

12

EUROPEAN PATENT APPLICATION

21 Application number: 88311966.1

51 Int. Cl. 4: **C10M 159/24 , C10M 163/00**

22 Date of filing: 16.12.88

**C10M 167/00 , //(C10M163/00,
129:93,129:95,133:52,137:10,
159:24),(C10M167/00,137:10,
159:24),C10N10:02,C10N30:04,
C10N60:00**

30 Priority: 29.12.87 GB 8730227
23.03.88 GB 8806973

43 Date of publication of application:
05.07.89 Bulletin 89/27

84 Designated Contracting States:
BE DE FR GB IT NL

71 Applicant: **EXXON CHEMICAL PATENTS INC.**
1900 East Linden Avenue
Linden New Jersey 07036(US)

72 Inventor: **Cleverley, John Artur**
9 Elbourne
Didcot Oxfordshire OX11 0BL(GB)
Inventor: **Marsh, John Frederick**
7 Cameron Avenue
Abingdon Oxfordshire(GB)
Inventor: **Swietlik, Joseph Marian**
18 Old Farm Close
Abingdon Oxfordshire OX14 3XU(GB)

74 Representative: **Northover, Robert Frank et al**
Exxon Chemical Limited Exxon Chemical
Technology Centre PO Box 1
Abingdon Oxfordshire, OX13 6BB(GB)

54 Improved overbased magnesium sulphonate.

57 Overbased magnesium sulphonates are treated with a dicarboxylic acid or anhydride, or a reaction product with an amine, alcohol, amino-alcohol or mixtures thereof, optionally in combination with an alcohol, to give increased resistance to interactions. Compositions comprising such overbased magnesium sulphonate, particularly in combination with high molecular weight dispersants and/or friction modifiers, provide stable sediment-free lubricating oil compositions which can meet the proposals for SG quality and the Tier II fuel economy requirements.

EP 0 323 087 A1

Improved Overbased Magnesium Sulphonate

This invention related to improved overbased magnesium sulphonates and to compositions containing them, particularly for use in lubricating oils for use in transport applications.

Magnesium sulphonates are well-known lubricant additives, and are described as "overbased" when they contain a stoichiometric excess of magnesium compared to that required to neutralize the sulphonic acid. Overbased magnesium sulphonates are commonly used as detergents in lubricating oils. They are generally prepared by carbonation of a reaction mixture comprising a sulphonic acid or sulphonate and an excess of a magnesium compound such as an alkoxide, oxide or hydroxide in oil, typically with a hydrocarbon solvent and usually in the presence of a promoter. Examples of preparations are found in US-A-3158009, GB-A-1166744, GB-A-1297150, GB-A-1399092, EP-A-0013808 and EP-A-0015341.

Lubricating oils for automobile are having to pass increasingly severe tests, usually engine tests, for approval by automobile manufacturers, and/or to meet industry standards. In particular, tests for sludge and varnish inhibition are becoming more severe requiring the use of more potent dispersants. The oils are also being required to be more resistant to thickening caused by oxidation, requiring the use of potent antioxidants. The SG quality level in the API Engine Service Categories for service station oils developed by API in conjunction with ASTM and SAE reflects this increased severity in requirements for passenger car applications.

Additionally, there is a desire to improve the effect of lubricating oils on fuel economy requiring the use of friction modifier. API in conjunction with ASTM and SAE has developed a more stringent engine test (Sequence 6 Test) for determining fuel economy performance, and a pass at the so-called "Tier II" level of fuel economy for a lubricating oil requires a 2.7 percent minimum improvement in fuel economy versus a standard lubricating oil run in the Sequence 6 engine test.

The use of overbased magnesium sulphonates in lubricating oils designed to meet these more stringent criteria can give rise to problems of interactions between the additives, either in concentrated form or in the finished lubricants, which may result in undesirable sediment or haze formation.

This invention relates to overbased magnesium sulphonates having increased resistance to interactions, to modifications to the manufacture of overbased magnesium sulphonates to reduce interactions and to compositions comprising overbased magnesium sulphonate, particularly in combination with high molecular weight dispersants and/or friction modifiers. The invention may provide stable sediment-free lubricating oil compositions (including lubricants and concentrates therefor) which can meet the proposals for SG quality and the Tier II fuel economy requirement (as defined hereinbefore).

