

(19)



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European Patent Office
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(11) Publication number:

0 421 765 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **90310832.2**(22) Date of filing: **03.10.90**

(51) Int. Cl.⁵: **C10M 107/34**, C10M 111/04,
C10M 169/04, C09K 5/04,
/(C10M111/04,105:52,107:34),
(C10M169/04,105:52,107:34,
107:34),C10N20:04,C10N40:30

(30) Priority: **03.10.89 JP 258079/89**

(43) Date of publication of application:
10.04.91 Bulletin 91/15

(84) Designated Contracting States:
DE FR GB

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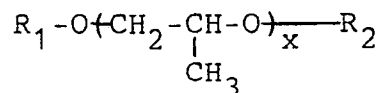
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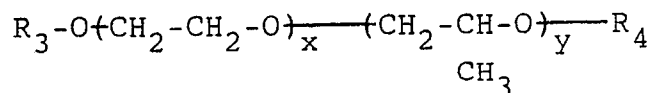
(54) **Polyoxyalkylene ethers as lubricants for a haloalkane refrigerant.**

(57) An oily lubricant for mixing with a refrigerant is a polyoxypropylene glycol alkylether of average molecular weight 500 - 1800, preferably 800 - 1600, of general formula:



where R_1 and R_2 each represent a C1-4 alkyl group (preferably both methyl or one methyl and one ethyl or butyl); the refrigerant is 1,1,1,2-tetrafluoroethane ("R134a").

The lubricant can also contain (a) up to 10 wt % of such alkylether of mol. wt. more than 1800; (b) a polyoxyalkylene glycol or monoalkylether thereof of average mol - wt 500 - 1800 and formula



where R_3 and R_4 are both hydrogen or one may be C_n-H_{2n+1} where n is 1 - 18, and x and y are not zero, and

preferably not more than 50 wt % of the ethylene and propylene oxide units being ethylene oxide; (c) anti-oxidants; (d) anti-wear agents or (e) rust preventatives.

The additives (a) and (b) have good miscibility with the refrigerant, do not react therewith, and can be selected so as to adjust the viscosity of the mixture as desired.

POLYOXYALKYLENE ETHERS AS LUBRICANTS FOR A HALOALKANE REFRIGERANT

The present invention relates to a lubricant for the refrigerant 1,1,1,2-tetrafluoroethane, and in particular to such lubricant which has excellent compatibility in a refrigerator and low hygroscopic property and high viscosity.

Conventionally, R11 (CCl_3F) is used as a refrigerant for refrigeration or air-conditioning systems in buildings, and R12 (CCl_2F_2) for refrigeration units in refrigerators, for food storage and in car air-conditioners. In the meantime, the destruction of ozone layer in stratosphere is now a serious environmental problem and there is an important need to develop an alternative refrigerant.

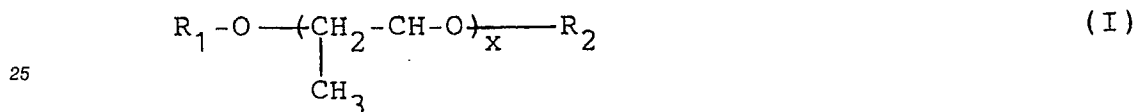
In recent years, R123 (CF_3CHCl_2) has been considered as an alternative to R11, but it has some problems such as high costs and unproven results in toxicity tests.

On the other hand, R22 (CHClF_2) is now being considered as an alternative to R12 because of its ease of decomposability. However, the operating pressure at normal temperature is high because of its low boiling point, and this requires high pressure-proofness of the equipment used. Also, there are problems of leakage from packings, hoses, etc., of or poor insulating property.

Like R22, 1,1,1,2-tetrafluoroethane (R134a) is known as an alternative product to R12, and attention is now given to this product because it does not cause ozone destruction. Although it is not yet proven in chronic toxicity tests, the product has already passed acute and subacute toxicity tests, and its practical use is attracting notice, but it is disadvantageous because of its poor compatibility with the lubricants for refrigerators.

It is therefore the object of the present invention to provide a lubricant suitable for use with 1,1,1,2-tetrafluoroethane refrigerant as an alternative fluid (chlorofluorocarbon).

