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REPLACEDOil & Fuel Oil Compositions

This invention relates to additive compositions and their use in improving the properties of oil and fuel oil compositions.

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It is known that wax separates out from oils and fuel oils at low temperatures thereby impairing certain properties. It is also known to use additives to improve those properties, for example to improve cold flow properties and to inhibit settling of the wax under gravity on standing. Additives for the former are sometimes called Cold Flow Improvers and additives for the latter are sometimes called Wax Anti-settling Additives.

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Examples of patent specifications describing such additives and their use are: US Patents 3 048 479; 3 961 916; 3 252 771; 2 542 542; 3 444 082; 4 211 534; 4 375 973 and 4 402 708; UK Patents 1 263 152; 1 469 016; 1 468 588; 2 129 012; 2 923 645; and 1 209 676; Japanese Patent Publications 56 54 038; 56 54 037; and 55 40 640.

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EP-A-0 225 688 describes the use of itaconate and citraconate polymers and copolymers for improving the cold flow properties of an oil (crude or lubricating) and fuel oils such as residual fuel, middle distillate fuels and jet fuel or as a dewaxing aid in lubricating oil, which polymers and copolymers can be tailored to suit the particular oil or fuel oil concerned. It describes polymers and copolymers having number average molecular weights as measured by Gel Permeation Chromatography of from 1,000 to 500,000 and exemplifies polymers and copolymers of molecular weights of 20,000 and higher.

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A problem using, in oils and fuel oils, polymers such as those embraced within EP-A-0 255 688 is that they may regress the cold flow performance of flow improving additives. The present invention can overcome this regression by using certain comb polymers in combination as will be described hereinafter and illustrated in the examples herein.

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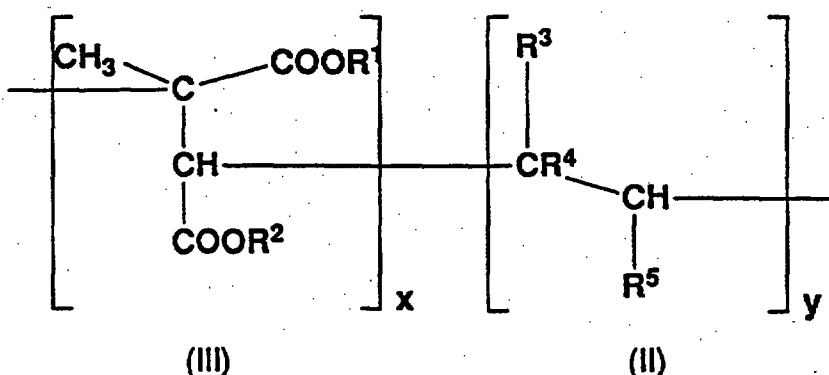
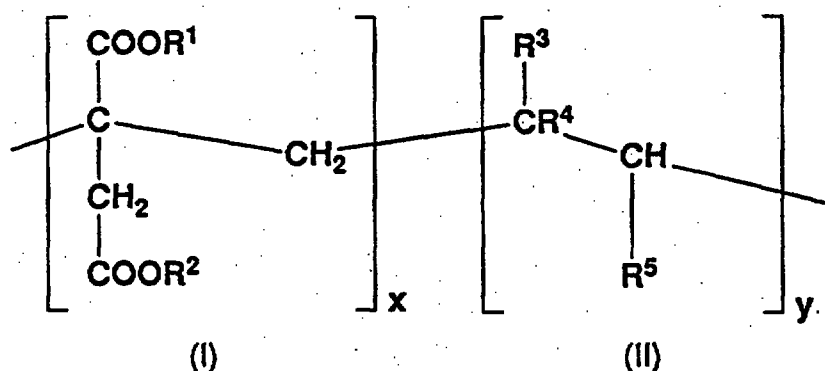
International Application Number PCT/GB91/00622 (Publication No WO 91/16407) describes the use of polymers embraced within EP-A-0 255 688 of number average molecular weight of 1,000 to 20,000 as low temperature flow improvers for distillate fuels, such as in combination with other

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additives, of which comb polymers are mentioned but not specifically exemplified.

In a first aspect, the invention provides an additive composition comprising, in combination,

(i) a polymer containing the units:



where x is an integer and y is 0 or an integer and wherein, in the polymer, the sum of x and y is at least two, the ratio of units (II) to units (I) is between 0 and 2, and the ratio of units (II) to (III) is between 0 and 2 and wherein:

R¹ and R² are the same or different, each representing a C₁₀ to C₃₀ alkyl,

R³ represents H, -OOCR⁶, C₁ to C₃₀ alkyl, -COOR⁶, -OR⁶, an aryl or alkaryl group or halogen,

R⁴ represents H or methyl,

R⁵ represents H, C₁ to C₃₀ alkyl, or -COOR⁶.

