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(54) Improved fuel oil compositions.

(57) Sediment and colour formation is reduced in fuels containing more than 0.04 wt. % sulphur and 100 ppm nitrogen by the incorporation of small amounts of basic lithium, sodium, potassium or calcium compounds, this is particularly beneficial in fuels containing cracked components where the preferred additives are basic calcium or sodium compounds.

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Description

IMPROVED FUEL OIL COMPOSITIONS

The present invention relates to fuel oil compositions and to fuel oil compositions containing cracked components which are stabilised against sediment formation and colour development during storage.

When diesel and heating oils are stored at ambient or elevated temperatures in air they become discoloured and precipitate sludge or sediment. It has been proposed that such fuels may be improved by the addition of various amines (for example, NN-dimethylcyclohexylamine as proposed in Japanese Patent 44-12034) or certain alkaline earth metal compounds as proposed in Japanese Patent Publication 61-143492 which uses a range of neutral metal salts whilst suggesting basic salts obtained from excess metal may be used.

It is clear that the problem of discoloration and sediment formation is exacerbated by the presence of cracked components in the fuel. This is demonstrated by the results in Table 1 which show the amount of sediment formed and the colour change when various fuel blends are tested in the AMS 77.061 accelerated stability test. Published research (see, for example, Offenhauer et. al, Industrial and Engineering Chemistry, 1957, Volume 49, page 1265, and the Proceedings of the 2nd International Conference on the Long Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, published October 1986) suggests that discolouration and sediment results from the oxidation of sulphur and nitrogen compounds present in the fuel. The analysis of cracked components is consistent with this idea. The results in Table 2 show that cracked components contain significantly larger quantities of nitrogen and sulphur compared with straight distillates. Also, the addition of nitrogen and sulphur compounds to a stable straight distillate causes an increase in both sediment and colour in the AMS 77.061 test (Table 3); with the worst result being obtained when both the nitrogen and the sulphur compounds are present in the fuel.

We have found that sediment and colour formation can be substantially reduced in fuels containing more than 0.04 wt.% especially more than 0.30 wt.% sulphur and more than 100 ppm nitrogen by the incorporation of small amounts of basic lithium, sodium, potassium or calcium compound.

The present invention therefore provides a fuel composition with improved stability, characterised in that it contains fuel oil obtained by cracking of heavy oil and a basic oil-soluble lithium, sodium, potassium or calcium compounds.

The invention further provides the use of basic compounds of lithium, sodium, potassium or calcium as additives to improve the storage stability of a fuel containing more than 0.04 wt.% especially more than 0.30 wt.% of sulphur and more than 100 ppm nitrogen.

We have found that whilst basic compounds are effective in reducing the sediment forming in distillate fuel the stronger bases such as the calcium and sodium salts are also effective in improving the colour stability of the fuels and these are our preferred additives.

The basic metal containing compounds may be present, for example, as the metal salts of sulphonic acids, alkyl phenols, sulphurised alkyl phenols, thiophosphonates, alkyl salicylates, naphtenates and other oil-soluble mono- and di-carboxylic acids. The basicity being provided by a stoichiometric excess of metal oxide, hydroxide or carbonate. Mixtures of two or more of these metal salts may be used.

The following compounds or mixtures are useful as the acidic dispersing agent.

(I) Sulphonic acids

(1) Alkylbenzene-sulphonic acid or alkylnaphthalene-sulphonic acid

Benzene-sulphonic acids with straight-chain or branched single or multiple substituted alkyl radicals with 4-24 (preferably 80-20) carbon atoms in the aromatic nucleus, for example dodecylbenzene-sulphonic acid, dinonylbenzenesulphonic acid, dodecylnaphthalenesulphonic acid etc.

(2) Alkane-sulphonic acids

Sulphonic acids possessing straight-chain or branched alkyl radicals usually with 10-30 carbon atoms, for example tetradecyl sulphonic acid etc.

(3) Alkene-sulphonic acids

Sulphonic acids which have straight-chain or branched alkenyl radicals usually with 15-30 carbon atoms, for example 2-eicosenyl sulphonic acid etc.