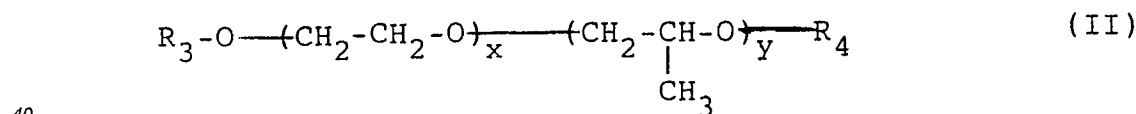
The synthetic oil lubricant according to this invention is represented by the general formula:



where R_1 and R_2 each represents an alkyl group having 1 to 4 carbon atoms which may be identical to or different from each other, and average molecular weight of 500 - 1800; these polyoxypropylene glycol alkylethers are hereinafter referred to as "diether oil".

The invention also includes a blend of said refrigerant and lubricant and optionally other additives.

Preferably the lubricant also includes as additives, to improve the mixture, a polyoxyalkylene glycol (referred to as a "diol oil") or polyoxyalkylene glycol monoalkylether (referred to as a "monool oil"), of average molecular weight of 500 - 1800 and represented by the general formula:



wherein R_3 and R_4 each represent a hydrogen atom or are a hydrocarbon group represented by $\text{C}_n\text{H}_{2n+1}$, where n is 1 - 18; R_3 and R_4 may be the same or different from each other, but they should not be a hydrocarbon group, and x and y are numbers not equal to zero.

In a refrigerator, gas-tightness to the refrigerant is important, and a polyether synthetic oil with high viscosity has been used as lubricant. However, the operating temperature of a refrigerator lubricant oil is normally from -30 to 100°C . When a polyether synthetic oil as lubricant is mixed with a refrigerant, they are (due to unknown causes) separated from each other at high temperature. Thus, it is important that a refrigerator lubricant oil has high compatibility with refrigerant, i.e. it does not separate therefrom at high or low temperature and it does not react with the refrigerant. If this compatibility is low, overheated equipment components may be burned out.

The diether oil of the invention has very high compatibility with said refrigerant, and the refrigerant used has a low hygroscopic property and is thermally and chemically stable compared with R12 (CCl_2F_2) as conventionally used. By properly selecting the range of molecular weight or by adjusting its viscosity

through addition of said diol oil or monool oil, it can be an excellent lubricant for 1,1,1,2-tetrafluorethane as refrigerant.

In the diether oil used as lubricant according to the invention, R_1 and R_2 may be a methyl group, ethyl group, propyl group or butyl group, and may be the same or different from each other. Preferably, R_1 and R_2 are both methyl groups, or one is a methyl group and the other is an ethyl or butyl group.

The average molecular weight is 500 - 1800, or more preferably, 800 - 1600. If it is less than 500, the compatibility with the refrigerant is high at high temperature, but its viscosity is decreased and thermal stability is lowered. If it exceeds 1800, its viscosity is high, but its compatibility with the refrigerant is decreased.

When a small quantity of a diether oil having average molecular weight of more than 1800 is mixed with this diether oil, the mixture has a viscosity suitable as a refrigerant liquid while it maintains compatibility with the refrigerant and the low hygroscopic property in the diether oil. It is preferable that the proportion of high molecular weight oil is 10 wt % or less; if the blending quantity is high, the compatibility with the refrigerant is decreased.

The same effect can be obtained by adding said diol oil or monool oil to the diether oil, and the characteristics of the diether oil can be thus improved. These blending substances are added as necessary to improve the viscosity, compatibility, etc., of the diether oil. There is no need to add any if the property of the diether oil itself is suitable for the refrigerator.

A diol oil or monool oil additive contains ethylene oxide and propylene oxide as monomer units. If the ethylene oxide is too high, the hygroscopic property of the lubricant is increased, and so its content is preferably 0.5 (weight ratio) or less of the total of such units.

The terminal alkyl group of a monool oil is preferably an alkyl group having 1 - 18 carbon atoms, more preferably, a methyl, ethyl, propyl or butyl group.

A diol oil or monool oil to be blended with the diether oil has a higher viscosity than a diether oil of similar molecular weight because of the presence of a terminal hydroxyl group, and the viscosity of the mixture can be increased when it is blended with diether oil. If too much is blended, the compatibility with refrigerant and low water absorption property are impaired.

