyl vinyl ether. This polymer may be a homopolymer, a mixture of homopolymers, a copolymer of alkyl vinyl ethers of different alkyl chain length, a copolymer of one or more alkyl vinyl ethers with one or more copolymerisable monomers or a mixture of such copolymers. Typical copolymers are copolymers of alkyl vinyl ethers with alkyl acrylates, alkyl methacrylates, olefins, dialkyl fumarates or maleates, eg copolymers of n-butyl vinyl ether with di(n-tetradecyl) fumarate. Other polymers are copolymers of an alkyl vinyl ether with an ethylenically unsaturated carboxylic acid or anhydride, subsequently reacted with an alcohol or an amine or both, eg a copolymer of methyl vinyl ether and maleic anhydride reacted with n-tetradecanol, n-hexadecanol or a mixture of these alcohols.

FUEL COMPOSITIONS

This invention concerns fuel compositions containing a cold flow improver.

Mineral oils containing paraffin wax such as the distillate fuels used as diesel fuel and heating oil have the characteristic of becoming less fluid as the temperature of the oil decreases. This loss of fluidity is due to the crystallisation of the wax into plate-like crystals which eventually form a spongy mass entrapping the oil therein, the temperature at which the wax crystals begin to form being known as the Cloud Point and the temperature at which the wax prevents the oil pouring being known as the Pour Point.

It has long been known that various additives act as Pour Point depressants when blended with waxy mineral oils. These compositions modify the size and shape of wax crystals and reduce the cohesive forces between the crystals and between the wax and the oil in such a manner as to permit the oil to remain fluid at a lower temperature so being pourable and able to pass through coarse filters.

Various Pour Point depressants have been described in the literature and several of these are in commercial use. For example, US Patent No. 3,048,479 teaches the use of copolymers of ethylene and C_1-C_5 vinyl esters, e.g. vinyl acetate, as Pour Point 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. US Patent 3,252,771 relates to the use of polymers of C_{16} to C_{18} alpha-olefins with aluminium trichloride/alkyl halide catalysts as pour depressants in distillate fuels of the "broad boiling", easy-to-treat types available in the United States in the early 1960's.

GB 1154966 discloses the use of certain polymers derived from mono olefinically unsaturated compounds which at least partly consist of at least one mono olefinically unsaturated aliphatic compound having an unbranched saturated hydrocarbon chain of at least 18 carbon atoms as pour point depressants for wax-containing fuels having at least 3 per cent by weight of waxes with a melting point above 35° C and a boiling point above 350° C.

UK Patent 1437132 suggests blends of polymers having long side chains which are particularly useful for flow improvers for petroleum fuel oils and crude oils.

For Europe in the late 1960's, early 1970's, greater emphasis was placed upon improving the filterability of oils at temperatures between the Cloud Point (CP) and the Pour Point as determined by the more severe Cold Filter Plugging Point (CFPP) Test (IP 309/80) and many patents have since been issued relating to additives for improving fuel performance in this test. Thus US Patent 3,961,916 teaches the use of a mixture of copolymers, to control the size of the wax crystals.

In operation of diesel engines at low temperatures, the wax crystals which are formed do not pass through the vehicle paper fuel filters but form a permeable cake on the filter allowing the liquid fuel to pass and the wax crystals will subsequently dissolve as the engine and the fuel heats up, which can be caused by the bulk fuel being heated by recycled fuel. A build up of wax can, however, block the filters, leading to diesel vehicle cold starting problems and problems during the first hour of driving in cold weather.

Such difficulties can be substantially overcome by adding certain homo polymers or copolymers of alkyl vinyl ethers to a middle distillate fuel oil in accordance with this invention. Since the wax crystals are smaller, the compositions of our invention unlike those of UK patent No 1437132, will better meet the conditions of the CFPP test and diesel vehicle operability in cold weather.

According to this invention a fuel oil composition comprises a major proportion by weight of a distillate fuel oil and a minor proportion by weight of a polymer of a hydrocarbyl vinyl ether wherein the hydrocarbyl group contains 1 to 17 carbon atoms. This invention also provides the use as a cold flow improver in a distillate fuel oil of a polymer of a hydrocarbyl vinyl ether wherein the hydrocarbyl group contains 1 to 17 carbon atoms.

The distillate fuel oils can be for example middle distillate fuels such as a diesel fuel, an aviation fuel, kerosene or jet fuel or a heating oil or a vacuum (process) gas oil, etc. Generally, suitable middle distillate fuels are those boiling in the range of 120° to 500° C (ASTM D1160), preferably those boiling in the range 150° to 400° C, for example, those having a relatively high final boiling point (FBP) of above 340° C. The low temperature flow problem is most usually encountered with diesel fuels and with heating oils.

The polymer of the hydrocarbyl vinyl ether, usually a polymer of an alkyl vinyl ether, (hereinafter sometimes referred to as AVE) added to the distillate fuel oil can be a homopolymer, a mixture of homopolymers, a copolymer of hydrocarbyl vinyl ethers of different hydrocarbyl chain length, a copolymer of one or more hydrocarbyl vinyl ethers with one or more copolymerisable monomers or a mixture of such copolymers in all cases in which the hydrocarbyl group has 1 to 17 carbon atoms. Thus the term polymer of a hydrocarbyl vinyl ether means a polymer derived from a hydrocarbyl vinyl ether as the or one of the monomers.

The polymers are derived from hydrocarbyl vinyl ethers. The hydrocarbyl group which has to have 1 to 17 carbon atoms can be alkyl, alkaryl, aralkyl, aryl, alkenyl, alkinyl, etc. Examples of alkaryl are tolyl, xylyl, 4-decylphenyl of aralkyl are 2-phenyl ethyl, benzyl of aryl are naphthyl and of alkenyl, pentenyl, dodecenyl, hexadecenyl. Preferably however the hydrocarbyl group is alkyl and the description which follows will be with reference to alkyl vinyl ethers.