The high molecular weight dispersants which may be used in the invention include those of number average molecular weight (M_n) of greater than 1300, e.g. those described in EP-A-0208560. Friction modifiers are well known and include polar materials such as partial esters of fatty acids such as glyceryl mono-oleate, various straight chain acids such as oleic acid and stearic acid and derivatives of linoleic acid dimers.

The overbased magnesium sulphonate, which may be prepared by a process as described hereinbefore, is treated with an oil-soluble hydrocarbyl-substituted C_4 to C_{10} mono-unsaturated dicarboxylic acid or anhydride or a reaction product thereof with an amine, alcohol, amino-alcohol or mixtures thereof, optionally in combination with a mono- or polyhydric alcohol.

The hydrocarbyl-substituted C_4 to C_{10} mono-unsaturated acid or anhydride, whether used as such or as a reaction product with an amine, alcohol, amino-alcohol or mixtures thereof, is preferably a hydrocarbyl succinic acid or anhydride comprising a hydrocarbon group substituted with one or more moles, per mole of hydrocarbon, of maleic acid. The preferred hydrocarbon is a long chain hydrocarbon having at least 50 carbon atoms, and polyolefins having a molecular weight of at least 900 are more preferred. The preferred polyolefin is polyisobutylene, and for convenience hereinafter polyisobutenyl succinic anhydride or acid will be referred to as PIBSA. A preferred category of PIBSA has a number average molecular weight of from 900 to 5000 (a particularly preferred range being 1300 to 2200), and more preferably also comprises at least 1 succinic moiety per polyisobutene.

When a reaction product of PIBSA with component b), as defined hereinbefore, is used it is preferred that b) is a polyamine (hereinafter referred to as PAM). A preferred group of PAMs are polyalkyleneamines with alkylene groups containing 2 to 6 carbon atoms and with 2 to 8 nitrogen atoms per molecule. The polyamines used may comprise a single polyalkyleneamine, or a commercial mixture comprising two more or more such amines.

Preferred PIBSA/PAM reaction products for use in the invention include those wherein the

polyisobutene group has a number average weight (M_n) of 900 to 2500, and specific examples of such products contain a polyisobutene group of $M_n = 950, 1300$ and 2200 . Each of these products may be used in a borated form (as described in US-A-3087936 or 3254025) or without boration.

When the treatment includes an alcohol, this may be, for example, a monohydric alkanol containing 10 to 30 carbon atoms, most preferably isodecanol, octadecanol, hexadecanol or a C_{20} alcohol. Glycols may also be employed and ethylene glycol is preferred.

The preferred treatment of the invention uses the acid, anhydride or reaction product, in an amount of from 1 to 10 wt % of the overbased product optionally with the alcohol, again in an amount of from 1 to 10 wt % of the overbased product, with an amount of 2 to 5 wt % of each compound used in the treatment being most preferred. It is preferred to carry out the treatment at elevated temperature, e.g. 150°C .

The overbased magnesium sulphonate on which the treatment is carried out may be prepared by a process which comprises carbonating a reaction mixture comprising:

- a) an oil-soluble sulphonic acid or sulphonate;
 - b) a stoichiometric excess of a magnesium compound such as an alkoxide, oxide or hydroxide;
 - c) oil;
 - d) hydrocarbon solvent such as benzene, toluene or xylene, with toluene being a preferred solvent;
 - e) promoter such as ketones, amines, oil-soluble carboxylic acids, amine salts or diketones
- and optional additional components such as water, lower (C_1 to C_5) alkanols, or additional surfactants such as oil-soluble alkyl phenols.

The sulphonic acid or sulphonate may be natural or synthetic with synthetic alkylaryl sulphonic acids and sulphonates being preferred. The alkyl substituent in such alkylaryl moieties may have 15 or more carbon atoms and is typically a polyolefin formed from an olefin having 2 to 5 carbon atoms.

The magnesium compound provides the basicity to the formed overbased magnesium sulphonate and is therefore present in excess of the amount stoichiometrically required to react with the sulphonic acid, the amount in the product dictating the total base number (TBN) of the product. It may however be introduced in stages with intervening carbonation steps.

The solvent is typically present in an amount of from 0.1 to 10 parts by weight of solvent per part of magnesium in the reaction mixture. The promoter is typically present in an amount of from 0.01 to 5 parts by weight per part of magnesium in the reaction mixture. Water may be present in an amount of from 0 to 2 parts by weight per part of magnesium in the reaction mixture.

An additional surfactant such as an alkyl phenol may be present in an amount of from 0 to 1 part by weight per part of magnesium present in the reaction mixture.