The sulphonic acids are typically obtained by sulphonation of alkyl substituted aromatic hydrocarbons, such as those obtained from the fractionation of petroleum by distillation and/or extraction, or by the alkylation of aromatic hydrocarbon, for example, benzene, toluene, xylene, naphthalene, diphenyl. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 30 carbon atoms, such as, for example, haloparaffins, olefins that may be obtained by dehydrogenation of paraffins, polyolefins, or, for example, polymers of ethylene, propylene, butene, etc. The alkaryl sulphonates usually contain from about 9 to about 20 or more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moeity.

The metal compounds which may be used in neutralising these alkaryl sulphonic acids to provide the sulphonates include the oxides, hydroxides and alkoxides, for example, calcium hydroxide or magnesium oxide or sodium hydroxide. Hydrocarbon solvents and/or diluent oil might also be included as well as neutralisation promoters and viscosity control agents, such as formates and halides. These additional materials are particularly useful when an excess of metal base is used to give a slightly basic salt.

The highly basic metal sulphonates are usually produced by neutralising an alkaryl sulphonic acid with a large excess of metal base over that required for complete neutralisation and thereafter forming a dispersed carbonate complex by reacting the excess metal base with carbon dioxide to provide the desired overbasing.

The reaction mixture may include organic solvents, for example, toluene, xylene, hexane, chlorobenzene and other materials, for example, alcohols, water, amines, salts of organic or inorganic acids, which serve to promote the overbasing process, and diluent oil. Volatile materials and undispersed solids are removed in the final stages of the process. Processes which use a metal alkoxide as the starting metal compound can proceed by a somewhat different route in which carbonation of the alkoxide to give an alkoxide-carbonate complex is followed by hydrolysis of the complex to give the metal carbonate. These reactions may be carried out in the presence of alkaryl sulphonate, solvents and diluents.

(II) Phenols

(1) Monohydric phenols substituted at the hydrocarbon radical, with single or multiple aromatic nuclei (containing phenols and naphthols; as below)

(a) Alkylphenols

Phenols with single or multiple substituted alkyl radicals possessing straight or branched chains usually with 1-40 and preferably 4-24 carbon atoms in the aromatic nucleus, for example n-butylphenol, tert.-butylphenol, 2-ethylhexylphenol, octylphenol, nonylphenol, decylphenol, dodecylphenol, hexadecylphenol, eicosylphenol, dibutylphenol, dinonylphenol, 1-dodecyl-2-naphthol, 5,7-dibutyl-2-naphthol, 4,6-dioctyl-1-naphthol, cyclohexylphenol, di-tert.-butylcresol etc.

(b) Alkenylphenols

Phenols with single or multiple substituted alkenyl radicals possessing straight or branched chains usually with 6-40 carbon atoms in the aromatic nucleus, for example, oleylphenol, linoleylphenol, polyisobutenylphenol (molecular weight 350), 4-oleyl-1-naphthol etc.

(c) Arylphenols

Phenols with single or multiple substituted aryl radicals, aryl-alkyl radicals or alkylaryl radicals with 6-30 carbon atoms in the aromatic nucleus, for example styrenated phenol, phenylphenol, butylphenylphenol, nonylphenylphenol etc.

(d)

Monohydric phenols possessing hydrocarbon radicals or halogen, alkoxyl, amino, nitro, hydroxyl radicals and other substituent radicals in the aromatic nucleus, for example 2-chloro-4-hexylphenol, 4-methoxyl-2-hexylphenol, p-aminobenzylphenol, p-nitrophenylphenol etc.

(e)

Monohydric phenols in which the hydrocarbon radicals and aromatic nuclei of the phenols are connected via oxygen, sulphur, nitrogen etc. atoms, for example nonylphenyloxyphenol, benzyloxyphenol, nonylphenylthionophenol, octylbenzylaminophenol etc.

(2) Polyhydric phenols

(a) Hydrocarbon-substituted bisphenols

Bisphenols substituted with single or multiple hydrocarbon radicals possessing straight or branched chains usually with 1-30 (preferably 4-20) carbon atoms in the aromatic nucleus, for example dibutyl-bisphenol A, diisopropyl-bisphenol A, dinonyl-bisphenol S etc.