If its average molecular weight is less than 500, an added diol oil or monool oil has high compatibility and low viscosity, but its viscosity is decreased and hygroscopic property is also worsened. If its molecular weight exceeds 1800, the viscosity can be increased, while the compatibility with refrigerant is decreased. When the molecular weight reaches 2000, separation from the refrigerant occurs already at room temperature, and this is not desirable. Therefore, the average molecular weight of diol oil and monool oil is 500 - 1800.

To the lubricant oil according to the present invention, various types of additives commonly in use can be added.

Suitable antioxidants are metal deactivators (metal trappers) such as benzotriazole, a benzotriazole derivative, thiadiazole, a thiadiazole derivative, triazole, a triazole derivative or dithiocarbamate, amine type antioxidants such as dioctyl-diphenylamine, phenyl- α -naphthylamine, alkyl-diphenylamine or N-nitrosophenylamine, phenol type antioxidants such as 2,6-di-t-butylpara cresol, 4,4'-methylene-bis (2,6-di-t-butylphenol) or 2,6-di-t-butylphenol, or phosphorus type antioxidants such as tris (2,4-di-t-butylphenyl)-phosphite, tris-nonylphenylphosphite or triphenyl phosphite. It is preferable to use an antioxidant in amount of 0.01 - 10 wt % to the base oil, more preferably 0.01 - 1.0 wt %.

Further, as phosphorus type anti-wear agents, tricresyl phosphate, trioctyl phosphite, dioleoyl hydrogenphosphite or zinc thiophosphate may be added. It is preferable to use the anti-wear agent in amount of 0 - 10 wt % of the base oil, more preferably, 0 - 1.0 wt %.

Suitable rust preventives are succinic acid and succinic acid ester, oleic acid beef tallow amide, barium sulfonate or calcium sulfonate. It is preferable to use a rust preventive in amount of 0.01 - 10 wt %, more preferably 0.01 - 1.0 wt %.

The present invention will now be illustrated by Examples and Comparative Examples. The methods used in the Examples to evaluate the refrigerator oils are as follows:

Compatibility Test Method

Into a glass tube there was put the lubricant oil and refrigerant (1,1,1,2-tetrafluorethane) to a total volume of 2 ml, with the specimen oil and refrigerant as 3 wt % and 10 wt % respectively. After mixing well, the glass tube was placed in a constant-temperature chamber furnished with heating and cooling units, and the temperature of separation into separate phases of the specimen oil and refrigerant was measured.

Hygroscopic Property Test Method

The specimen oil was placed in a dessicator containing water, and its hygroscopic property was measured over time at room temperature and humidity of 95%.

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Example 1

Table 1 shows the results of the performance evaluation as refrigerator lubricant oil when various types of diether oil were added to 1,1,1,2-tetrafluoroethane, which is the refrigerant according to the present invention.

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EO/PO refers to the ratio of ethylene oxide to propylene oxide units in the diether oil.

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Table 1

Specimen oil	1	2	3	4	5	6	7	8	9	10
	The present invention			The present invention	The present invention			The present invention		The present invention
End alkyl group in polyalkylene glycol	Methyl/methyl	Methyl/methyl	Methyl/methyl	Butyl/methyl	Butyl/methyl	Butyl/methyl	Butyl/methyl	Ethyl/methyl	Ethyl/methyl	Methyl/methyl
EO/PO ratio in polyalkylene glycol	0/100	0/100	25/75	0/100	0/100	25/75	50/50	0/100	25/75	0/100
Average molecular weight	1,000	2,000	1,000	900	1,000	1,000	1,000	1,000	1,000	700
Viscosity (cSt 100 °C)	8.9	18.9	8.1	6.8	9.8	7.9	10.0	7.7	7.8	4.0
Compatibility with refrigerant										
High temperature 2-phase separation temperature										
° Oil content 10 wt %	74 °C	38	79	78	63	73	70	79	73	90 or more
° Oil content 3 wt %	80 °C	-	-	-	-	-	-	83	-	-
Low temperature 2-phase separation temperature										
° Oil content 10 wt %	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	Turbidity at -30 °C	-40 °C or lower	-40 °C or lower	-40 °C or lower
Hygroscopic property (moisture %)										
7 days	1.6	-	3.2	1.5	1.2	3.1	3.2	1.5	3.2	2.5
14 days	1.9	-	4.7	1.7	1.6	4.2	4.9	1.8	4.6	2.8
21 days	2.0	-	5.5	1.7	1.7	5.2	5.7	2.0	5.4	3.0
28 days	2.1	-	5.8	1.8	1.7	5.5	6.0	2.1	5.7	3.2

As is evident from Table 1, a diether oil with higher molecular weight (specimen oil No. 2) has lower compatibility at high temperature.