The reaction mixture is carbonated by passing carbon dioxide gas through the mixture at a typical temperature of 25° to 200°C , with a preferred range being 50° to 150°C .

After carbonation the product may be stripped to remove volatiles, and filtered to remove solids, but these operations may be carried out in either order. Further carbonation may be carried out during stripping and further oil may be added to replace material lost in stripping.

The formed product may be post-treated prior to the treatment of the invention to improve the water tolerance and/or stability and/or foaming performance and/or seal compatibility thereof, by known post-treatments.

The overbased magnesium sulphonate preferably has a total base number (TBN) as measured by ASTM D2896 of at least 300, more preferably 300 to 450, and most preferably about 400.

The overbased magnesium sulphonates may be used in oleaginous compositions, e.g. lubricants and concentrates therefor, and in particular those comprising:

- (i) high molecular weight ashless dispersant, and preferably an ashless dispersant of the type described hereinbefore for use in the carbonation, but having M_n of at least 1300, more preferably 1500-5000 and optionally
- (ii) friction modifier, preferably even when used at the levels required to meet the Tier II fuel economy requirement (as defined hereinbefore) which may require levels of friction modifier in a concentrate of greater than 0.5 wt%, and/or
- (iii) copper compound as antioxidant, and/or
- (iv) a zinc dihydrocarbyl dithiophosphate (ZDDP), and/or
- (v) other conventional additives.

The overbased magnesium sulphonate will typically comprise from 0.01 to 5 wt % of such compositions for use as crankcase lubricants, but concentrates may contain up to 50 wt % of the overbased magnesium sulphonate. The tendency for such compositions and concentrates to give interactions may be tested by blending the additives required for the composition or concentrate which are then stored at an elevated

temperature, typically 54° C or 66° C and observing the appearance of haze/sediment.

A lubricating oil composition or concentrate may be regarded as being acceptably stable if it is clear and substantially free from haze and/or sediment after at least 3 months at 66° C. The compositions of the invention may provide a means of meeting more severe testing regimes with acceptably stable formulations and packages.

The compositions contain a major amount of a lubricating oil which may be a mineral lubricating oil, a synthetic lubricating oil or mixtures thereof. The synthetic oils include polyalpha olefins, diester oils, such as di(2-ethylhexyl) sebacate, azelate and adipate, complex ester oils such as those formed from dicarboxylic acids, glycols and either monobasic acids or monohydric alcohols and silicone oils.

In addition to the additives specifically listed above, the compositions may contain additives such as viscosity modifiers, corrosion inhibitors, other oxidation inhibitors, other friction modifiers, other dispersants, anti-foaming agents, anti-wear agents, pour point depressants, detergents, rust inhibitors and the like.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures.

Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties.

These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6 , preferably 10^4 to 10^5 , e.g. 20,000 to 250,000, as determined by gel permeation chromatography or membrane osmometry.

Representative examples of suitable viscosity modifiers are any of the types known to the art including polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and vinyl compound, interpolymers of styrene and acrylic esters, and styrene/isoprene copolymers.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulphurized hydrocarbons and the products obtained by reaction of a phosphosulphurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulphurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from 5 to 30 wt % of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 150° F to 600° F. Neutralization of the phosphosulphurized hydrocarbon may be effected in the manner taught in US Patent No. 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include ZDDP's, aromatic amines such as alkylated diphenylamines and phenyl alpha naphthylamine, hindered phenols, copper compounds, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, eg, calcium nonylphenol sulphide, barium t-octylphenyl sulphide, dioctylphenyl-amine, phenylalphanaphthylamine and phosphosulphurized or sulphurized hydrocarbons.

Friction modifiers serve to impact the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in US Patent No. 3,933,659 which discloses fatty acid esters and amides; US Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; US Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; US Patent No. 3,779,928 which discloses alkane phosphonic acid salts; US Patent No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; US Patent No. 3,852,205 which discloses S-carboxyalkylene hydrocarbyl succinimide, s-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; US Patent No. 3,879,306 which discloses N-(hydroxyalkyl)alkenyl-succinamic acids or succinimides; US Patent No. 3,932, 290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and US Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulphurized N-(hydroxyalkyl) alkenyl succinimides. The most preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis alkanols such as described in US Patent No. 4,344,853.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation or deposition on metal parts. High molecular weight ashless dispersants for use in the invention have a number average molecular weight of at least 1300 and

preferably comprise an alkenyl succinimide, the reaction product of oil-soluble polyisobutylene succinic anhydride with an amine such as an ethylene amine which may optionally be borated.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Such depressants are well known. Typically of those additives which usefully optimize the low temperature fluidity of the fluid are C₈-C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, eg silicone oil and polydimethyl siloxane.

