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(54) Lubricant oil composition with improved friction reducing properties.

(57) A lubricating oil composition having improved friction reducing properties and the method of reducing friction in internal combustion engines by lubricating said engines with said lubricating oil which contains an effective friction reducing amount of an additive which is the reaction product of dimer carboxylic acid and a polyhydric alcohol having at least 2 hydroxy groups in combination with an oil soluble alkanol or an oil soluble alkyl phosphate.

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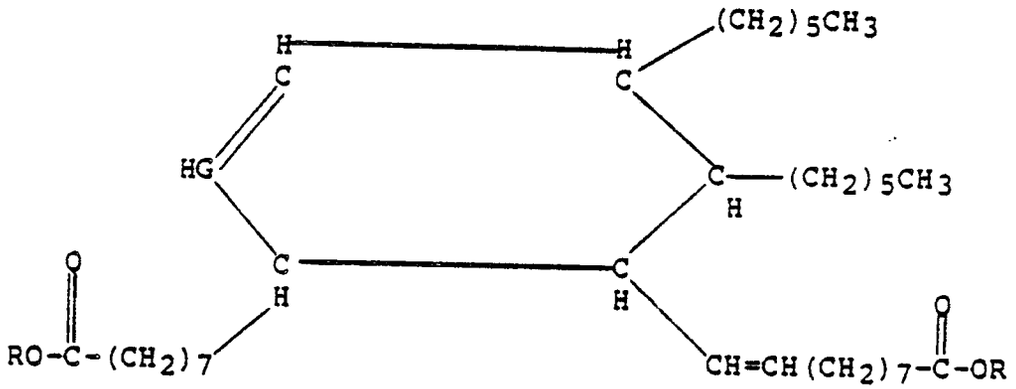
LUBRICANT OIL COMPOSITION WITH IMPROVED FRICTION REDUCING PROPERTIES

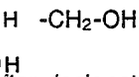
DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to a lubricating oil composition containing an oxygenated (hydroxy) ester of a dimer acid in combination with an oil soluble alkanol or alkyl phosphate to provide improved friction reducing properties and to a method of reducing friction in an internal combustion engine by using a lubricating oil composition which contains said additives.

The friction reducing additive which is used in this invention is an oil soluble oxygenated (hydroxy) ester of a dimer acid (HEDA hydroxy ester of dimer acid) in combination with an oil soluble alkanol or alkyl phosphate, wherein the oxygenated (hydroxy) ester is characterized by the formula:



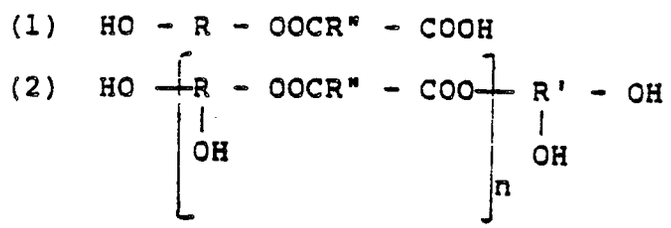
where R is selected from the group consisting of
$-CH_2-CH_2-[OCH_2CH_2]_nOH$;
with n being equal to 1 to 5 (hereafter designated as HEDA);
$-CH_2-CH_2-N(CH_2CH_2OH)_2$
(hereinafter designated as LA214);
and



(hereinafter designated as LA200).

The use of an oxygenated (hydroxy) ester of the dimer acid as a friction-reducing agent for oils in a gasoline engine can be limited by poor solubility in the lubricating oil and adverse interactions with other lubricating oil components, wherein some of these interactions show up as sediment formation. The present invention teaches that the solubilization and stabilization of the dimer acid esters in the lubricating oils is improved by the addition of an oil-soluble alkanol or alkyl phosphate.