R⁶ represents C₁ to C₂₂ alkyl,

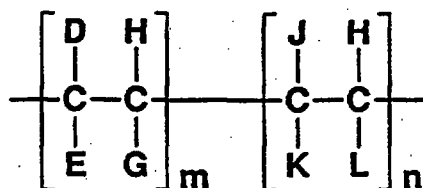
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optionally, each of the groups R^1 , R^2 , R^3 , R^4 , R^5 and R^6 being inertly substituted, and

- (ii) a comb polymer having, from a polymer backbone, aryl groups and hydrocarbyl groups, which hydrocarbyl groups contain 10 or more carbon atoms. Preferably, component (ii) is a polymer of the general formula:



where

D = R^7 , $C(O).OR$, $OC(O).R^7$, $R^8C(O).OR^7$ or OR^7

E = H or CH_3 or D or R^8

G = H, or D

m = 1.0 (homopolymer) to 0.4 (mole ratio)

J = H, R^8 , aryl or heterocyclic group, $R^8CO. OR^7$

K = H, $C(O).OR^8$, $OC(O).R^8$, OR^8 , $C(O)OH$

L = H, R^8 , $C(O).OR^8$, $OC(O).R^8$, Aryl, $C(O)OH$

n = 0 to 0.6 (mole ratio)

R^7 is a hydrocarbyl group containing 10 or more carbon atoms

R^8 is a C_1 or higher hydrocarbyl group,

provided that at least one of J and L is an aryl group.

Advantageously, R^7 has from 10 to 30 carbon atoms and R^8 has from 1 to 30 carbon atoms.

In a second aspect, the invention provides the use as a flow improver in a crude oil, lubricating oil or fuel oil or as a dewaxing acid in a lubricating oil of an additive composition of the first aspect of this invention.

In a third aspect, the invention provides a crude oil, lubricating oil or fuel oil composition comprising a major proportion by weight of a crude oil, lubricating oil or fuel oil and a minor proportion by weight of an additive composition of the first aspect of this invention.



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In a fourth aspect, the invention provides an additive concentrate comprising an admixture of an additive composition of the first aspect of this invention dispersed in a liquid medium compatible with a crude oil, lubricating oil or fuel oil.

In a fifth aspect, the invention provides a process for improving the flow properties of a crude oil, lubricating oil or fuel oil or for aiding dewaxing of a lubricating oil which comprises incorporating into the oil an additive composition of the first aspect of this invention.

The individual features of the invention will now be described in further detail.

COMPONENT (i)

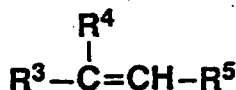
Polymer (i) may be a homopolymer of a dialkyl itaconate or citraconate or a copolymer of a dialkyl itaconate or citraconate with an aliphatic olefin, a vinyl ether, a vinyl ester of an alkanolic acid, an alkyl ester of an unsaturated acid, an aromatic olefin, a vinyl halide or a dialkyl fumarate or maleate; or polymer (i) may be a copolymer of dialkyl itaconate or dialkyl citraconate with an aliphatic olefin, a vinyl ester or an alkyl substituted vinyl ester of a C₂ to C₃₁ alkanolic acid.

R¹ and R² are each preferably straight chain although they can be branched. If branched, the branch is preferably a single methyl in the 1 or 2 position.

Examples of R¹ and R² are decyl, dodecyl, hexadecyl and eicosyl. Each of R¹

and R² may be a single C₁₀ to C₃₀ alkyl group or a mixture of alkyl groups. Polymers where R¹ and R² are each mixtures of C₁₂ to C₂₀ alkyl groups are particularly useful as flow improvers in middle distillate fuel oils. Polymers where R¹ and R² are each C₁₆ to C₂₂ are particularly useful in heavy fuel oils and crude oils, and polymers where R¹ and R² are each C₁₀ to C₁₈ are particularly useful in lubricating oils. Such particularly useful polymers may be homopolymers or copolymers.

The dialkyl itaconate or dialkyl citraconate, when a comonomer, has the formula:





where R^3 , R^4 and R^5 are as defined above. Such a comonomer can be a mixture.

When such a comonomer is an aliphatic olefin, R^3 and R^5 represent hydrogen or C_1 to C_{30} alkyl groups, preferably n-alkyl groups, that are the same or different. Thus, when each of R^3 , R^4 and R^5 is hydrogen, the olefin is ethylene, and, when R^3 is methyl, and R^4 and R^5 are hydrogen, the olefin is n-propylene. When R^3 is an alkyl group, R^4 and R^5 are preferably hydrogen. Examples of other suitable olefins are butene-1, butene-2, isobutylene, pentene-1, hexene-1, tetradecene-1, hexadecene-1 and octadecene-1 and mixtures thereof.

Other such comonomers are vinyl esters or alkyl substituted vinyl esters of C_2 to C_{31} alkanolic acids: in vinyl esters when R^3 is R^6COO- , R^4 is H and R^5 is H, and in alkyl substituted vinyl esters when R^3 is R^6COO- and R^4 is methyl and/or R^5 is C_1 to C_{30} alkyl. Un-substituted vinyl esters are preferred, examples being vinyl acetate, vinyl propionate, vinyl butyrate, vinyl decanoate, vinyl hexadecanoate and vinyl stearate.