Alkyl vinyl ethers are inexpensive derivatives of alcohols and can be obtained by reaction of an alcohol with acetaldehyde followed by dehydration, i.e. $R\text{-}OH + CH_3CHO\ R\text{-}O\underset{OH}{CH}\ \text{-}CH_3\ ROCH = CH_3$

or by the reaction of acetylene with an alcohol catalysed by a potassium (or sodium) alkoxide.

The alkyl vinyl ethers readily polymerise under cationic conditions using an acidic catalyst, for example $SnCl_2$, BF_3, $Al_2\ (SO_3)_3\ H_2SO_4\ 7H_2O$,

Usually, it is desirable for the polymer, ie homopolymer or copolymer, to be derived from a monomer having at least one relatively long chain alkyl group, eg at least 12 carbon atoms, either as the alkyl group of the alkyl vinyl ether in homopolymers or, in the case of copolymers, as the alkyl group in the alkyl vinyl ether and/or as part of the monomer copolymerisable therewith.

Suitable and preferred polymers of AVE include the following:

1. Homopolymers of AVE. The alkyl group can be of any chain length from C_1 to C_{17} but is preferably C_{12} to C_{16}. The alkyl group is preferably straight-chained, but a certain proportion (up to 25%) may contain a low level of branching (e.g. 2- + 3-methyl substituted chains). Examples of suitable AVEs are those where the alkyl group is n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-hepta or n-eicosyl.

2. Mixtures of homopolymers of AVE such as those described in 1 above, for example a mixture of n-hexadecyl vinyl ether and n-tetradecyl vinyl ether.

3. Copolymers of AVEs. Suitable and preferred alkyl groups in the AVE are as described above in connection with homopolymers of AVE 1. Very suitable copolymers are copolymers of mixtures of n-alkyl vinyl ethers where the alkyl group ranges from 1 to 17 carbon atoms, often giving an average alkyl chain length of 12 to 13 eg about 12.5 carbon atoms. Thus a suitable copolymer is a copolymer of a substantially equimolar mixture of AVES wherein the alkyl groups are n-alkyl groups of chain lengths 8, 10, 12, 14 and 16. Another suitable copolymer is a copolymer of a short chain, alkyl vinyl ether, e.g. C_3 or C_4 alkyl vinyl either, with mixed C_{12} to C_{16} n-alkyl vinyl ethers.

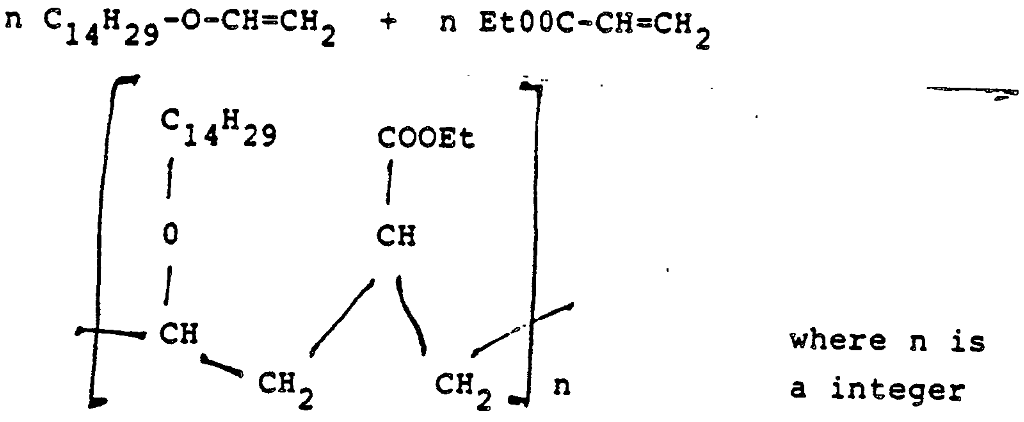
4. Copolymers of one or more alkyl vinyl ethers with one or more copolymerisable monomers. Usually these copolymerisable monomers are ethylenically unsaturated. Examples of these monomers include olefins or haloolefins; dienes, for example alkoxybutadienes; acrylate or methacrylate esters; acrylonitrile, maleic anhydride, maleate or fumarate esters; and allyl or vinyl substituted heterocyclic compounds, for example allyl or vinyl pyrrole or allyl or vinyl carbazole. Alkyl vinyl ethers copolymerise with such monomers using free-radical initiators (e.g. AIBN (azo-iso butyro nitrile) di-t-butyl peroxide, t-butyl per-octanoate or t-butyl perbenzoate) or coordination - type catalysts.

It is preferred with these copolymers that there is at least one relatively long chain alkyl group, eg of at least 12 carbon atoms, derived either from the AVE and/or from the copolymerisable monomer.

More specific examples are as follows:

4(a) Long chain alkyl vinyl ethers copolymerised with short chain monomers for example C_{12} to C_{16} alkyl vinyl ethers copolymerised with C_1 to C_{10} alkyl acrylates, C_1 to C_{10} alkyl methacrylates, C_1 to C_6 olefins or di(C_1 to C_{10} alkyl) fumarates or maleates.

Examples of C_{12} to C_{17} alkyl vinyl ethers include the n-dodecyl, tetradecyl and hexadecyl vinyl ethers, examples of C_1 to C_{10} alkyl acrylates and methacrylates include the ethyl and n-hexylacrylates and methacrylates, examples of C_1 to C_{10} olefins are ethylene, propylene, 1-butene, 1-hexene, and examples of di(C_1 to C_{10} alkyl) fumarates and maleates, include di-methyl di-ethyl, di-n-butyl and di-n-octyl fumarates and maleates. A specific example is a copolymer of n-tetradecyl vinyl ether copolymerised with ethyl acrylate ie,