The oxygenated (hydroxy) esters of the dimer acid are classified as reaction products of a dimer carboxylic acid and a polyhydric alcohol. Such a reaction product may be a partial, di- or polyester, with typical formulae represented as follows when using a trihydric alcohol:



wherein R" is the hydrocarbon radical of the dimer acid; each R and R' may be the same or different hydrocarbon radicals associated with a trihydric alcohol; and n is an integer which typically is 1 to 5 or higher. It will, of course, be appreciated that the ester reaction products can be obtained by reacting a

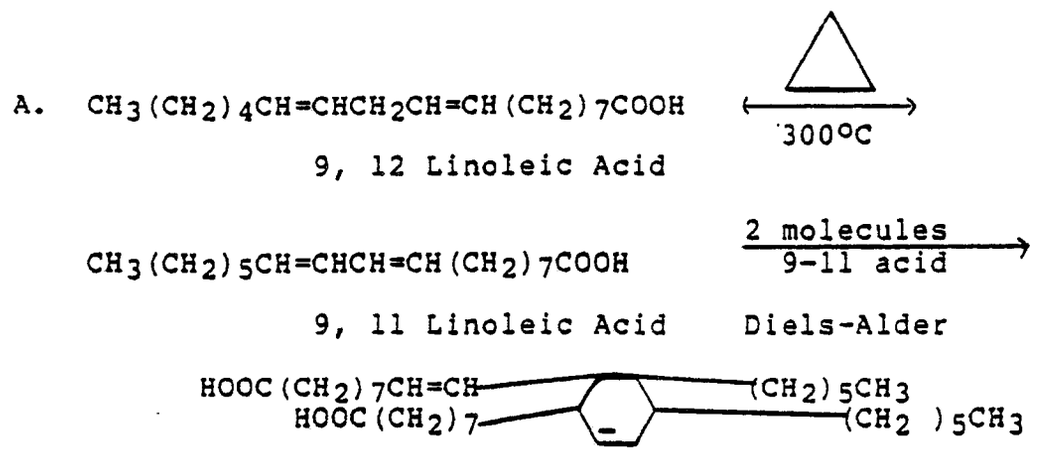
dimer carboxylic acid or a mixture of such acids with a trihydric alcohol or other polyhydric alcohol or mixtures of such alcohols.

The alcohol used in preparing the friction reducing reaction product additive of this invention is a polyhydric alcohol having at least 2 hydroxy groups and from 3 to 18 carbon atoms. Generally, such compounds will be aliphatic and may contain branched or unbranched hydrocarbon groups, as well as other functional groups, such as nitrogen, sulfur and phosphorus. Such polyhydric alcohols will contain at least 2 hydroxyl groups and may contain more, generally from 3 to 6 hydroxyl groups, with the upper amount limited by the degree of solubility and effectiveness of the reaction product in the lubricating oil composition. Preferably, such polyhydric alcohol will contain 2 to 4 hydroxyl groups and 3 to 12 carbon atoms. More preferably, such polyhydric alcohol will be saturated, contain 3 hydroxyl groups and 3 to 8 carbon atoms. Compounds of this type include diethylene glycol, glycerol (i.e., 1, 2, 3, propane triol), 1, 2, 6-trihydroxyhexane and 2, 2′, 2″ nitrilotriethanol.

The carboxylic acid used in preparing the oxygenated (hydroxy) esters of the dimer acid friction reducing reaction product of this invention will be a dimer of an aliphatic saturated or unsaturated carboxylic acid, said dimer acid having a total of 24 to 90 carbon atoms, and from 9 to 42 carbon between the carboxylic acid groups. Preferably, the dimer acid will have a total of 24 to 60 carbon atoms and 12 to 42 carbon atoms between the carboxylic acid groups, and more preferably a total of 24 to 44 carbon atoms and 16 to 22 carbon atoms between the carboxylic acid groups.

The molar quantities of the dimer acid and polyhydric alcohol reactants may be adjusted so as to secure either a complete ester or partial ester and generally from 1 to 3 or more moles of polyhydric alcohol will be used per mole of dimer acid and preferably from 2 to 3 moles of alcohol per mole of acid.