When ethylene oxide is present as a monomer component (specimen oils Nos. 3, 6, 7 and 9), the hygroscopic property increases. When the ethylene oxide content is high, the compatibility at low temperature is decreased. As is evident in the specimen oil 7, turbidity appears at -30°C , and phase separation occurs.

In contrast, in the diether oils Nos. 1, 4, 5, 8 and 10 according to this invention, a good balance is kept between viscosity, compatibility and low hygroscopic property.

Table 2 summarizes the results of an evaluation similar to Table 1, using a diol oil and monool oil (butyl group as alkyl group) having the molecular weight similar to the above diether oil.

Table 2

15	Specimen oil	11	12	13	14	15	16
	Type of polyalkylene glycol	Diol	Diol	Diol	Diol	Monool	Monool
20	EO/PO ratio in polyalkylene glycol	0/100	0/100	0/100	70/30	0/100	50/50
	Average molecular weight	700	1,000	2,000	1,000	1,100	1,000
25	Viscosity (cSt 100°C)	7.5	11.0	22.6	13.3	11.5	11.6
	Compatibility with refrigerant						
30	High temperature 2-phase separation temperature						
	$^{\circ}\text{C}$ Oil content 10 wt %	83°C	64	Separated at room temperature	45	50	55
35	$^{\circ}\text{C}$ Oil content 3 wt %	90°C or higher	84	-	-	-	-
40	Low temperature 2-phase separation temperature						
	$^{\circ}\text{C}$ Oil content 10 wt %	-40°C or lower	-40°C or lower	-	-40°C or lower	-40°C or lower	-40°C or lower
45	Hygroscopic property (moisture %)						
	7 days	4.8	2.9	2.1	5.0	1.9	3.6
	14 days	6.0	4.1	2.7	8.5	2.3	5.7
50	21 days	7.3	4.6	2.8	-	2.4	6.5
	28 days	8.3	5.0	2.9	-	2.5	7.3

As it is evident from Table 2, when only propylene oxide is contained as monomer component, hygroscopic property is high even when viscosity and compatibility can be adjusted (specimen oil 12), and both hygroscopic property and compatibility are worsened in the copolymer with ethylene oxide (specimen oil 14). Also, it is apparent that even a monool oil cannot satisfy three conditions of viscosity, compatibility and hygroscopic property (specimen oils 15 and 16).

Example 2

Table 3 shows the results of the evaluation similar to Example 1 when diol oil or monool oil is added to the mixed oil of diether oil or diether oil to use as refrigerator oil.

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Table 3

Specimen oil	17	18	19	20	21	22	23	24	25
	The present invention			The present invention	The present invention	The present invention			
Base oil	Specimen oil 5	Specimen oil 5	Specimen oil 5	Specimen oil 1	Specimen oil 1	Specimen oil 1	Specimen oil 1	Specimen oil 1	Specimen oil 1
Added oil	Specimen oil 12	Specimen oil 7	Specimen oil 11	Specimen oil 2	Specimen oil 16	Specimen oil 15	Specimen oil 11	Specimen oil 12	Specimen oil 2
Blending ratio 1)	50/50	50/50	24/76	97/3	90/10	90/10	38/62	88/12	80/20
Viscosity (cSt 100 °C)	10.3	9.9	8.0	9.0	9.0	9.0	8.0	9.1	10.6
Compatibility with refrigerant									
High temperature 2-phase separation temperature									
° Oil content 10 wt %	64 °C	67	80	72	71	71	81	73	60
° Oil content 3 wt %	-	-	90 or more	81	-	-	90 or more	82	-
Low temperature 2-phase separation temperature									
° Oil content 10 wt %	-40 °C or lower	Turbidity at -30 °C	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower	-40 °C or lower
Hygroscopic property (moisture %)									
7 days	2.1	2.3	4.3	1.6	2.0	1.8	3.9	1.9	1.5
14 days	3.0	3.5	5.4	1.9	2.5	2.1	4.9	2.4	1.8
21 days	3.5	4.0	6.5	2.0	2.7	2.2	5.8	2.6	1.9
28 days	3.7	4.2	7.4	2.1	2.9	2.3	6.5	2.7	2.0

1) Blending ratio: Base oil:added oil (weight ratio)

1) Blending ratio: Base oil:added oil (weight ratio)

As it is evident from Table 3, the mixed oil of this invention is a mixed oil, containing diether oil of the specimen oil 1 added to a diether having molecular weight of 2000 of specimen oil 2 in a weight ratio of 97/3. The viscosity is apparently improved from the specimen oil 1 shown in Table 1.