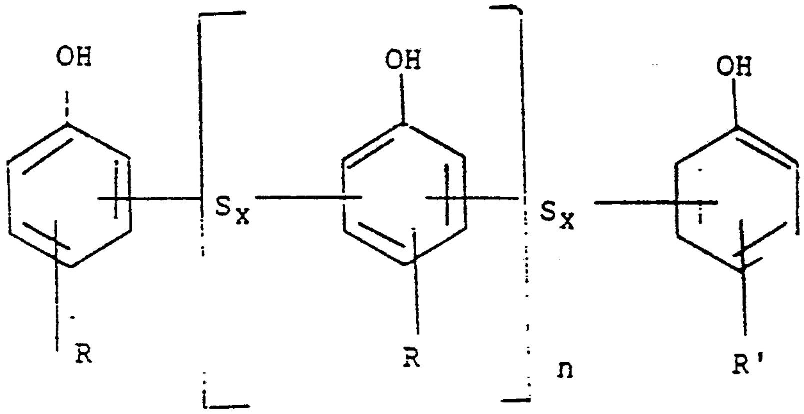
(b) Hydrocarbon-substituted polyhydric phenols

Polyhydric phenols with single or multiple substituted hydrocarbon radicals usually with 4-20 carbon atoms, with two or more substituent hydroxyl radicals per aromatic nucleus, for example nonylcatechol, tert.-butylresorcinol, octylhydroquinone etc.

Preferred among these phenols are the alkylphenols, with single or multiple substituted alkyl radicals possessing straight or branched chains usually with 1-40 and preferably 4-24 carbon atoms in the aromatic nucleus, for example n-butylphenol,

(3) Sulphurised Phenols

Sulphurised alkyl phenols have the general structure:



where R is an alkyl radical, n is an integer from 0 to 4 and x is an integer from 1 to 4. The average number of carbon atoms in all of the R groups is preferably at least about 9 in order to ensure adequate solubility in oil. The individual R groups may contain from 5 to 40, preferably 8 to 20 carbon atoms. Alkylation of phenol may be carried out with alkylating agents of the types used to alkylate aromatic hydrocarbons in the manufacture of alkaryl sulphonates. Sulphurisation may be by reaction of the alkyl phenol with sulphur chloride or by reaction with sulphur. In the latter case, the alkyl phenol is usually present as the metal salt, although other sulphurisation promoters may be used, such as amines.

Highly basic metal phenates may be made by methods similar to those used to prepare highly basic metal sulphonates.

Highly basic metal salicylates, naphthenates and thiophosphonates may also be used in lubricating compositions and may be prepared by methods similar to those used to prepare highly basic sulphonates and phenates.

(III) Carboxylic acids

(1) Monocarboxylic acids

(a) Aliphatic monocarboxylic acids

Aliphatic monocarboxlic acids possessing saturated or unsaturated straight or branched chains usually with 4-35 (preferably 6-28) carbon atoms, for example capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, eleostearic acid, 2-ethylhexanoic acid, isostearic acid, mixed fatty acids obtained from natural animal and vegetable oils (sperm-oil fatty acids, coconut-oil fatty acids, tall-oil fatty acids etc.) etc.

(b) Alicyclic monocarboxylic acids

Saturated or unsaturated alicyclic carboxylic acids usually with 6-40 carbon atoms, for example naphthenic acid (average molecular weight 280), hexahydrobenzoic acid etc.

(c) Aromatic monocarboxylic acids

Aromatic monocarboxylic acids with single or multiple substituted hydrocarbon radicals possessing saturated or unsaturated straight or branched chains usually with 1-35 (preferably 4-24) carbon atoms in the aromatic nucleus, for example P-octyl substituted benzoic acid, P-nonyl substituted benzoic acid, P-oleyl substituted benzoic acid, dibutylbenzoid acid, isopropyl salicylic acid etc.

(2) Polycarboxylic acids

(a) Aliphatic polycarboxylic acids

Aliphatic polycarboxylic acids possessing saturated or unsaturated straight or branched chains usually with 4-80 (preferably 6-50) carbon atoms, for example sebacic acid, azelaic acid, polymeric fatty acids (dimeric acid, trimeric acid etc.), alkenyl succinic acid (polyisobutenyl succinic acid etc.) etc. or the anhydrides of such polycarboxylic acids.