Another class of comonomers are the alkyl esters of unsaturated acids, i.e. when R^3 is a R^6OOC- and R^5 is H or C_1 to C_{30} alkyl. When R^4 and R^5 are hydrogen, the comonomers are alkyl esters of acrylic acid. When R^4 is methyl, the comonomers are esters of methacrylic acid or C_1 to C_{30} alkyl substituted methacrylic acid. Examples of alkyl esters of acrylic acid are methyl acrylate, n-hexyl acrylate, n-decyl acrylate, n-hexadecyl acrylate, n-octadecyl acrylate, and 2-methyl hexadecyl acrylate. Examples of alkyl esters of methacrylic acid are propyl methacrylate, n-butyl methacrylate, n-octyl methacrylate, n-tetradecyl methacrylate, n-hexadecyl methacrylate and n-octadecyl methacrylate. Other examples are the corresponding esters where R^5 is alkyl, e.g. methyl, ethyl, n-hexyl, n-decyl, n-tetradecyl and n-hexadecyl.

Another class of comonomers is that where both R^3 and R^5 are R^6OOC- , i.e. when they are C_1 to C_{22} dialkyl fumarates or maleates and the alkyl groups may be n-alkyl or branched alkyl, e.g. n-octyl, n-decyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Other examples of comonomer are those where R^3 is an aryl group. When R^4 and R^5 are hydrogen and R^3 is phenyl the comonomer is styrene and when one

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of R^4 and R^5 is methyl and comonomer is a methyl styrene, e.g. α -methyl styrene. Another example when R^3 is aryl is vinyl naphthalene. Other examples when R^3 is alkaryl are, for example, substituted styrenes such as vinyl toluene, or 4-methyl styrene.

5 Another comonomer is that where R^3 is halogen, e.g. chlorine, such as vinyl chloride (i.e. R^4 and R^5 hydrogen).

10 As stated, some or all of the groups R^1 , R^2 , R^3 , R^4 , R^5 and R^6 can be inertly substituted; examples are by one or more halogen atoms such as chlorine or fluorine. For example, the comonomer may be vinyl trichloroacetate. Alternatively, the inert substituent may be an alkyl group, e.g. methyl.

15 When the ratio of units (II) to units (I) and of units (II) to (III) is 0 the polymer is an itaconate or citraconate homopolymer and when the ratio is 2 the polymer is a copolymer. The ratio is preferably between 0.5 and 1.5. Usually the copolymer consists of units (I) and (II) only, or of units (II) and (III) only, but other units are not excluded. However, the weight percentage of units (I) and (II) or of units (II) and (III) in the copolymer is desirably at least 60%, preferably at least 70%.

20 The molecular weight of the polymer of component (i), whether a homopolymer or copolymer, may be between 1,000 and 500,000, preferably 1,000 and 20,000, more preferably between 1,000 and 10,000, even more preferably between 2,200 and 5,000, the molecular weights being measured by gel permeation chromatography (GPC) relative to polystyrene standards and being number average molecular weights.

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The homopolymers and copolymers are generally prepared by polymerising the monomers alone or in solution in a 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 by a peroxide or azo type catalyst such as benzoyl peroxide or azodiisobutyronitrile under a blanket of an inert gas such as nitrogen or carbon dioxide in order to exclude oxygen. The polymer may be prepared under pressure in an autoclave or by refluxing.

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To prepare copolymers, the polymerisation reaction mixture may contain up to 2 moles of comonomer (e.g. vinyl acetate) per mole of dialkyl itaconate or dialkyl citraconate.

5 In the practice of the invention, more than one components (i) may be used.

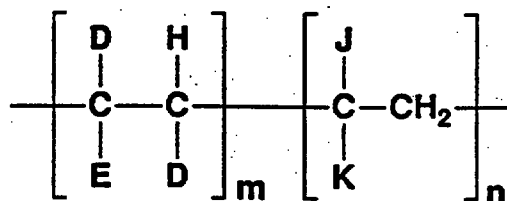
The ratio of component (i) to component (ii) may, for example, be in the range of 10:1 to 1:10 (weight:weight).

10 COMPONENT (ii)

Comb polymers are intermediate in structure between linear and branched polymers and have long aliphatic side chains from a polymer backbone such as a polymethylene backbone which may or may not be interrupted. They are
15 described in, for example, "Comb-like Polymers, Structure and Properties" by N.A. Platé and V.P. Shibaev, J. Polymer Science: Macromolecular Reviews Vol. 8, pps. 117-253 (1974) - John Wiley and Son.

"Hydrocarbyl" means a group containing hydrogen and carbon such as an
20 aliphatic group and which may be interrupted by one or more hetero atoms such as O, N, S insufficient to alter the hydrocarbyl nature of the group.

Preferably, the polymer is of the general formula



25 wherein D, E, K, m and n are defined as above, and J is an aryl group which may be unsubstituted or substituted.