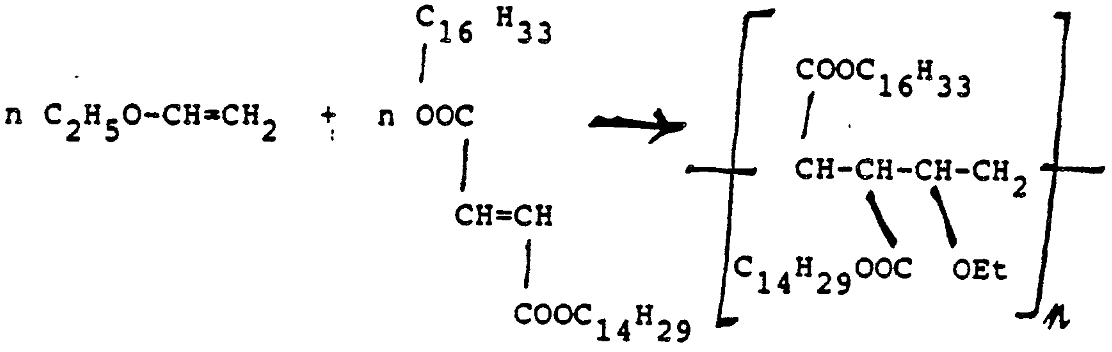


where n is a integer

4(b) Short chain alkyl vinyl ethers, for example C_1 to C_{10} alkyl vinyl ethers copolymerised with long chain monomers for example di (C_{12} to C_{18}) alkyl fumarates and maleates, C_{12} to C_{18} alkyl acrylates and methacrylates and N,N di (C_{12} to C_{18}) alkyl acrylamides.

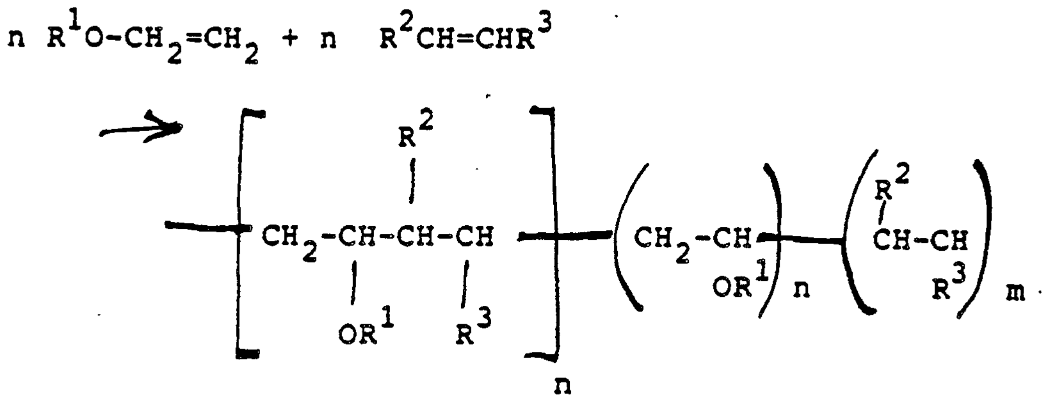
Examples of short chain alkyl vinyl ethers include the methyl, propyl, n- and iso-butyl and hexyl vinyl ethers, examples of the long chain dialkyl fumarates, maleates and N,N dialkyl acrylamides include the di-dodecyl, tetradecyl and hexadecyl fumarates, maleates and acrylamides, examples of the C_{12} to C_{18} alkyl acrylates and methacrylates include the dodecyl, hexadecyl and octadecyl acrylates and methacrylates.

A specific example is the copolymer of ethyl vinyl ether with tetradecyl, octadecyl fumarate.



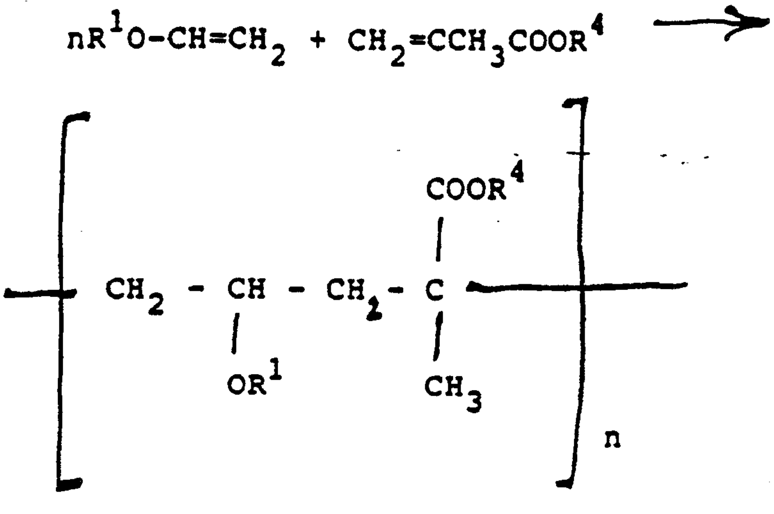
where n is an integer.

General equations for the reactants and the resulting polymers for 4(a) and 4(b) above are



where n and m are integers, R^1 is an alkyl group, R^2 is - H or-COOR^4, R^3 is -COOR^5, CONR$^6_2$ or R^7 and R^4, R^5, R^6 and R^7 are alkyl groups.

For reacting an AVE with a methacrylate the reaction is



$$nR^1O-CH{=}CH_2 + CH_2{=}CCH_3COOR^4 \longrightarrow \left[CH_2 - \underset{OR^1}{CH} - CH_2 - \overset{COOR^4}{\underset{CH_3}{C}} \right]_n$$

where n, R^1 and R^4 are as defined above.

For 4(a) R^1 is long chain alkyl and R^4, R^5, R^6 and R^7 are short chain alkyl and for 4(b) R^1 is short chain alkyl and R^4, R^5, R^6 and R^7 are long chain alkyl.