(b) Aromatic polycarboxylic acids

Aromatic polycarboxylic acids with single or multiple substituted hydrocarbon radicals possessing saturated or unsaturated straight or branched chains usually with 1-35 (preferably 4-24) carbon atoms in the aromatic nucleus, for example dodecyl-substituted phthalic acid etc.

Preferred among the carboxylic acids are the aliphatic monocarboxylic acids, and especially preferred are lauric acid, myristic acid, palmitic acid, stearic aid, oleic acid, linoleic acid, coconut-oil fatty acids, tall-oil fatty acids and mixtures of two or more of these. Also preferred are the alkenyl succinic acids, especially the polyisobutenyl succinic acids.

Preferred among these organic acids containing oil-soluble radicals are sulphurised phenols and sulphonic acids and polyisobutenyl succinic acids or anyhydrides.

The cracked component in the fuel oil which leads to the undesirable colour formation and sediment is generally obtained by cracking of heavy oil and may be fuel oil in which the main constituent is a fraction obtained from residue oil after removal of distillate oil by distillation or by thermal cracking treatment or catalytic treatment of heavy distillate oil obtained by distillation. The cracked component may then be distilled further by atmospheric or vacuum distillation (called cracked fraction hereinafter), or mixture of cracked fraction with a fraction obtained by direct ordinary-pressure distillation reduced-pressure distillation (called direct-distillation fraction hereinafter).

Typical methods available for the thermal cracking are visbreaking and delayed coking. Alternatively the fuels may be obtained by catalytic cracking, the principal methods being moving-bed cracking and fluidised-bed cracking. After cracking, the distillate oil is extracted by normal or vacuum distillation, the boiling point of the distillate oil obtained usually being 60-500°C, and is a fraction called light-cycle oil, preferably corresponding to the boiling point range of light oil of 150-400°C. The invention may be applied to composites composed entirely of this fuel or to fuels which are mixtures of the cracked fraction and normal distillates as main constituent.

The proportion by weight of direct-distillation fraction and cracked fraction in the fuel oil composition according to the present invention can vary considerably, but is usually 1 : 0.03 - 1 : 2 and preferably 1 : 0.05 - 1 : 1. Typically the content of cracked fraction is usually 5-97%, and preferably 10-50%, based on the weight of the composition.

The fuel oil compositions of the present invention may contain other additives such as antioxidants, anticorrosion agents, fluidity improvers, agents absorbing ultraviolet radiation, detergents, dispersants cetane improvers in small amounts (for example, usually less than 2% based on the weight of the composition).

The amount of oil-soluble alkali or alkaline earth metal compound added to the fuel according to the present invention, based on the weight of the composition, is usually 5-1000 ppm, preferably 10-500 ppm, and even more preferably 20-200 ppm.

The alkaline earth metal compounds may be added to the fuel oil directly, or may first be diluted in an appropriate diluent. As these compounds usually have fairly high viscosity, it is preferable to supply them as additive concentrates. Suitable diluents include common fuel oils, organic solvents readily miscible with petroleum-type fuel oils hydrocarbon mixtures normally used as lubricant basestocks, and mixtures of two or more of these. Preferred among these are xylene, toluene and similar aromatic solvents. The amount of diluent, per 1 part by weight of oil-soluble is usually 0.1-100 parts by weight, and preferably 0.2-20 parts by weight.

Examples

The present invention is illustrated by the following examples:

Table 1 shows the effect of blending different amounts of a straight distillate fuel with an unhydrofined catalytically cracked gas oil, on sediment and colour in the AMS 77.061 test.

Table 2 shows typical nitrogen and sulphur levels for straight run distillates and unhydrofined catalytically cracked gas oils.

Table 3 shows the effect of doping a stable fuel with compounds containing nitrogen and sulphur.

Table 4 shows the effect of adding 200 ppm of an amine, polyisobutenyl succinic anhydride/polyamine (PIBSA-PAM) dispersants and basic magnesium detergents on sediment and colour formed by a fuel containing 20% of cracked components according to the AMS 77.061 test. Comparison with the results for the untreated fuel shows that all the additives give good control of sediment but very little control of colour. In contrast as shown in Table 5, basic calcium and sodium additives give good control of both sediment and colour in the same fuel blend. Furthermore, as Table 6 shows, the calcium and sodium additives are effective at relatively low concentrations.