However, when a diether oil of molecular weight of 2000 of the specimen oil 2 is added to diether oil of the specimen oil 1 by 80/20, i.e. in more than 10 wt % (specimen oil 25), the separation property at high temperature decreases.

Also, when polyethylene oxide is contained as monomer component as in the specimen oil 18, phase separation occurs at low temperature, and hygroscopic property is also generated, and this is not desirable.

When diol oil of the specimen oil 12 is added to diether oil of specimen oil 1 (specimen oil 24), or when monool oil of specimen oil 15 is added (specimen oil 22), or when monool oil of specimen oil 16 is added (specimen oil 21), viscosity can be apparently improved without impairing compatibility and low hygroscopic property, and it is apparently suitable as refrigerator oil.

On the other hand, when diol oil of specimen oil 11 having low molecular weight is added to diether oil of specimen oil 1 of this invention (specimen oil 23), hygroscopic property is worsened, and it is not suitable as refrigerator oil.

Diether oil of specimen oil 5 has butyl group at the end group, and it has lower compatibility with refrigerant at low temperature as molecular weight increases, whereas, when specimen oil 12 is added (specimen oil 17), the compatibility at low temperature is improved, and it is suitable as a refrigerator oil.

However, when specimen oil 11 is added instead of specimen 12 (specimen oil 19), hygroscopic property is increased although compatibility is improved, and it is apparently not suitable as a refrigerator oil.

Example 3

A sealed tube test at high temperature was performed, using mixtures of various amounts (and controls without the additive) of the specimen oils 1 and 24 of this invention added to 1,1,1,2-tetrafluoroethane refrigerant.

In the testing method (sealed tube test), 1 g of the specimen oil, 1,1,1,2-tetrafluoroethane and one each of iron, copper and aluminum test pieces (shape: 1.7 mm in diameter, 40 mm in length) were placed into a glass tube and the tube was sealed by welding. Then, the tube was heated at 175°C for 14 days (336 hours). At the completion of the test, the discoloration degree of the specimen oil was measured, and the metal pieces were examined.

Thus, to each of the above specimen oils, 0.1 wt % of antioxidant benzotriazole (BTA), or 0.5 wt % of 2,6-di-*t*-butylparacresol (DBPC) and 0.5 wt % of anti-wear agent tricresyl phosphate (TCP) were added, and the above test was performed. The results of the test are summarized in Table 4.

Table 4

	Specimen oil			Hue of specimen oil		External appearance of test piece		
	Base oil	Additive	Added quantity (%)	Before test	After test	Iron	Copper	Aluminum
5	Specimen oil 1	-	-	L0.5	L1.0	Good	Good	Good
10	Specimen oil 1	BTA	0.1	L0.5	L1.0	Good	Good	Good
	Specimen oil 1	DBPC	0.5	L0.5	L1.0	Good	Good	Good
	Specimen oil 1	TCP	0.5	L0.5	L1.0	Good	Good	Good
15	Specimen oil 1	DBPC	0.3	L0.5	L1.0	Good	Good	Good
	Specimen oil 1	TCP	0.3	L0.5	L1.0	Good	Good	Good
	Specimen oil 24	-	-	L0.5	L1.0	Good	Good	Good
	Specimen oil 24	BTA	0.1	L0.5	L1.0	Good	Good	Good
20	Specimen oil 24	DBPC	0.5	L0.5	L1.0	Good	Good	Good
	Specimen oil 24	TCP	0.5	L0.5	L1.0	Good	Good	Good

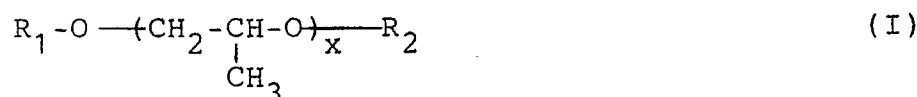
25 As is evident from Table 4, the hue may not be worsened after the test with the compatibility substance of 1,1,1,2-tetrafluoroethane and refrigerator oil of this invention, and less sludge is generated after the test. The external appearance of the test samples were also satisfactory and they were chemically and thermally stable.