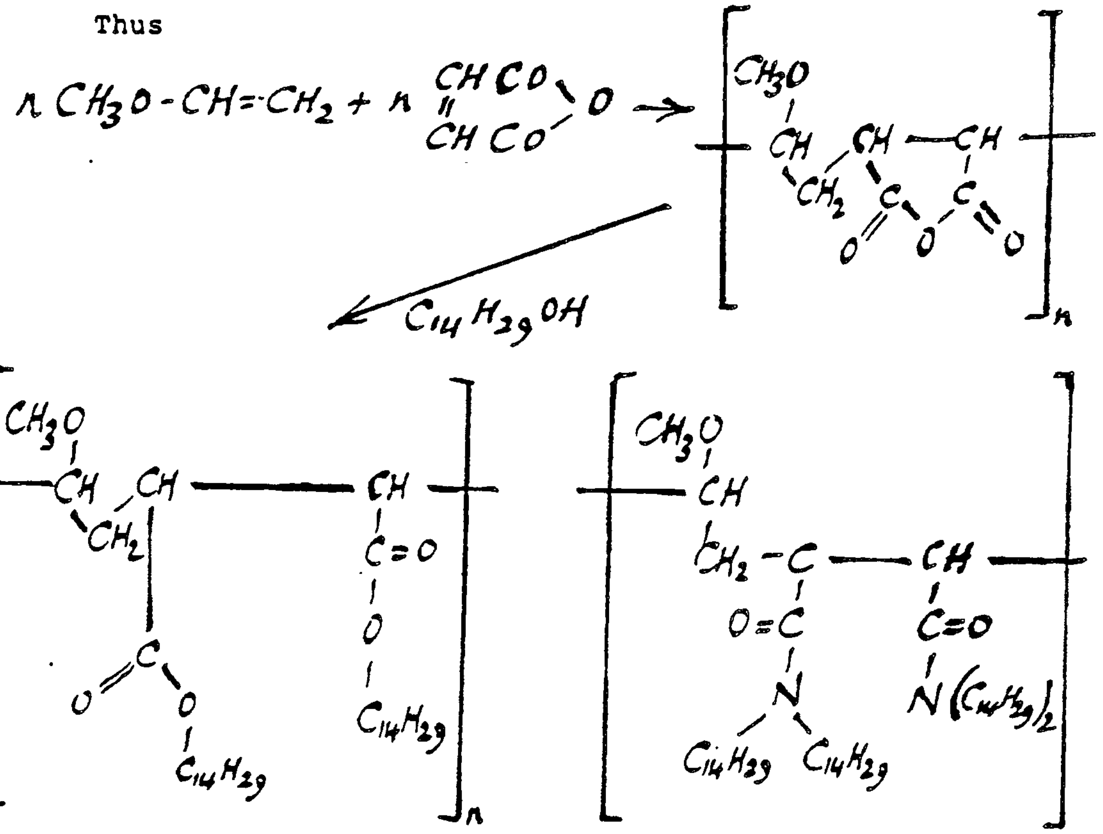
4(c) Copolymers of short chain length AVE, eg a C_1 to C_{10} alkyl vinyl ether, with an ethylenically unsaturated carboxylic acid or carboxylic acid anhydride subsequently reacted with an alcohol or an amine or both. Thus one may copolymerise a C_1 to C_{10} alkyl vinyl ether with acrylic acid, methacrylic acid or maleic anhydride and react the copolymer with a long-chain alcohol, eg a C_{12} to C_{18} alcohol and/or a long-chain primary or secondary amine, eg an amine in which at least one of the hydrocarbyl groups contains at least 12 carbon atoms.

Suitable examples of short chain AVEs are given in 4(b) above. Examples of long chain alcohols are the aliphatic alcohols, R^8OH where R^8 is a C_{12} to C_{18} substituted or unsubstituted alkyl group. Suitable examples are dodecanol, tetradecanol and octadecanol.

The long chain primary or secondary amine may have the formula where $R^9R^{10}HN$ where R^9 is hydrogen or an alkyl group, and R^{10} is an alkyl group. Examples of hydrocarbyl groups are alkyl, aralkyl or cycloalkyl groups. The alkyl and the alkyl portion of the alkaryl groups can be branched but are preferably straight chain. Preferred alkyl groups contain 10 to 18, especially 12 to 16 carbon atoms and preferred alkaryl and aralkyl groups contain 16 to 24 carbon atoms. Especially preferred alkyl groups are C_{12} to C_{18} alkyl groups eg tetradecyl, hexadecyl, octadecyl, or a mixture such as hexadecyl/tetradecyl.

Specific examples are the copolymerisation of methyl vinyl ether with maleic anhydride followed by reaction of the copolymer with tetradecanol or with dihexadecyl amine.

Thus



In general the AVE copolymers should have a molecular weight of between 1,500 and 50,000, preferably between 2,500 and 15,000.

Compared with the olefin copolymers where the methylene link is much less flexible than the ether link in the AVE polymers used in the fuel oil compositions of this invention, the AVE polymers have similar wax crystal modifier properties to for example poly-1-octadecene polymers but better oil solubility.

The amount of hydrocarbyl vinyl ether polymer added to the fuel oil is a minor proportion by weight and preferably this is between 0.0001 and 5.0% by weight, for example 0.001 to 0.5% by weight (active matter) based on the weight of the fuel oil.

The hydrocarbyl vinyl ether polymer may be conveniently dissolved in a suitable solvent to form a concentrate of from 20 to 90%, e.g. 30 to 80 weight % of polymer in the solvent. Suitable. solvents include kerosene, aromatic naphthas, mineral lubricating oils, etc.

Other additives which may be included in the fuel oil with the alkyl vinyl ether polymer include for example other flow improvers.

The flow improver can be one of the following:-

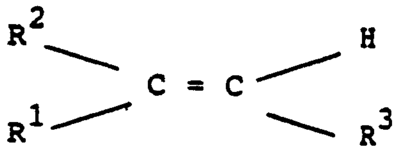
(i) Linear copolymers of ethylene and some other comonomer, for example a vinyl ester, an acrylate, a methacrylate, an -olefin, styrene, etc,

(ii) Comb polymers, ie polymers with C_8-C_{30} alkyl side chain branches;

(iii) Linear polymers derived from ethylene oxide, for example polyethylene glycol esters and amino derivatives thereof;

(iv) Monomeric compounds, for example amine salts and amides of polycarboxylic acids such as citric acid and phthalic acid. Also amide/amine salts of sulpho-carboxylic acids such as o-sulpho benzoic and sulpho-succinic acid may be used.