TABLE 1

Fuel 3* wt %	Fuel 4** (%)	Sediment (mgs/100 ccs)	ΔColour[a]
100	0	(0.14 ± 0.09)	≃0.5, < 0.5, < 0.5
80	20	(0.61 ± 0.13)	≃1.0, 1.0, 1.0, 1.0
60	40	(1.12 ± 0.10)	≃1.0, ≃1.0, ≃1.0, ≃1.0
40	60	(1.80 ± 0.04)	~2.0, ~2.0
20	80	(2.10 ± 0.10)	~2.0, ~2.0
0	100	2.90	~6.0

* Straight distillate

** Unhydrofined catalytically cracked gas oil (CCGO)

(a) Colour Change (ASTM D1500 test)

TABLE 2

The Nitrogen and Sulphur Contents of Various Fuels

Type of Fuel	Nitrogen (ppm)	Sulphur (%)
Unhydrofined CCGO	695	1.11
" "	650	1.70
Straight distillate	50	0.24
" "	70	0.25
" "	97	0.23
" "	128	0.24

TABLE 3

The Effect of Doping with Dimethyl Pyrrole (DMP) and a Sulphonic Acid (SA) on the Stability of a Straight Distillate Fuel in the AMS 77.061 Test

DMP (ppm)[a]	SA (ppm)[b]	Sediment (mgs/100 ccs)	Colour		
			Before	After	ΔC
NIL	Nil	0.06, 0.10	< 0.5	<1.0	0.5
Nil	50	0.02, 0.00	< 0.5	<1.5	1.0
			< 0.5	< 1.5	1.0
50	Nil	0.76, 0.59	< 0.5	< 1.0	0.5
			< 0.5	< 1.0	0.5
50	50	1,06, 1.01	< 1.5	< 3.0	1.5
			< 1.5	< 3.0	1.5

(a) 2,5-dimethylpyrrole

(b) a commercially available alkyl-aryl sulphonic acid having a SAN of approximately 80 mgs KOH/grm of acid

TABLE 4

The Effect of an Amine, PIBSA-PAM Dispersants and Magnesium Detergents on Sediment and Colour

Additive	Sediment (a)	Colour (b)
None	(0.61 ± 0.13)	~ 1.0,1.0,1.0,1.0
A mixture of an alkyl imidazoline dispersant and a Mannich condensation product available as NALCO 5300	(0.18 ± 0.19)	< 1.0,<1.0
Aliphatic Primary Amine	(0.09 ± 0.02)	~ 1.0,~1.0
PIBSA-PAM Dispersant	(0.06 ± 0.06)	< 1.0,~1.0
PIBSA-PAM Dispersant	(0.09 ± 0.12)	< 1.0,~1.0
400 TBN Overbased Mg Sulphonate	(0.00 ± 0.00)	> 1.0,>1.0
250 TBN Overbased Mg Phenate	(0.03 ± 0.04	~ 1.0,~1.0
Neutral Magnesium Sulphonate	(0.05 ± 0.06)	~ 1.0,~1.0
Magnesium PIBSATE	(0.13 ± 0.04)	~ 1.0, 1.0
Magnesium Salicylate	(0.00 ± 0.00)	~ 1.0,~1.5

(a) mgs/100 ccs of fuel

(b) colour change during test (ASTM D1500 colour)

TABLE 5

The Effect of Calcium and Sodium Detergents on Sediment and Colour

Additive	Sediment (a)	ΔColour (b)
Nil	(1.19 ± 0.12)	∼ 1.0 → ∼ 1.5
300 TBN Overbased Ca Sulphonate (100 ppm)	0.00	∼ 1.0
150 Ca Phenate (100 ppm)	0.00	∼ 0.0
250 TBN Overbased Ca Phenate (100 ppm)	0.07	∼ 0.5
400 TBN Overbased Na Sulphonate (80 ppm)	(0.9 ± 0.06)	∼ 0.5, ∼ 0.5
400 TBN Overbased Na Phenate (100 ppm)	0.00	< 1.0
100 TBN Neutral Na Phenate (100 ppm)	(0.00 ± 0.00)	∼ 1.0, > 0.5