30 More specifically, component (ii) is preferably a copolymer of the monomers (a) and (b) where

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- (a) is an ester, being a mono- or di-alkyl fumarate, maleate, itaconate, citraconate, mesaconate, trans- or cis-glutaconate, in which the alkyl group has 8 to 23 carbon atoms, and
- 5 (b) is an aromatic substituted olefin having 8 to 40 carbon atoms per molecule, for example of the formula Ar-CH=CH_2 where Ar is the aromatic substituent.
- (a) is preferably a dialkyl ester, e.g. fumarate, but mono-alkyl esters, e.g. fumarates, are suitable. The alkyl group is preferably straight chain although, if
10 desired, branched chain alkyl groups can be used. Examples of suitable alkyl groups are decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, behenyl or mixtures thereof. Preferably, the alkyl group contains 10 to 18 carbon atoms, such as 10 to 14 carbon atoms. Where the ester is a dialkyl ester such as a
15 dialkyl fumarate the two alkyl groups can be different.

In (b), the aromatic substituent is preferably a phenyl substituent, particularly preferred monomers being styrene, and α - and β -alkyl styrenes such as α -methyl styrene and β -methyl styrene, which may be substituted on the
20 benzene ring, e.g. with one or more alkyl groups or halogen atoms. Such alkyl substituents may, for example, have 1 to 20 carbon atoms.

The molar proportions of (b) to (a) may, for example, be between 1:1.5 and 1.5:1, preferably between 1:1.2 and 1.2:1, e.g. about 1:1. The number average
25 molecular weight of the copolymer of (a) and (b) may be between 2,000 and 100,000, preferably between 5,000 and 50,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standard.

Preferred examples of the component (ii) are styrene-maleate copolymers or
30 styrene-fumarate copolymers, it being preferred to use them in this invention in combination with polyitaconates of number average molecular weight between 1,000 and 20,000 as component (i).

In the practice of this invention, more than one component (ii) may be used.



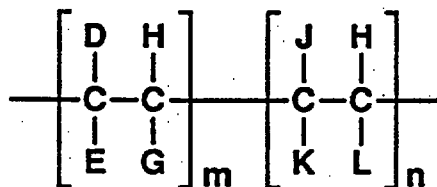
OTHER COLD FLOW IMPROVERS

The additive composition of the invention may be used in combination with one or more other Cold Flow Improvers as co-additives such as those known in the art. Examples are comb polymers other than those constituting component (i) or component (ii); polyoxyalkylene esters, ethers, ester/ethers, amide/esters and mixtures thereof; ethylene unsaturated ester copolymers; polar compounds, either ionic or non-ionic (such as described in EP-A-0 225 688); sulphur carboxy compounds and hydrocarbon polymers.

The other cold flow improvers will now be described in further detail as follows:

COMB POLYMERS

Examples are those having the general formula



- where
- D = R, CO.OR, OCO.R, R¹CO.OR or OR
 - E = H or CH₃ or D or R¹
 - G = H, or D
 - m = 1.0 (homopolymer) to 0.4 (mole ratio)
 - J = H, R¹, Aryl or Heterocyclic group, or R¹CO.OR
 - K = H, CO.OR¹, OCO.R¹, OR¹ or CO₂H
 - L = H, R¹, CO.OR¹, OCO.R¹, Aryl or CO₂H
 - n = 0.0 to 0.6 (mole ratio)
 - R ≥ C₁₀
 - R¹ ≥ C₁

Another monomer may be terpolymerized if necessary.

Examples of suitable comb polymers are fumarate/vinyl acetate copolymers, particularly those described in European Patent Applications 0153176 and 0153177; esterified olefin/maleic anhydride copolymers; polymers and copolymers of alpha olefin/maleic anhydride copolymers; polymers and

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copolymers of alpha olefins; esterified copolymers of styrene and maleic anhydride; and polymers of alkyl esters of itaconic acid or citraconic acid such as those where the alkyl groups have from 16 to 18 carbon atoms and the polymer has a number average molecular weight of from 1,000 to 20,000..

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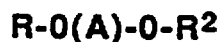
POLYOXYALKYLENE COMPOUNDS

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Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two C₁₀ to C₃₀ linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular weight up 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 0 061 895 A2. Other such additives are described in United States Patent 4 491 455.

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The preferred esters, ethers or ester/ethers which may be used may be structurally depicted by the formula



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where R and R² are the same or different and may be

(a) n-alkyl;

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(b) $n\text{-alkyl}-\overset{\text{O}}{\parallel}{\text{C}}$

(c) $n\text{-alkyl}-O-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_n-$

(d) $n\text{-alkyl}-O-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_n-\overset{\text{O}}{\parallel}{\text{C}}-$

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n being, for example, 1 to 30, the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyalkylene 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 that the glycol should be substantially linear. A may also contain nitrogen.

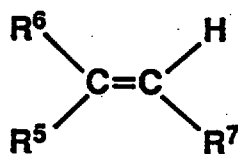
Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C₁₈-C₂₄ fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for additive performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Examples of other compounds in this general category are those described in Japanese Patent Publication Nos 2-51477 and 3-34790 (both Sanyo), and EP-A-117,108 and EP-A-326,356 (both Nippon Oil and Fats).