The unsaturated comonomers from which the linear copolymers (i) are derived and which may be copolymerized with ethylene, include unsaturated mono and diesters of the general formula:



wherein R^2 is hydrogen or methyl; R^1 is a $-OOCR^4$ group or hydrocarbyl wherein R^4 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 groups or R^1 is a $-COOR^4$ group wherein R^4 is as previously described but is not hydrogen and R^3 is hydrogen or $-COOR^4$ as previous defined. The monomer, when R^1 and R^3 are hydrogen and R^2 is $-OOCR^4$ 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 copolymerized with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. 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 No 3961916.

Other linear copolymers (i) are derived from comonomers of the formula:

$CHR^5 = CR^6X$ where

R^5 is H or alkyl, R^6 is H or methyl and X is $-COOR^7$ or hydrocarbyl where R^7 is alkyl. This includes acrylates, $CH_2 = COOR^7$, methacrylates, $CH_2 = CMeCOOR^7$, styrene $CH_2 = CH.C_6H_5$ and olefins $CHR^5 = CR^6R^8$ where R^8 is alkyl. The group R^7 is preferably C_1 to C_{28}, more usually C_1 to C_{17} and more preferably a C_1 to C_8 straight or branched chain alkyl group. For the olefins R^5 and R^6 are preferably hydrogen and R^8 a C^1 to C_{20} alkyl group. Thus suitable olefins are propylene, hexene-1, octene-1, dodecene-1 and tetradecene-1.

For this type of copolymer it is preferred that the ethylene content is 50 to 65 weight per cent although higher amount can be used eg 80 weight % for ethylene -propylene copolymers.

It is preferred that these copolymers have a number average molecular weight as measured a by vapour phase osmometry of 1000 to 6000, preferably 1000 to 3000.

Particularly suitable linear copolymeric flow improvers (i) are copolymers of ethylene and a vinyl ester.

The vinyl ester can be a vinyl ester of a monocarboxylic acid, for example one containing 1 to 20 carbon atoms per molecular. Examples are vinyl acetate, vinyl propionate and vinyl butyrate. Most preferred however is vinyl acetate.

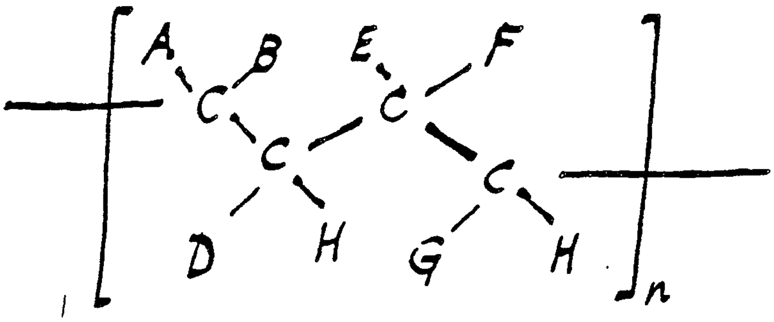
Usually the copolymer of ethylene and a vinyl ester will consist of 3 to 40, preferably 3 to 20, molar proportions of ethylene per molar proportion of the vinyl ester. The copolymer usually has a number average molecular weight of between 1000 and 50,000, preferably between 1,500 and 5,000. The molecular weights can be measured by cryoscopic methods or by vapour phase osmometry, for example by using a Mechrolab Vapour Phase Osmometer Model 310A.

Particularly preferred comb copolymeric flow improvers are (ii) copolymers of an ester of fumaric acid and a vinyl ester. The ester of fumaric acid can be either a mono- or a di-ester and alkyl esters are preferred. The or each alkyl group can contain 6 to 30, preferably 10 to 20 carbon atoms, and mono- or di-(C_{14} to C_{18}) alkyl esters are especially suitable, either as single esters or as mixed esters. Generally di-alkyl esters are preferred to mono- esters.

Suitable vinyl esters with which the fumarate ester is copolymerised are those described above in connection with ethylene/vinyl ester copolymers. Vinyl acetate is particularly preferred.

The fumarate esters are preferably copolymerised with the vinyl ester in a molar proportion of between 1.5:1 and 1:1.5, for example about 1:1. These copolymers usually have a number average molecular weight of from 1000 to 100,000, as measured for example by Vapour Phase Osmometry such as by a Mechrolab Vapour Pressure Osmometer.

Comb polymers (ii) have the following general formula:



where
A is H, Me or CH_2CO_2R' (where $R' = C_{10} - C_{22}$ alkyl) (Me = methyl) B is CO_2R or R'' (where $R'' = C_{10} - C_{30}$ alkyl, PhR' (Ph = phenyl)
D is H or CO_2R'
E is H or Me, CH_2CO_2R'
F is $OCOR''$ ($R''' = C_1 - C_{22}$ alkyl), CO_2R', Ph, R' or PhR'
G is H or CO_2R'
and n is an integer

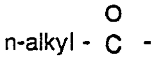
In general terms, such polymers include a dialkyl fumarate/vinyl acetate copolymer eg ditetradecyl fumarate/vinyl copolymer; a styrene dialkyl fumarate ester copolymer eg styrene/dihexadecyl fumarate copolymer; a poly dialkyl fumarate, eg poly (di octadecyl fumarate); an alpha-olefin dialkyl maleate copolymer eg copolymer of tetradecene and di hexadecyl maleate, a dialkyl itaconate/vinyl acetate copolymer eg dihexadecyl itaconate/vinyl acetate; poly-(n-alkyl methacrylates) eg poly(tetradecyl methacrylate); poly (n-alkyl acrylates) eg poly (tetra decyl acrylate); poly - alkenes eg poly (1-octadecene) etc.