While any of the dimer acids and polyhydric alcohols described above may be used in preparing the friction reducing additive of this invention, the most preferred esters, as set forth above, are those wherein the carboxyl groups are separated from the closest caboxyl group by from 2 to 12 carbon atoms. Particularly useful ester additives are obtained when the acid used is a dimer of a fatty acid, preferably those fatty acids containing 12 to 22 carbon atoms. Such dimers are, of course, clearly taught in U. S. Patent No. 3,180,832, which was granted on April 27, 1965, and U. S. Patent No. 3,429,817, which was granted on February 25, 1969, and as here indicated the hydrocarbon portion of the dimer carboxylic acid thus obtained may contain a 6 member ring. The formation of the dimer from linoleic acid, oleic acid and mixtures of these acids is illustrated by the following reactions:



Linoleic Acid Dimer (dilinoleic acid)

B. $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ —(2 molecules oleic acid, Diels Alder)→

Oleic Acid

$CH_3(CH_2)_7CH{=}C(CH_2)_7COOH$
|
$CH_3(CH_2)_7CH_2CH(CH_2)_7COOH$
Oleic Acid Dimer (Dioleic Acid)

C. 9,11 Linoleic Acid + Oleic Acid —(Diels Alder, △)→

$CH_3(CH_2)_6CHCH{=}CH(CH_2)_7COOH$
|
$CH_3(CH_2)_4CHCH{=}CHCH{=}CH(CH_2)_7COOH$
Mixed Dimer

It will, of course, be appreciated that while the reactions illustrated produce the dimers, commercial application of the reactions will generally also lead to trimer formation and, in some cases, the product thus obtained will contain minor amounts of unreacted monomer or monomers. As a result, commercially available dimer acids may contain as much as 25% trimer and the use of such mixtures is within the scope of the present invention. It is also noted that prepared dimer acids may be saturated or unsaturated. While in some instances the unsaturated dimer acids are preferred, it is also contemplated that if desired dimer acids formed having one or more saturated bonds may have such unsaturation removed, e.g., by hydrogenation.

The ester friction reducing additive of this invention will generally be used at a concentratoin level of from 0.1 to 2.0 parts by weight per 100 parts of lubricating oil composition, more preferably from 0.1 to 1.0, and most preferably from 0.2 to 1.0 parts.

The oil soluble alkanols which are added to the lubricating base oil and the oxygenated (hydroxy) ester of the dimer acid are:

$$RCH_2\text{-}\underset{\displaystyle R'}{\underset{|}{CH}}\text{-}OH$$

wherein R = 2-16 carbon atoms and is straight chained or branched and R' is H or a straight or branched hydrocarbon chain containing 1 to 5 carbon atoms.

The oil-soluble alkanol will generally be used at a concentration of from 1 to 10 parts by weight per part of the ester friction reducing additive, more preferably 1 to 5, and most preferably about 2 to about 4.

The lubricating base oil will generally comprise a major amount of the lubricating composition, i.e., at least 50% by weight thereof, and will include liquid hydrocarbons, such as the mineral lubricating oils and the synthetic lubricating oils, and mixtures thereof. The synthetic oils which can be used include 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; silicone oils; sulfide esters; organic carbonates; and other synthetic oils known in the art.

Other additives, known in the art, may be added to the oil composition of the present invention to form a finished oil. Such additives include dispersants, antiwear agents, antioxidants, corrosion inhibitors, detergents, pour point depressants, extreme pressure additives, viscosity index improvers, etc. These additives are typically disclosed, for example, in Lubricant Additives by C. V. Smalheer and R. Kennedy Smith, 1967, pages 1-11, and in U. S. Patent No. 4,105,571.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following Examples are further illustrative of this invention and are not to be construed as limitations thereof.

Example 1

Oils A and B are fully formulated SF quality SAE 10W-30 passenger car engine oils. Each oil is formulated with standard additives used in the industry to meet the requirements of current gasoline engines. Oils A and B contain the sam viscosity index improvers, dispersants, detergents, antioxidants, pour depressants and antifoamant additives. Oil A contains a zinc dialkyl dithiophosphate antiwear additive made with primary alcohols, while oil B contains a zinc dialkyl dithiophosphate antiwear additive made with secondary alcohols. This is the only difference between oils A and B.

Oil A and oil B, each formulated with 0.5 weight percent HEDA solubilized with C_8Oh at a 3/1 alcohol/HEDA weight ratio were tested for relative friction using a ball on cylinder test, described in the Journal of the American Society of Lubricating Engineers, entitled ASLE Transactions, Volume 4, pages 1-11, 1961. In essence, the apparatus consists basically of a fixed metal ball loaded against a rotating cylinder. The weight on the ball and the rotation of the cylinder can be varied during any given test or from test to test. Also, the time of any given test can be varied. Generally, however, steel on steel is used at a constant load, constant rpm, and a fixed time and in each of the tests of these examples a 4 Kg load, 0.26 rpm and 70 minutes was used.