ETHYLENE/UNSATURATED ESTER COPOLYMERS

Examples are one or more oil-soluble copolymers of ethylene and an unsaturated monomer of the general formula



wherein R⁶ is hydrogen or methyl, R⁵ is a -OOCR⁸ group

wherein R⁸ is a hydrogen formate or a C₁ to C₂₈, more usually C₁ to C₁₇, and preferably a C₁ to C₈, straight or branched chain alkyl group; or R⁵ is a -COOR⁸ group



wherein R^8 is as previously described but is not hydrogen and R^7 is hydrogen or $-COOR^8$ as previously defined

The monomer, when R^6 and R^7 are hydrogen and R^5 is $-OOCR^8$, includes vinyl alcohol esters of C_1 to C_{29} , more usually C_1 to C_5 , mono-carboxylic acid, and preferably C_2 to C_{29} , more usually C_1 to C_5 mono-carboxylic acid, and preferably C_2 to C_5 mono-carboxylic acid. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. It is preferred that these copolymers have a number average molecular weight as measured by vapour phase osmometry of 1,000 to 10,000, preferably 1,000 to 5,000. If desired, the copolymer may be derived from additional comonomers, e.g. it may be a terpolymer or tetrapolymer or higher, for example where the additional comonomer is an iso-olefin such as di-isobutylene.

POLAR ORGANIC, NITROGEN-CONTAINING COMPOUNDS

Examples comprise one or more of the compounds (a) to (c) below.

- (a) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride;

Ester/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US Patent 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 contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8 to C_{40} , preferably C_{14} to C_{24} 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, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl. Amine mixtures are also suitable



such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine of the formula HNR^1R^2 where in 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 and their anhydrides for preparing the nitrogen compounds include cyclohexane, 1,2 dicarboxylic acid, cyclohexene 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid. Generally, these acids 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, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

Other examples are condensates such as described in EP-A-327,423.

- (b) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R^1 and R^2 are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof;

Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

"Hydrocarbyl" in this specification means an organic moiety composed of hydrogen and carbon which, unless the context states otherwise, may be

aliphatic, including alicyclic; aromatic; or any combination thereof. It may be substituted or unsubstituted alkyl, aryl or aralkyl and may optionally contain unsaturation. Examples where it is substituted are oxy-, halogeno- and hydroxy-hydrocarbyl.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

Examples of such polycyclic assemblies include

- condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;
- condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene;
- rings joined "end-on" such as diphenyl;
- heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine;
- non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene), a-pinene, cardinene, and bornylene; and



- three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

Each hydrocarbyl group constituting R¹ and R² in the invention (Formula I) may for example be an alkyl or alkylene group or a mono- or poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with two only substituents of the general formula (I) and that A is a methylene group.

Examples of salts of the chemical compounds are the acetate and the hydrochloride.

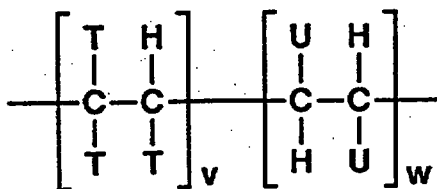
The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride.

- (c) a condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanoloamines such as described in US-A-4,639,256; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

30 HYDROCARBON POLYMERS

Examples are those represented by the following general formula



where T = H or R¹
U = H, T or Aryl
v = 1.0 to 0.0 (mole ratio)
w = 0.0 to 1.0 (mole ratio)

where R¹ is alkyl.

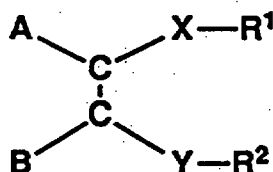
These polymers may be made directly from ethylenically unsaturated monomers or indirectly by hydrogenating the polymer made from monomers such as isoprene, butadiene etc.

A particularly preferred hydrocarbon polymer is a copolymer of ethylene and propylene having an ethylene content preferably between 20 and 60% (w/w) and is commonly made via homogeneous catalysts.

Examples of hydrocarbon polymers are described in WO-A-9111488.

SULPHUR CARBOXY COMPOUNDS

Examples are those described in EP-A-0,261,957 which describes the use of compounds of the general formula



in which -Y-R² is SO₃⁽⁻⁾⁽⁺⁾NR₃³R², -SO₃⁽⁻⁾⁽⁺⁾HNR₃³R²,

-SO₃⁽⁻⁾⁽⁺⁾H₂NR₃³R², -SO₃⁽⁻⁾⁽⁺⁾H₃NR²,

-SO₂NR₃³R² or -SO₃R²;

-X-R¹ is -Y-R² or -CONR₃³R¹,

-CO₂⁽⁻⁾⁽⁺⁾NR₃³R¹, -CO₂⁽⁻⁾⁽⁺⁾HNR₃³R¹,

-R⁴-COOR₁, -NR₃³COR¹,

-R⁴OR¹, -R⁴OCOR¹, -R⁴,R¹,

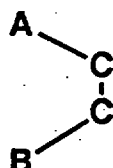
-N(COR₃³)R¹ or Z⁽⁻⁾⁽⁺⁾NR₃³R¹;

-Z⁽⁻⁾ is SO₃⁽⁻⁾ or -CO₂⁽⁻⁾;



R¹ and R² are alkyl, alkoxy alkyl or polyalkoxy alkyl containing at least 10 carbon atoms in the main chain;

5 R³ is hydrocarbyl and each R³ may be the same or different and R⁴ is nothing or is C₁ to C₅ alkylene and in



10 the carbon-carbon (C-C) bond is either a) ethylenically unsaturated when A and B may be alkyl, alkenyl or substituted hydrocarbyl groups or b) part of a cyclic

structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic, it is preferred that X-R¹ and Y-R² between them contain at least three alkyl, alkoxyalkyl or polyalkoxyalkyl groups.