Linear polymer derived from ethylene oxide (iii) include the poly oxyalkylene esters, ethers, esters/ethers, amide/esters and mixtures thereof, particularly those containing at least one, preferably at least two C_{10} to C_{30} linear saturated alkyl groups of a polyoxyalkylene glycol group of molecular weight 100 to 5,000, preferably 200 to 5,000, the alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. European patent publication No 0,061,985 A2 describe some of these additives. The preferred esters, ethers or ester/ethers may be structurally depicted by the formula:

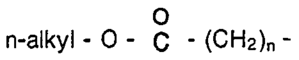
$R-O-(A)-O-R^1$

where R and R^1 are the same or different and may be

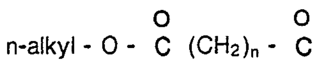
i) n-alkyl

ii) 

$\text{n-alkyl} - \overset{O}{C} -$

iii) 

$\text{n-alkyl} - O - \overset{O}{C} - (CH_2)_n -$

iv) 

$\text{n-alkyl} - O - \overset{O}{C}\ (CH_2)_n - \overset{O}{C} -$

the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyoxyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred the glycol should be substantially linear.

Suitable glycols generally are the substantially linear polyethylene glycol (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives and it is preferred to use a C_{18}-C_{24} fatty acid, especially behenic acids. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Examples of the monomeric compounds (iv) as flow improver include polar nitrogen containing compounds, for example an amine salt of, a mono amide or a diamide of, or a half amine salt, half amide of a dicarboxylic acid, tricarboxylic acid or anhydride thereof. These polar compounds are generally formed by reaction of at least one molar proportion of hydrocarbyl substituted amines with a molar proportion of hydrocarbyl acid having 1 to 4 carboxylic acid groups or their anhydrides; ester/amides may also be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US patent No 4,211, 534. Suitable amines are usually long chain C_{12}-C_{40} primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally containing about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8-C_{40}, preferably C_{14} to C_{24} alkyl segment.

The amine salt or half amine salt can be derived from a primary, secondary, tertiary or quaternary amine but the amide can only be derived from a primary or secondary amine. The amines are preferably aliphatic amines and the amine is preferably a secondary amine in particular an aliphatic secondary amine of the formula R^1R^2NH. Preferably R^1 and R^2 which can be the same or different contain at least 10 carbon atoms, especially 12 to 22 carbon atoms. Examples of amines include dodecyl amine, tetradecyl amine, octadecyl amine, eicosyl 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 cyclo-hexane, 1,2 dicarboxylic acid, cyclohexane dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid, naphthalene dicarboxylic acid, citric acid and the like. Generally, these acids will have about 3-13 carbon atoms in the cyclic moiety. Preferred acids are benzene dicarboxylic acids such as phthalic acid, terephthalic acid, and iso-phthalic acid. Phthalic acid or its anhydride is particularly preferred.

Examples of suitable sulpho carboxylic acids are ortho sulpho benzoic acid and mono-alkyl sulpho succinic acid.

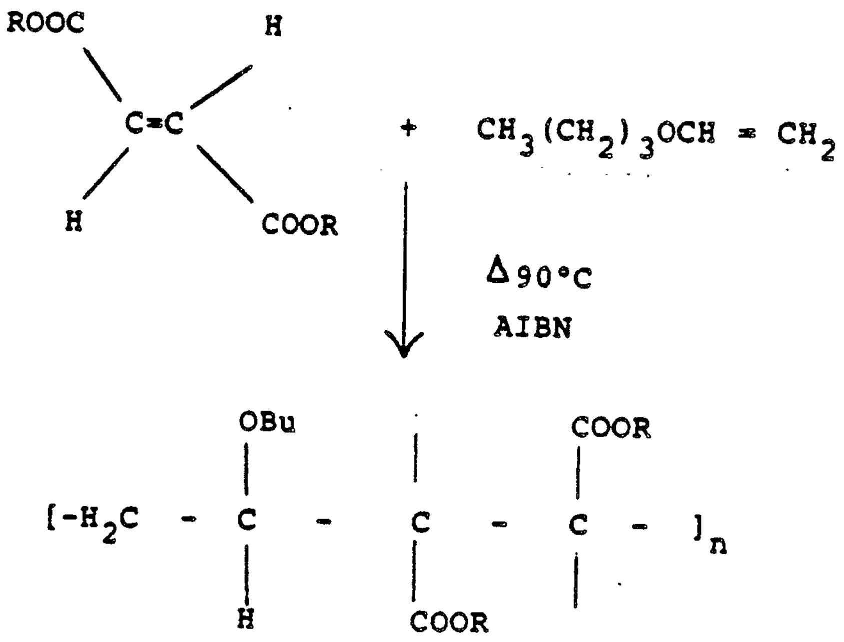
One suitable compound is the half amine salt, half amide of the dicarboxylic acid in which the amine is a secondary amine. Especially preferred is the half amine salt, half amide of phthalic acid and dihydrogenated tallow amine - Armeen 2HT (approx 4 wt% n-C_{14} alkyl, 30 wt% n-C_{16} alkyl, 60 wt% n-C_{18} alkyl, the remainder being unsaturated).

Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

Example 1

A copolymer having a number average molecular weight of about 20,000 as determined by membrane osmometry was prepared by copolymerising methyl vinyl ether and maleic anhydride using a free radical catalyst. The anhydride groups of the resulting copolymer were then esterified with either n-tetradecanol, n-hexadecanol or a mixture of these two alcohols. The resulting esterified copolymers are identified as C1, C2 and C3 respectively.

A copolymer (C4) of a di(n-tetradecyl) fumarate and n-butyl vinyl ether was prepared according to the following reaction conditions:



$R = C_{14}H_{29}$

AIBN = Catalyst tl/2 = 25 mins at 90° C. This was added as initial charge 0.6g followed by 0.1g each hour for six hours. The reaction was monitored by IR and GC (to determine free fumarate content).

Copolymers C1, C2, C3 and C4 were added in conjunction with a prior art copolymer (X) which was an ethylene/vinyl acetate copolymer containing 36 weight % of vinyl acetate units, $\overline{M}n$ about 2,500, to three middle distillate fuel oils F1, F2 and F3 having the following ASTM D 86 distillation characteristics (all ° C):

	IBP	20%	90%	FBP%	Cloud Pt	CFPP base
F1	170	228	316	347	-6	-12
F2	164	240	330	356	-10.5	-14
F 3	232	270	326	344	-7	-9

The results of the Wax Appearance Temperature measurements are expressed in Table 1 as degrees depression below the WAT of the fuel without the additive polymers to illustrate their effectiveness as WAT (hence Cloud Point) depressants.