Ball-on-Cylinder (BOC) Test

Test Conditions

Load on Ball, kg = 4
Cylinder Speed, rpm = .26
Oil Sump Temp., °C = 104
Test Duration, Minutes = 70

BOC Coefficient of Friction (COF) at 70 Minutes (0 = Best)

Oil	Fresh Oil	After 3 Hours LST*
Reference	0.260	0.280
Oil A + HEDA/OXOC$_8$OH = 1/3)	0.050	0.065
Reference	0.250	--
Oil B + HEDA/OXOC$_8$OH = 1/3)	0.055	0.070
Reference	0.220	--
Oil A	0.090	--
Oil B	0.125	0.105

*See U. S. Patent No. 4,479,883, column 6, lines 55-60.

As summarized above, oil A and oil B, each with 0.5 weight percent HEDA and 1.5 weight percent C_8OH, gave lower BOC friction than the base case oils without HEDA/C_8 alcohol (oil A or oil B). As

indicated in U. S. Patent No. 4,479,883, the BOC data on the oxidized oil from the 3 hour Lube Stability Test (LST) is a better predictor of fuel economy differences during field service than fresh oil data.

Example 2

Table I lists the surfactants and alcohols tested as solubilizers for dimer acid esters. The designation CO for the solubilizer refers to a series of ethoxylated nonyl phenols produced by GAF Corp. under the trademark name Igepal®. The prefix OXO refers to oil soluble alcohols manufactured by the OXO process. The designation DM refers to the Igepal DM® series of ethoxylated dinonyl phenols manufactured by the GAF Corp. Spans® are products of ICI Americas, Inc.; Tetronics® are products of BASF Wyandott Corp.; Tritons® are products of Rohm and Haas, Inc.; Aerosol® are products of American Cyanamid; and Emphos® designates a series of alkyl phosphates manufactured by Witco Chemical Corp. Of all the materials tested, only the alkanols and alkyl phosphates formed clear solutions, with HEDA in oil A at the ratios of solubilizer/ester indicated in the second column of Table I.

TABLE I

Solubilization of Dimer Acid Esters

CONCENTRATES			OILS PLUS CONCENTRATES		
Solubilizer/Additive	Ratio	Appearance[1]	S150N	Oil A	Oil B
C_9Phenol/HEDA	2:1,4:1	1, 1	-, 2	4, 3	5, 3
CO210/HEDA	2:1,4:1	1,1	-, 3	3, 2	5, 2
CO430/HEDA	2:1,4:1	1, 1	-, -	3, 3	5, 3
CO530/HEDA	-,4:1	-, 1	-, 5	-, 4	-, 4
CO630/HEDA	-,4:1	-, 1	-, 5	-, 5	-, 5
CO710/HEDA	-,4:1	-, 1	-, 5	-, 5	-, 5
C_9Phenol/LA200	2:1,4:1	1,1	-, -	5, 5	5, 5
CO210/LA200	2:1,4:1	1,1	-, -	5, 5	5, 5
CO430/LA200	2:1,4:1	1, 1	-, -	5, 5	5, 5
C_9Phenol/LA214	2:1,4:1	1, 1	-, -	5, 5	5, 5
CO210/LA214	2:1,4:1	1,1	-, -	5, 5	5, 5
CO430/LA214	2:1,4:1	1, 1	-, -	5, 5	5, 5
$OXOC_6OH$/HEDA	2:1,3:1,4:1	1, 1, 1	-, -, -	1, 1, 1	2, 1, 1
$OXOC_8OH$/HEDA	2:1,3:1,4:1	1, 1, 1	-, -, -	1, 1, 1	2, 2, 1
$OXOC_{13}OH$/HEDA	-,-,4:1	-, -, 1	-, -, 2	-, -, 2	-, -, 2
$OXOC_6OH$/LA200	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_8OH$/LA200	,-,-,4:1	-, -, 1	-, -, -	-, -, 5	-, -, 5
$OXXOC_{10}OH$/LA200	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_{13}OH$/LA200	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_6OH$/LA214	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_8OH$/LA214	2:1,3:1,4:1	-, -, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_{10}OH$/LA214	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5
$OXOC_{13}OH$/LA214	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	5, 5, 5