(c) mgs/100 ccs of fuel

(d) Colour change during test (ASTM D1500 colour)

TABLE 6

The Effect of Additive Concentration on Sediment and Colour Formed

Concentration (ppm)	Additive							
	300 TBN Calcium Sulphonate		150 TBN Calcium Phenate		250 TBN Calcium Phenate		400 TBN Sodium Sulphonate	
	Sediment(a)	ΔC(b)	Sediment(a)	ΔC(b)	Sediment(a)	ΔC(b)	Sediment (a)	ΔC(b)
0	$\Delta C = \sim 1.0 \dashrightarrow \sim 1.5$; Sediment = 1.19 ± 0.12 mgs/100 ccs							
20	0.83	~ 1.0	0.19	~ 1.0	0.31	~ 0.5	—	—
40	0.19	~ 1.0	0.11	~ 0.5	0.31	~ 0.5	(0.04±0.05)	0.5,0.5
60	0.13	~ 1.0	0.09	~ 0.5	0.00	~ 0.5	—	—
80	0.00	~ 1.0	0.00	~ 0.5	0.00	~ 0.5	(0.09±0.06)	0.5,0.5
100	0.00	~ 1.0	0.00	~ 0.0	0.07	~ 0.5	—	—

(a) mgs/100 ccs of fuel

(b) Colour change during the test

Claims

1. A fuel composition with improved stability, characterised in that it contains fuel oil obtained by cracking of heavy oil and a basic oil-soluble lithium, potassium, sodium or calcium compound.

2. A fuel composition according to claim 1 containing more that 0.04 wt.% sulphur and 100 ppm nitrogen.

3. A fuel oil according to claim 1 or claim 2 containing more than 0.30 wt.% sulphur.

4. A fuel composition according to any of the preceding claims containing from 1:0.03 to 1:2 parts by weight of the cracked component.

5. A fuel composition according to any of the preceding claims containing 5 to 1000 ppm of the basic oil soluble compound.

6. The use of a basic salt of one or more of lithium, sodium, potassium or calcium as an additive to improve the storage stability of a fuel containing more than 0.04 wt. % sulphur and more than 100 pm nitrogen.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 2364

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	GB-A- 674 765 (DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) * Whole document *	1,3-5	C 10 L 1/18 C 10 L 1/24 C 10 L 10/00
Y		2,6	
Y	B. RIEDIGER: "DIE VERARBEITUNG DES ERDÖLES", 1971, pages 38-43, Springer-Verlag, Berlin, DE * Whole document *	2,6	
X	GB-A- 685 117 (H.I. DOWNES) * Claims; example; pages 1,2; page 3, lines 59-70 *	1,3-5	
Y		2,6	
X	FR-A-1 194 439 (SOCONY MOBIL OIL) * Abstract; page 1; page 12, column 2; page 13 *	1,3-5	
Y		2,6	
Y	FR-A-1 582 348 (MOBIL OIL) * Whole document *	1-6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Y	FR-A-1 485 522 (LUBRIZOL) * Whole document *	1-6	C 10 L
X	US-A-3 635 686 (GEE et al.) * Whole document *	1,3-5	
X	US-A-3 951 613 (KIELE) * Claims; column 1, lines 16-47; column 4, line 62 - column 3, line 2; column 5, lines 14-20; column 6, lines 9-31 *	1,3-5	

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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	06-06-1988	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

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
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Y	FR-A-1 594 227 (MOBIL OIL) * Whole document * ---	1,3-5	
Y	US-A-2 658 823 (ANDRESS) * Whole document * ---	1,3-5	
A	EP-A-0 212 922 (EXXON) * Whole document * ---	1-6	
A	EP-A-0 192 323 (NIPPON) * Whole document * ---	1-6	
A	US-A-4 016 093 (KOFT, Jr.) * Claims * ---	1-6	
A	GB-A-1 184 020 (SHELL) * Claims * ---	1-6	
A	US-A-2 692 821 (AMBROSE et al.) * Whole document * -----	1-6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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