Additional detergents and metal rust inhibitors may be present including the metal salts of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl saliscylates, naphthenates and other oil soluble mono- and di-carboxylic acids.

Highly basic (viz, overbased) metal salts, such as highly basic alkali and alkaline earth metal sulphonates (especially Na, Ca and Mg salts) are frequently used as detergents, alone and in combination. Mixtures of calcium and magnesium salts, and of calcium, magnesium and sodium salts are preferred.

Copper and lead corrosion inhibitors and antiwear agents include borate esters, thiadiazoles such as derivatives of 2, 5 dimercapto 1,3,4-thiadiazole and benzotriazoles.

Some of these numerous additives can provide a multiplicity of effects, eg a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

Additive	Vol %	Wt % a.i.
Viscosity Modifier	.01-4	.01-4
Corrosion Inhibitor	0.01-1	.01-1.5
Oxidation Inhibitor	0.01-1	.01-1.5
Dispersant	0.1-7	0.1-8
Pour Point Depressant	0.01-1	.01-1.5
Anti-Foaming Agents	0.001-0.1	.001-0.15
Anti-Wear Agents	0.001-1	.001-1.5
Friction Modifiers	0.01-1	.01-1.5
Detergents/Rust Inhibitors	.01-2.5	.01-3
Mineral Oil Base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the dispersant (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the dispersant additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the combination of additives of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 5 to about 75%, and most preferably from about 8 to about 50% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt % of the additive-package with the remainder being base oil.

When otherwise stated, all weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package, or formulation, which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

The following Examples and Test Results are given, though only by way of illustration, to show certain aspects of the invention in more detail.

Examples 1-9 and Comparative Example A

An overbased magnesium sulphonate was prepared by carbonation at 40-70° C of a reaction mixture comprising:

- a) an alkylbenzene sulphonic acid
- b) excess magnesium oxide
- 5 c) ethylene diamine in an amount of 0.06 parts by weight per part of magnesium in b), the ethylene diamine being introduced as a carbamate solution prepared by reacting ethylene diamine, water, methanol and carbon dioxide
- d) oil.

10 Carbonation was continued until breakthrough and the formed product after stripping and filtration was post-treated with 2 wt % (based on product) fumaric acid to form a nominal 400 TBN product. This product is Comparative Example A, and contains approximately 47 wt % active ingredient.

The product of Comparative Example A was treated with various amounts of PIBSA and PIBSA/PAM materials, alone or in combination with an alcohol, to give products which are examples of the invention as
15 detailed in Table I below.

Test Results

20 The formed overbased magnesium sulphonates were blended into a typical service station oil additive package including in addition to other conventional additives 18.2% of a borated PIBSA/PAM dispersant in which the polyisobutene moiety has a number average molecular weight of about 2200, 120 ppm of added copper as antioxidant and 0.75 wt % of glyceryl monooleate as friction modifier. The overbased magnesium sulphonate comprised 9.85 wt % of this package.

25 The packages were evaluated by storing them at 150° F (66° C) and observing them at regular intervals. The results are given in Table 1 below as the number of days after which incompatibility manifested itself as haze and/or sediment. A '+' sign indicates the test was still running at the number of days given without sign of incompatibility.

TABLE 1

Example	Dispersant	% ¹	Days ⁴
A	-	-	7 ²
1	950 M.W. ³ PIBSA/PAM + ethylene glycol	3% + 2%	12
2	950 M.W. PIBSA	2%	7
3	950 M.W. PIBSA	5%	18
4	1300 M.W. PIBSA	2%	10
5	500 M.W. PIBSA/PAM	2%	10
6	2200 M.W. PIBSA	2%	68
7	1300 M.W. PIBSA	5%	17
8	500 M.W. PIBSA/PAM	5%	10
9	2200 M.W. PIBSA	5%	90

1. as wt. percentage of 400 TBN overbased magnesium sulphonate product

2. average of 10 repeats

3. M.W. = number average molecular weight.

4. Test halted after 90 days.

Claims

55 1. An oleaginous composition comprising a high molecular weight ashless dispersant having a number average molecular weight of at least 1300, and an overbased magnesium sulphonate treated with an oil-soluble hydrocarbyl-substituted C₄ to C₁₀ mono-unsaturated dicarboxylic acid or anhydride or a reaction product thereof with an amine, alcohol, amino-alcohol or mixtures thereof.