15

Multicomponent additive systems may be used and the ratios of additives to be used will depend on the oil to be treated.

OIL AND FUEL OIL

20

The oil may be a crude oil, i.e. an oil as obtained from drilling and before refining, when the inventive composition may be used as a flow improver or dewaxing aid.

25

The oil may be a lubricating oil which may be an animal, vegetable or mineral oil, for example petroleum oil fractions ranging from naphthas or spindle oil to lubricating oil grades, castor oil, fish oils or oxidised mineral oil. The additive composition of the invention may be used as a flow improver, pour point depressant or dewaxing aid in lubricating oils. Other additives may be present

30

in a final lubricating oil, examples being viscosity index improvers such as ethylene-propylene copolymers, succinic acid based dispersants, metal containing dispersant additives and zinc dialkyl-dithiophosphate antiwear additives.





Examples of fuel oils are middle distillate fuel oils, i.e. fuels obtained in refining crude oil as the fraction between the lighter kerosene and jet fuels fraction and the heavy fuel oil fraction. Examples are diesel fuel, aviation fuel, kerosene, fuel oil, jet fuel and heating oil etc. Generally, suitable 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 360°C. The fuel oil may be an animal, vegetable or mineral oil. The fuel oil may also contain other additives such as stabilisers, dispersants, antioxidants, corrosion inhibitors and/or demulsifiers.

Heating oils may be made of a blend of virgin distillate, e.g. gas oil, naphtha, etc and cracked distillates, e.g. catalytic cycle stock. A representative specification for a diesel fuel includes a minimum flash point of 38°C and a 90% distillation point between 282 and 338°C (see ASTM Designations D-396 and D-975).

The total amount of additive composition provided in the fuel in this invention is preferably 0.0001 to 5.0 wt%, for example 0.001 to 0.5 wt% (active matter), based on the weight of fuel.

Where the invention is a concentrate, the additive composition may form from 20 to 90, e.g. 30 to 80 wt% thereof. Examples of liquid carriers for use in a concentrate are solvents such as kerosene, aromatic naphthas and mineral lubricating oils.

EXAMPLES

The invention will now be particularly described, by way of example only, as follows. The examples include comparative examples in addition to examples of the invention as will be indicated. $\bar{M}_n$ means number average molecular weight as measured by GPC relative to polystyrene standards.

ADDITIVES

The additives used were as follows, designated by the indicated code letters.

A: For tests on Fuels I and II (see below), A was a mixture of two ethylene/vinyl acetate copolymers: a copolymer of $\bar{M}_n$ 2500 containing

36.5 wt% vinyl acetate and containing 3-4 methyl groups per 100 methylene groups, and a copolymer of $\bar{M}_n$ 5000 containing 13.5 wt% vinyl acetate and containing 6 methyl groups per 100 methylene groups, the ratio of the two copolymers being 93:7 (weight:weight); for tests on the remaining fuels (see below), A was an ethylene/vinyl acetate copolymer of $\bar{M}_n$ 3000 containing 29.0 wt% vinyl acetate and containing 4 methyl groups per 100 methylene groups.

B: the reaction product of one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt.

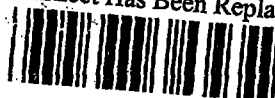
D: a homopolymer of an ester of itaconic acid whose linear alkyl groups have 16 carbon atoms made by polymerising the monomer using a free radical catalyst, the homopolymer having an $\bar{M}_n$ of 3,500.

G-K: a group of styrene/fumarate copolymers whose alkyl groups have the following number of carbon atoms and a number average molecular weight of 15,000 to 30,000,

G	10
H	10-12
I	12
J	12-14
K	14

FUELS

The test fuels used were Fuels I to VI whose characteristics are listed in Diagram 1 below, all temperatures being in °C.



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Diagram 1

FUEL

Fuel Properties	I	II	III	IV	V	VI
Cloud Point	-6	-5	-6	-7	-2	+3
Base CFPP	-8	-8	-9	-7	-4	0
D-86 IBP	166	168	135	136	178	179
20%	231	248	213	200	261	257
50%	276	279	277	248	291	293
90%	325	327	332	329	341	350
FBP	348	358	361	364	368	373
Test Temperature:	-17	-15	-17	-17	-15	-9

5

GENERAL PROCEDURE

10 An additive (which includes a combination of individual additive components as identified by juxtaposition of additive code letters in the results hereinafter) was added to a test diesel fuel (I to VI) by standard methods at an additive concentration of 200 ppm (active ingredient) for A, 200 ppm (active ingredient) for B, and 200 ppm (active ingredient) for each of the other additive components where used. The following tests were then carried out on the so-treated fuel.