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Claims

1. A lubricant for the refrigerant using 1,1,1,2-tetrafluoroethane, which is a polyoxypropylene glycol alkylether oil having an average molecular weight of 500 - 1800 and represented by the formula:

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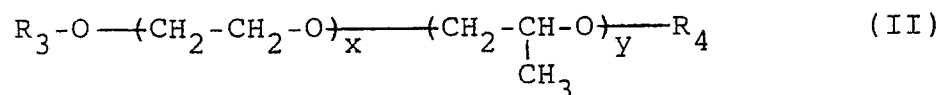


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where R_1 and R_2 each represent an alkyl group having 1 - 4 carbon atoms which may be the same or different from each other.

2. A lubricant as claimed in Claim 1, which also includes a polyoxyalkylene glycol or polyoxyalkylene glycol monoalkylether represented by the formula:

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wherein R_3 and R_4 each represent a hydrogen atom or a hydrocarbon group C_nH_{2n+1} where n is 1 - 18 and they may be the same or different from each other, but they are not both hydrocarbon groups at the same time, and x or y are numbers not equal to zero, and having average molecular weight of 500 - 1800.

3. A lubricant as claimed in Claim 2, wherein the proportion of ethylene oxide units in the ethylene oxide and propylene oxide monomer components of the glycol (II) is not more than 50 wt %.

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4. A lubricant as claimed in any preceding claim, which includes up to 10 wt % of a polyoxypropylene glycol alkyl ether oil of molecular weight more than 1800.

5. A refrigerant composition which comprises 1,1,1,2-tetrafluoroethane and a lubricant as claimed in any

preceding claim.

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EUROPEAN SEARCH REPORT

EP 90 31 0832

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
X	US-A-4 851 144 (P.W. McGRAW) * Column 3, lines 4-7; column 3, lines 22-25; claims 9,14 * - - -	1,5	C 10 M 107/34 C 10 M 111/04		
X	DATABASE WPIL, accession no. 89-274103 [38], Derwent Publications Ltd, London, GB; & JP-A-01 198 694 (IDEMITSU KOSAN) 10-08-1989 * Abstract * - - -	1,5	C 10 M 169/04 C 09 K 5/04 // (C 10 M 111/04 C 10 M 105:52 C 10 M 107:34)		
X	US-A-2 717 242 (E.G. FOEHR) * Column 4, example 2; column 6, line 30; claim 4 * - - -	1	(C 10 M 169/04 C 10 M 105:52		
A	US-A-4 755 316 (H. MAGID) * Column 6, table A, lines 22-29; column 8, example 2, table B * - - -	1-5	C 10 M 107:34 C 10 M 107:34) C 10 N 20:04 C 10 N 40:30		
A	DATABASE WPI, accession no. 78-75637A [42], Derwent Publications Ltd, London, GB; & RD-A-174 063 (DU PONT DE NEMOURS) 20-09-1978 * Abstract * - - -	4,5			
A	DE-A-2 943 446 (NIPPON OIL) * Page 5, line 28 - page 6, line 7; page 7, lines 24-27 * - - -	1,2,5	TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
X	US-A-2 520 612 (F.H. ROBERTS) * Column 4, lines 48-58; column 5, example 1 * - - -	1	C 10 M C 09 K		
A	DE-A-2 820 640 (NIPPON OIL) - - -				
P,X	DATABASE WPIL, accession no. 89-345395 [47], Derwent Publications Ltd, London, GB; & JP-A-01 259 094 (KYOSEKI SEIHIN GIJU) 16-10-1989 * Abstract * - - - -/-	1,5			
The present search report has been drawn up for all claims					
Place of search The Hague		Date of completion of search 23 November 90	Examiner HILGENGA K.J.		
<table><tr><td>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</td><td>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</td></tr></table>				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
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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 0832

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	DATABASE WPIL, accession no. 89-345394 [47], Derwent Publications Ltd, London, GB; & JP-A-01 259 093 (KYOSEKI SEIHIN GIJU) 16-10-1989 * Abstract * -----	1,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		23 November 90	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			