TABLE I - Continuation 1

CONCENTRATES			OILS PLUS CONCENTRATES		
Solubilizer/Additive	Ratio	Appearance[1]	S150N	Oil A	Oil B
C_8OH/HEDA	2:1,3:1,4:1	1, 1, 1	-, -, -	5, -, 1	-, -, -
C_8OH/LA200	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	-, -, -
C_8OH/LA214	2:1,3:1,4:1	1, 1, 1	-, -, -	5, 5, 5	-, -, -
OXOC_8ACET/HEDA	4:1	1	3	4	4
OXOC_9ACET/HEDA	2:1,3:1	1,1	2,2	-, -	-, -
OXOC_{13}ACET/HEDA	4:1	1	1	5	5
OXOC_9ACET/LA200	2:1,3:1	5, 4	5, 5	-, -	-, -
OXOC_9ACET/LA214	2:1,3:1	5, 4	5, 5	-, -	-, -

TABLE I - Continuation 2

CONCENTRATES			OILS PLUS CONCENTRATES		
Solubilizer/Additive	Ratio	Appearance	S150N	Oil A	Oil B
DM430/HEDA	4:1	1	5	3	
DM530/HEDA	4:1	1	5	4	4
DM710/HEDA	4:1	1	5	5	5
$OXOC_8OH$/(HEDA/LA200) = (95/5)	4:1	-	-	1	-
= (90/10)	4:1	-	-	1	-
= (85/15)	4:1	-	-	2	-
= (80/20)	4:1	-	-	3	-
= (75/25)	4:1	-	-	4	-
= (70/30)	4:1	-	-	5	-
= (60/40)	4:1	-	-	5	-
= (50/50)	4:1	-	-	5	-
Butyl Cellulose/LA200	4:1	1	-	5	-
Oleic Acid/LA200	4:1	1	-	5	-
Span 80/LA214	4:1	1	-	5	-
Span 85/LA214	4:1	1	-	5	-
Tetronic 150l/LA214	4:1	5	-	-	-
Tetronic 610l/LA214	4:1	5	-	-	-

TABLE I - Continuation 3

CONCENTRATES			OILS PLUS CONCENTRATES		
Solubilizer/Additive	Ratio	Appearance	S150N	Oil A	Oil B
Triton X-15/LA214	4:1	1	-	5	-
Aerosol MA80/LA200	4:1	1	-	5	-
Siloxane/LA200	4:1	5	-	-	-
Emphos PS121/HEDA	4:1	1	-	1	-
Emphos PS220/HEDA	4:1	1	-	1	-
Emphos CS1361/HEDA	4:1	1	-	1	-
Emphos CS1361/LA200	4:1	1	-	5	-
Emphos PS220/LA200	4:1	1	-	5	-
Emphos PS121/LA200	4:1	1	-	5	-

(1) 1-Excellent; 2-Very good; 3-Good; 4-Fair; 5-Poor. The friction reducing dimer acid product is used in all cases at the 0.5 weight percent level.

Example 3

A series of alkanols, including C_6, C_8 and C_{13}, were used as solubilization agents with HEDA in lubricating oils A and B. Shown in Table II is the appearance of the oils using 0.5 weight percent HEDA solubilized by the alkanols. As illustrated, solubilization of HEDA in oil B requires more alkanol than required by oil A to obtain a bright and clear oil. To test the stability of these systems, oil A containing 0.5 weight percent of HEDA, solubilized with 3 parts of C_8OH per part of HEDA was stored two months at 22° C with no apparent change. In addition, this oil was temperature cycled for one-half hour at 100° C, one and one-half hours at -14° C, one-half hour at -40° C and one hour at 100° C with no apparent change in clarity. Also indicated is the criticality of the chain length in the alkanol. $C_{13}OH$ is less effective in solubilizing HEDA in both oil A and oil B relative to C_8OH and C_6OH.