15 THE COLD FILTER PLUGGING POINT TEST (OR CFPP TEST)

20 The test which is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285, is designed to correlate with the cold flow of a middle distillate in automotive 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 centigrade starting from above the cloud point),

the cooled oil 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 screen 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, the temperature at which failure occurs being reported as the CFPP temperature.

WAX ANTI-SETTLING (WAS) TEST

The extent of the settled layer (WAS) was visually measured as a percentage of the total fuel volume by leaving the treated fuel in a measuring flask. Extensive wax settling would be indicated by a low number whilst an unsettled fluid fuel would be indicated by 100%. Poor samples of gelled fuel with large wax crystals almost always exhibit high values; such results are therefore recorded as "gel" where they occur.

DETERMINATION OF CRYSTAL SIZE

The wax crystal average particle size was measured by analysing an Optical Micrograph of a fuel sample and measuring the longest axis of up to 50 crystals over a predetermined grid.

RESULTS

Additives, or combinations thereof, were tested in each of the Fuels I-VI. The results for CFPP, WAS and Crystal Size are shown in each of the following three tables, designated TABLES 1, 2 and 3 respectively where the following explanations are to be noted:

TABLE 1 (CFPP): all results are in °C below 0°C, i.e. negative values.



TABLE 2 (WAS):

all results are percentage dispersed, 100 being fully dispersed and the observations being taken after 2 to 3 hours at the test temperature.

5 TABLE 3 (Crystal Size):

all values are on a scale of 1 to 10 where

10 is	< 10 microns
9 is	10 microns
8 is	10-20 microns
7 is	20-50 microns
6 is	50-100 microns
5 is	100-200 microns
4 is	200-300 microns
3 is	300-500 microns
2 is	500-700 microns
1 is	>700 microns

The following general conclusions can be drawn from the results shown in TABLES 1-3:

- Additive AB (comparison example) gave good overall CFPP performance but inconsistent WAS and Crystal Size performance.
- Additive ABD (comparison example) gave good WAS and Crystal Size performance but regression in CFPP performance.
- the above regression was remedied, at least partly, by any of additives G-K in combination with ABD.



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Table 1 (CFPP)

FUEL

Additive	I	II	III	IV	V	VI	Average
AB	13	19	20	14	18	13	16.2
ABD	8	18	15	16	7	3	11.2
ABDG	11	19	17	15	15	7	14
ABDH	11	18	19	15	14	7	14
ABDI	11	18	20	15	14	10	14.7
ABDJ	10	17	20	16	15	9	14.5
ABDK	11	15	16	17	13	10	13.7

5

Table 2 (WAS)

FUEL

Additive	I	II	III	IV	V	VI	Total
AB	70	80	10	15	80	40	49.2
ABD	100	100	80	100	75	100	92.5
ABDG	95	40	100	100	100	20	75.8
ABDH	95	50	100	100	100	20	77.5
ABDI	95	50	100	100	100	20	77.5
ABDJ	95	50	95	100	100	80	86.7
ABDK	95	100	15	100	100	90	88.3

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Table 3 (Crystal Size)

Additive	FUEL						Average
	I	II	III	IV	V	VI	
AB	6	9	9	9	6	6	7.5
ABD	6	9	10	10	9	8	8.7
ABDG	6	9	10	10	7	6	8
ABDH	6	9	10	10	7	5	7.8
ABDI	6	9	10	10	7	6	8
ABDJ	6	9	10	10	9	5	8.2
ABDK	6	9	6	10	9	7	7.8

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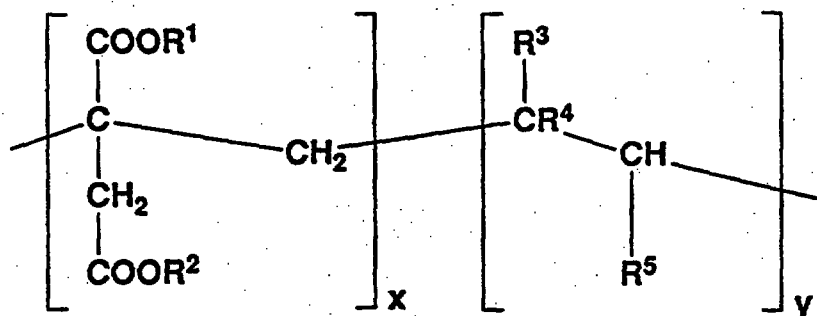
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Claims:

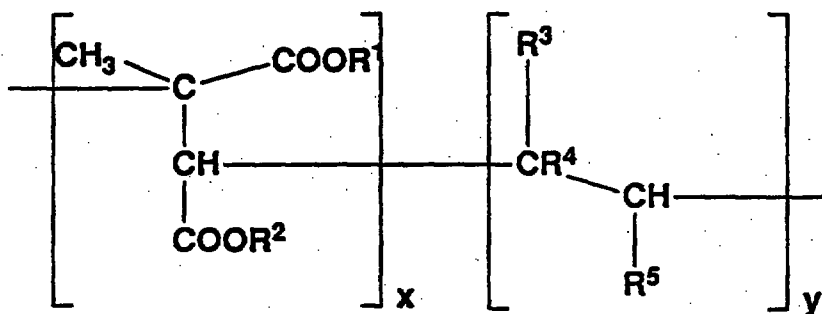
1. An additive composition comprising, in combination,

(i) a polymer containing the units:



(I)

(II)



(III)

(II)

or

where x is an integer and y is 0 or an integer and wherein, in the polymer, the sum of x and y is at least two, the ratio of units (II) to units (I) is between 0 and 2, and the ratio of units (II) to (III) is between 0 and 2 and wherein:

R¹ and R² are the same or different, each representing a C₁₀ to C₃₀ alkyl group,

R³ represents H, -OOCR⁶, C₁ to C₃₀ alkyl, -COOR⁶, -OR⁶, an aryl or alkaryl group or halogen,

R⁴ represents H or methyl,

R⁵ represents H, C₁ to C₃₀ alkyl, or -COOR⁶.

R⁶ represents C₁ to C₂₂ alkyl

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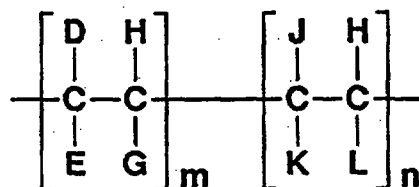
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optionally, each of the groups R¹, R², R³, R⁴, R⁵ and R⁶ being inertly substituted, and

- (ii) a comb polymer, having from a polymer backbone, aryl groups and hydrocarbyl groups, which hydrocarbyl groups contain 10 or more carbon atoms.

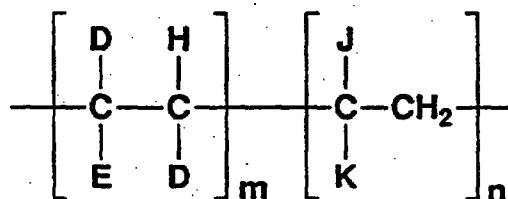
2. A composition of claim 1 wherein component (ii) has the general formula:



- where
- D = R⁷, C(O).OR, OC(O).R⁷, R⁸C(O).OR⁷ or OR⁷
 - E = H or CH₃ or D or R⁸
 - G = H, or D
 - m = 1.0 (homopolymer) to 0.4 (mole ratio)
 - J = H, R⁸, aryl or heterocyclic group, R⁸CO.OR⁷
 - K = H, C(O).OR⁸, OC(O).R⁸, OR⁸, C(O)OH
 - L = H, R⁸, C(O).OR⁸, OC(O).R⁸, Aryl, C(O)OH
 - n = 0 to 0.6 (mole ratio)
 - R⁷ is a hydrocarbyl group containing 10 or more carbon atoms
 - R⁸ is a C₁ or higher hydrocarbyl group,

provided that at least one of J and L is an aryl group.

3. The composition of claim 1 or claim 2 wherein the polymer as defined in (ii) is of the general formula



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wherein D, E, K, m and n are defined as in claim 2 and J is a substituted or unsubstituted aryl group.

4. The composition of claim 3 wherein the polymer is a styrene-maleate copolymer or a styrene-fumarate copolymer.

5. The composition of claim 4 wherein the maleate or fumarate have alkyl groups containing 10 to 18 carbon atoms.

6. The composition of any of the preceding claims wherein the composition contains, in combination, another low temperature flow improver for distillate fuels.

7. The composition of any of the preceding claims wherein the polymer as defined in (i) is a homopolymer of a dialkyl itaconate or a dialkyl citraconate or is a copolymer of a dialkyl itaconate or a dialkyl citraconate with an aliphatic olefin, a vinyl ether, a vinyl ester of an alkanolic acid, an alkyl ester of an unsaturated acid, an aromatic olefin, a vinyl halide, a dialkyl fumarate, or a dialkyl maleate.

8. The composition of any of the preceding claims wherein one or both of the polymers as defined in (i) and (ii) has a number average molecular weight in the range of 1,000 to 50,000.

9. The composition of claim 8 wherein the range is 1,000 to 20,000.

10. A crude oil, lubricating oil or fuel oil composition comprising a major proportion by weight of a crude oil, lubricating oil or fuel oil and a minor proportion by weight of an additive composition of any of the preceding claims.

11. An additive concentrate comprising an admixture of a composition of any of claims 1 to 9 dispersed in a liquid medium compatible with a crude oil, lubricating oil or fuel oil.

12. The use as a flow improver in a crude oil, lubricating oil or fuel oil or as a dewaxing aid of an additive composition of any of claims 1 to 9.

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13. The use or oil composition of claim 10 or claim 12 wherein the oil is a middle distillate fuel oil.
14. A process for improving the flow properties of a crude oil, lubricating oil or fuel oil or for aiding dewaxing of a lubricating oil which comprises incorporating into the oil an additive composition of any of to claims 1 to 9.

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