Table 1

Fuel F1	Δ WAT/° C
100 ppm X + 500 ppm C1	1.9
100 ppm X + 500 ppm C3	3.0
100 ppm X + 500 ppm C2	2.9
100 ppm X + 1000 ppm C1	2.7
100 ppm X + 1000 ppm C3	3.7
100 ppm X + 1000 ppm C2	3.2
100 ppm X + 1000 ppm C4	2.7
Fuel F2	
100 ppm X + 500 ppm C1	2.0
100 ppm X + 500 ppm C3	2.6
100 ppm X + 500 ppm C2	1.1
100 ppm X + 1000 ppm C1	2.8
100 ppm X + 1000 ppm C3	3.4
100 ppm X + 1000 ppm C2	1.1
100 ppm X + 1000 ppm C4	2.8
Fuel F3	
100 ppm X + 500 ppm C1	0.7
100 ppm X + 500 ppm C3	0.8
100 ppm X + 500 ppm C2	0.4
100 ppm X + 1000 ppm C1	1.1
100 ppm X + 1000 ppm C3	1.4
100 ppm X + 1000 ppm C2	0.4
100 ppm X + 1000 ppm C4	1.1

The Wax Appearance Temperature (WAT) is measured by different scanning calorimetry using a Du Pont 990 differential scanning calorimeter. In the test a 10 microlitre sample of the fuel is cooled at 10° C/min from a temperature at least 30° C above the expected cloud point of the fuel. The observed onset of crystallisation is estimated, without correction for thermal lag (approximately 2° C), as the wax appearance temperature (WAT) is indicated by the differential scanning calorimeter.

The depression of the wax appearance temperature WAT is shown by comparing the result of the treated fuel (WAT_1) with that of the untreated fuel (WAT_0) as $\Delta WAT = WAT_0 - WAT_1$. Depression of the WAT is indicated by a positive result.

Example 2

Copolymer C4 of Example 1 was added to three further fuel oils F4, F5 and F6 having the following ASTM D86 distillation characteristics (all ° C):

	IBP	20%	90%	FBP%	Cloud Pt	CFPP base
F4	159	210	316	350	-12	0
F5	184	226	368	398	6	
F6	168	231	325	350	-9	

The results of adding C4 to F4 are shown in Table 2.

Table 2

ppm ai Polymer	0	250	500	750	1000	1500
WAP Depression (ASTM D 3117-72)			3.4		5.8	
WAT (D.S.C.Mettler)	-18.0	-20.9	-22.0	-22.6	-22.1	-23.9

In Table 3 the CFPP results of adding to fuel oil F5 (CFPP 0°C) a mixture of 1 part by weight of C4 with 4 parts by weight of a prior art copolymer mixture Y and Y alone are given. Y was a 3:1 (by weight) mixture of respectively an ethylene-vinyl acetate copolymer containing about 36 wt % vinyl acetate of number average mol. wt. 2,500 and a copolymer containing about 17 wt % vinyl acetate of number average molecular weight 3000.

Table 3

ppm ai -	50	100	150	175	200	250	300	500
C4:Y(1:4)	3	13	19		20	19	20	
Y alone				-6	-11		-13	-16

The Cold Filter Plugging Point Test (CFPPT)

The cold flow properties of the blend were determined by the Cold Filter Plugging Point Test (CFPPT). This test is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Vol 52, No 510, June 1966 pp 173-185. In brief, a 40 ml sample of the oil to be tested is cooled by a bath maintained at about -34°C. Periodically (at each one degree Centrigrade drop in temperature starting from 10°C above the cloud point) the cooled oil is tested for its ability to flow through a fine screen within 1 minute. This cold property is tested with a device consisting of a pipette to whose lower end is attached an inverted funnel 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 of about 0.45 square inch. The periodic tests are each initiated by applying a vacuum of 20cm of water to the upper end of the pipette whereby the oil is drawn through the screen up into the pipette to a mark indicating 20 ml of oil. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds. The results of the test can be quoted as CFPP (°C) which is the fail temperature of the fuel treated with the flow improver.

In this case what is quoted is ΔCFPP(°C) which is the difference between the fail temperature of the untreated fuel (CFPP_0) and the fuel treated with the additive (CFPP_1) ie $\Delta\text{CFPP} = \text{CFPP}_0 - \text{CFPP}_1$.

In Table 4 the results of adding different amounts of copolymer C4, prior art copolymer X and prior art cloud point depressing additive Z to fuel oil F6 are shown. Z is a C_{14} dialkyl fumarate/vinyl acetate copolymer.

Table 4

ppm X	0	0	0	100	100	100
ppm Polymer C4	0	500	1000	0	500	1000
Cloud Point	-6	-10	-10	-6	-9(-9)	-10
Wax Appearance Point	-11	-14	-15(-14)	-12	-14	-14(-12)
DSC WAT	-11	-12.5	-13(-13)	-10	-11.5	-12.5(-12)
Pour Point	-15	-29.0	-25(-24)	-30	-35	-45(-21)
Results in ° C						
Results in brackets C_{14} dialkyl fumarate/vinyl acetate copolymer,Z.						

Table 4 shows WAP, CP and WAT depressions by the C4 alone or in fuels with X added are equivalent to those with Z. Pour points with X are improved on adding C4 whereas pour point regression occurs on adding Z. This result is confirmed by slow cool tests where the sample is cooled from room temperature to -25° C in a cold box. Here Z/X 1000/100 ppm ai gave a gelled sample whereas C4/X 1000/100 ppm ai gave a completely fluid sample.

Claims

1. A fuel oil composition comprising a major proportion by weight of a distillate fuel oil and a minor proportion by weight of a polymer of an hydrocarbyl vinyl ether wherein the hydrocarbyl group contains 1 to 17 carbon atoms.