TABLE II

Solubilization of 0.5 Wt.% HEDA by Oxo-Alcohols

Alcohol	B. P. oC	Alcohol Ester Ratio	Appearance(1 Oil A	Oil B
C_6OH	151°	2/1	1	2
		3/1	1	1
		4/1	1	1
C_8 OH	183°	2/1	1	2
		3/1	1	
		4/1	1	1
C_{13} OH	260°	4/1	2	2

(1) 1-Bright and Clear; 2-Clear

Claims

1. A lubricating oil composition having improved friction reducing properties comprising:

(a) a major amount of a lubricating base oil;

(b) from 0.1 to 2.0 parts by weight per 100 parts by weight of said lubricating oil composition of the reaction product of a dimer carboxylic acid having a total of 24 to 90 carbon atoms with 9 to 42 carbon atoms between carboxylic acid groups and a polyhydric alcohol having at least 3 to 18 carbon atoms, said reaction product being formed using from 1 to 3 moles of alcohol per mole of dimer acid; and

(c) from 1 to 10 parts by weight of an oil soluble compound per part of the reaction product of (b) wherein said oil soluble compound is selected from the alkanols and alkyl phosphates.

2. The composition of claim 1 wherein said dimer carboxylic acid has 24 to 60 carbon atoms and said polyhydric alcohol has 3 to 12 carbon atoms.

3. The composition of claim 1 or claim 2 wherein said polyhydric alcohol has 2 or more hydroxyl groups.

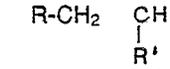
4. The composition of any one of claims 1 to 3 wherein from 0.1 to 1.0 parts by weight of said reaction product is used per 100 parts by weight of lubricating oil composition.

5. The composition of any one of claims 1 to 4 wherein said alcohol is selected from diethylene glycol, glycerol, 1, 2, 6 trihydroxyhexane and 2, 2′, 2″ nitrilotriethanol.

6. The composition of any of claims 1 to 5 wherein said carboxylic acid is a fatty acid which contains 12 to 22 carbon atoms.

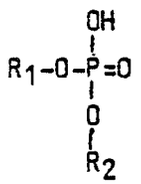
7. The composition of any of claims 1 to 6 wherein from 0.1 to 1.0 parts by weight (pbw) of said reaction product is used per 100 pbw of the composition, and said alcohol is selected from diethylene glycol, glycerol, 1, 2, 6 trihydroxyhexane and 2, 2′, 2″ nitrilotriethanol.

8. The composition of any one of claims 1 to 7 wherein said alkanol is characterized by the formula:



where R = 2-16 carbon atoms and can be linear or branched and R′ is H or a straight or branched hydrocarbon chain containing 1 to 5 carbon atoms.

9. The composition of any of claims 1 to 8 wherein said alkyl phosphate is characterized by the formula:



where R_1 is an alkyl or alkyl aryl group of 6-18 carbons on the alkyl chain and R_2 is the same as R_1 or H.

10. A method of reducing friction in an internal combustion engine comprising lubricating said engine using a lubricating oil composition containing an effective friction reducing amount of an additive which is the reaction product of a dimer carboxylic acid having 24 to 90 carbon atoms and a polyhydric alcohol having at least 2 hydroxyl groups and 3 to 18 carbon atoms, in combination with an oil soluble compound selected from the group consisting of alkanols and alkyl phosphates.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 6874

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)
Y	EP-A-0 093 598 (EXXON RESEARCH AND ENGINEERING CO.) * Whole document * ---	1-10	C 10 M 129/02 C 10 M 141/06 C 10 M 141/10 // (C 10 M 129/02 C 10 M 129:06 C 10 M 129:76) (C 10 M 141/06 C 10 M 129:06 C 10 M 133:08) (C 10 M 141/10 C 10 M 129:76 C 10 M 133:08 C 10 M 137:04) C 10 N 40:00
Y	GB-A- 708 017 (STANDARD OIL DEVELOPMENT CO.) * Page 1, lines 35-83; claims 1,10 * ---	1-10	
Y	FR-A-1 047 117 (N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) * Page 1, column 2, lines 19-38; page 2, columns 1,2; claims 1,3,13 * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-12-1987	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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