2. A composition as claimed in claim 1 in which the hydrocarbyl-substituted C₄ to C₁₀ mono-unsaturated acid or anhydride, whether used as such or as a reaction product with an amine, alcohol, amino-alcohol or mixtures thereof, is a hydrocarbyl succinic acid or anhydride comprising a hydrocarbon group having at least 50 carbon atoms substituted with one or more moles, per mole of hydrocarbon, of maleic acid.

3. A composition as claimed in claim 2, in which the hydrocarbon is a polyisobutylene having a number average molecular weight of from 900 to 5000.

4. A composition as claimed in claim 3, in which a reaction product of the anhydride or acid with a polyamine is used.

5. A composition as claimed in claim 4, in which the polyisobutene group of the reaction product has a number average weight (M_n) of 900 to 2500.

6. A process as claimed in any of claims 1 to 5, in which the acid, anhydride or reaction product is used in an amount of from 1 to 10 wt % of the overbased product.

7. A process as claimed in claim 6, in which the acid, anhydride or reaction product is used in an amount of 2 to 5 wt % of the overbased product.

8. A composition as claimed in any of claims 1 to 7, in which the overbased magnesium sulphonate is also treated with a mono- or polyhydric alcohol.

9. A process as claimed in claim 8, in which the alcohol is a monohydric alkanol containing 10 to 30 carbon atoms of a glycol.

10. A composition as claimed in any of claims 1 to 9, for use as a lubricant or a concentrate therefor, which further comprises:-

- (i) friction modifier, and/or
- (ii) copper compound as antioxidant, and/or
- (iii) a zinc dihydrocarbyl dithiophosphate.

11. A composition as claimed in claim 10 in which the ashless dispersant has a number average molecular weight of 1500-5000.

12. A composition as claimed in claim 10 or claim 11, which contains a major amount of oil, from 0.01 to 5 wt % of the overbased magnesium sulphonate and friction modifier at a level required to meet the Tier II fuel economy requirement of the API Sequence 6 test.

13. A composition as claimed in claim 10 or claim 11, in the form of a concentrate containing up to 50 wt % of the overbased magnesium sulphonate and friction modifier in an amount of greater than 0.5 wt %.

14. A composition as claimed in any of claims 10 to 13, which contains calcium and magnesium.

15. A composition as claimed in claim 14, which contains calcium, magnesium and sodium.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 31 1966

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	DE-A-2 014 880 (LUBRIZOL) * Page 2, lines 6-19; page 3, lines 1-15; page 3, line 27 - page 4, line 4; page 6, lines 12-21; page 7, line 10 - page 8, line 16; page 11, line 20 - page 12, line 14; page 12, lines 23-28; claims 1,2,10,12 * ---	1-7,10-12	C 10 M 159/24 C 10 M 163/00 C 10 M 167/00 // (C 10 M 163/00 C 10 M 129:93 C 10 M 129:95 C 10 M 133:52 C 10 M 137:10 C 10 M 159:24) (C 10 M 167/00 C 10 M 137:10 C 10 M 159:24) (C 10 N 10/02 C 10 N 30:04 C 10 N 60:00)
A	EP-A-0 041 851 (EXXON RESEARCH AND ENGINEERING CO.) * Page 2, line 5 - page 3, line 20; page 4, lines 4-12; page 5, lines 7-19,27-34; page 7, line 35 - page 8, line 5; page 11, lines 1-9 * ---	1-3,6,7,10-13	
A	EP-A-0 096 539 (EXXON RESEARCH AND ENGINEERING CO.) * Page 1, line 31 - page 3, line 3; page 4, line 12 - page 6, line 10; page 12, line 22 - page 13, line 5; page 16, line 22 - page 17, line 14; page 23 * ---	1-7,10,11	
A	EP-A-0 212 922 (EXXON RESEARCH AND ENGINEERING CO.) * Page 24, line 28 - page 6, line 11; page 10, lines 16-32 * -----	10	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 M
Place of search THE HAGUE		Date of completion of the search 23-03-1989	Examiner HILGENGA K.J.
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 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 L : document cited for other reasons & : member of the same patent family, corresponding document			