2. A composition according to claim 1 wherein the hydrocarbyl vinyl ether is an alkyl vinyl ether.

3. A composition according to claim 2 wherein the polymer is derived from a monomer having at least one alkyl group having at least 12 carbon atoms.

4. A composition according to either of claims 2 and 3 wherein the polymer is a homopolymer of a C_{12} to C_{16} alkyl vinyl ether.

5. A composition according to either of claims 2 and 3 wherein the polymer is a copolymer of mixtures of alkyl vinyl ethers having 1 to 17 carbon atoms in the alkyl group.

6. A composition according to either of claims 2 and 3 wherein the polymer is a copolymer of one or more alkyl vinyl ethers with one or more copolymerisable monomers.

7. A composition according to claim 6 wherein the copolymer is a copolymer of a C_{12} to C_{16} alkyl vinyl ether with a C_1 to C_{10} alkyl acrylate, a C_1 to C_{10} alkyl methacrylate, a C_1 to C_6 olefin or a di (C_1 to C_{10} alkyl) fumarate or maleate.

8. A composition according to claim 6 wherein the copolymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with a di(C_{12} to C_{18}) alkyl fumarate or maleate, a C_{12} to C_{18} acrylate or methacrylate or a N,N di (C_{12} to C_{18}) alkyl acrylamide.

9. A composition according to either of claims 2 and 3 wherein the polymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with an ethylenically unsaturated carboxylic acid or carboxylic acid anhydride subsequently reacted with an alcohol or an amine or both.

10. A composition according to any one of the preceding claims which contains 0.0001 to 5.0% by weight of the polymer.

11. A composition according to any one of the preceding claims which includes another flow improver.

12. The use as a cold flow improver in a middle distillate fuel oil of a polymer of an hydrocarbyl vinyl ether wherein the hydrocarbyl group has 1 to 17 carbon atoms.

13. The use according to claim 12 wherein the hydrocarbyl vinyl ether is an alkyl vinyl ether.

14. The use according to claim 13 wherein the polymer is derived from a monomer having at least one alkyl group having at least 12 carbon atoms.

15. The use according to either of claims 13 and 14 wherein the polymer is a homopolymer of a C_{12} to C_{16} alkyl vinyl ether.

16. The use according to either of claims 13 and 14 wherein the polymer is a copolymer of mixtures of alkyl vinyl ethers having 1 to 17 carbon atoms in the alkyl group.

17. The use according to either of claims 13 and 14 wherein the polymer is a copolymer of one or more alkyl vinyl ethers with one or more copolymerisable monomers.

18. The use according to claim 17 wherein the copolymer is a copolymer of a C_{12} to C_{16} alkyl vinyl ether with a C_1 to C_{10} alkyl acrylate, a C_1 to C_{10} alkyl methacrylate, a C_1 to C_6 olefin or a di (C_1 to C_{10} alkyl) fumarate or maleate.

19. The use according to claim 17 wherein the copolymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with a di(C_{12} to C_{18}) alkyl fumarate or maleate, a C_{12} to C_{18} acrylate or methacrylate or a N,N di (C_{12} to C_{18}) alkyl acrylamide.

20. The use according to either of claims 13 and 14 wherein the polymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with an ethylenically unsaturated carboxylic acid or carboxylic acid anhydride subsequently reacted with an alcohol or an amine or both.

21. A concentrate comprising a solvent and 20 to 90% by weight of hydrocarbyl vinyl ether wherein the hydrocarbyl group has 1 to 17 carbon atoms.

22. A concentrate according to claim 21 wherein the hydrocarbyl vinyl ether is an alkyl vinyl ether.

23. A concentrate according to claim 22 wherein the polymer is dervied from a monomer having at least one alkyl group having at least 12 carbon atoms.

24. A concentrate according to either of claims 22 and 23 wherein the polymer is a homopolymer of a C_{12} to C_{16} alkyl vinyl ether.

25. A concentrate according to either of claims 22 and 23 wherein the polymer is a copolymer of mixtures of alkyl vinyl ethers having 1 to 17 carbon atoms in the alkyl group.

26. A concentrate according to either of claims 22 and 23 wherein the polymer is a copolymer of one or more alkyl vinyl eithers with one or more copolymerisable monomers.

27. A concentrate according to claim 26 wherein the copolymer is a copolymer of a C_{12} to C_{16} alkyl vinyl ether with a C_1 to C_{10} alkyl acrylate, a C_1 to C_{10} alkyl methacrylate, a C_1 to C_6 olefin or a di (C_1 to C_{10} alkyl) fumarate or maleate.

28. A concentrate according to claim 26 wherein the copolymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with a di(C_{12} to C_{18}) alkyl fumarate or maleate, a C_{12} to C_{18} acrylate or methacrylate or a N,N di (C_{12} to C_{18}) alkyl acrylamide.

29. A concentrate according to either of claims 22 and 23 wherein the polymer is a copolymer of a C_1 to C_{10} alkyl vinyl ether with an ethylenically unsaturated carboxylic acid or carboxylic acid anhydride subsequently reacted with an alcohol or an amine or both.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 8510

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.5)
X	GB-A-1 161 188 (SHELL) * Claims 1-19; page 3, line 87 - page 4, line 3 *	1-3,6,10-14,17,21-23,26	C 10 L 1/18 C 10 L 1/22 C 10 L 1/14
O,X	GB-A-1 154 966 (SHELL) * Page 10, example 4; page 3, lines 70-117 *	1-29	
X	FR-A-2 080 410 (MOBIL OIL) * Claims; pages 2,3 *	1-3,6-14,17-23,26-29	
X	FR-A-2 189 503 (TEXACO) * Whole document *	1-5,10-16,21-24	
X	DE-A-1 941 581 (MOBIL OIL) * Whole document *	1-3,6,8-14,17,19-23,26,28,29	
X	DE-A-2 047 448 (BADISCHE ANILIN- & SODA-FABRIK) * Whole document *	1-4,10-15,21-24	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 10 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-12-1989	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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