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(57) Abstract

A lubricant comprising as a base oil an ester composition consisting essentially of: (1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6; and optionnally (2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6, wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

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LUBRICANTS FOR HEAT TRANSFER DEVICES

The present invention relates generally to lubricants for heat transfer devices and more particularly to lubricants for heat transfer devices which use a hydrofluorocarbon, especially 1,1,1,2-tetrafluoroethane (HFC-134a), as the refrigerant. In particular, the present invention is concerned with the provision of a lubricant for reciprocal or rotary type domestic refrigerators, and small air conditioning systems (excluding car air conditioners) which use a hydrofluorocarbon refrigerant.

Heat transfer devices of the mechanical compression type such as refrigerators, freezers, heat pumps and air conditioning systems are well known. In such devices a refrigerant liquid of a suitable boiling point evaporates at low pressure taking heat from a surrounding zone. The resulting vapour is then compressed and passes to a condenser where it condenses and gives off heat to a second zone. The condensate is then returned through an expansion valve to the evaporator so completing the cycle. The mechanical energy required for compressing the vapour and pumping the liquid may be provided by an electric motor or an internal combustion engine.

Hitherto, heat transfer devices have tended to use fully and partially halogenated chlorofluorocarbon refrigerants such as trichlorofluoromethane (Refrigerant R-11), dichlorodifluoromethane (Refrigerant R-12) and chlorodifluoromethane (Refrigerant R-22). However, these compounds have been implicated in the destruction of the earth's protective ozone layer and as a result the use and production thereof is to be severely limited by international agreement.

The use of certain hydrofluorocarbons, i.e. compounds which contain only carbon, hydrogen and fluorine atoms in their structure, in place of the fully and partially halogenated chlorofluorocarbons has been proposed. Particular mention may be made of 1,1,1,2-tetrafluoroethane (HFC-134a).

In a heat transfer device, the refrigerant forms part of a working fluid composition which also comprises a lubricant. The lubricant provides for lubrication of the moving parts of the compressor, and in order to function satisfactorily needs to be compatible with the refrigerant. Lubricants based on mineral oils have the desired compatibility with chlorofluorocarbon refrigerants and hitherto have been widely used in heat transfer devices. Unfortunately, however, lubricants based on mineral oils tend to exhibit poor compatibility with the replacement hydrofluorocarbon refrigerants and cannot be used as a lubricant with such refrigerants. Accordingly, there is a need to develop a lubricant for use with the replacement hydrofluorocarbon refrigerants, especially HFC-134a.

US-4,755,316 discloses a lubricant for use in refrigeration systems containing HFC-134a which comprises a polyoxyalkylene glycol (PAG) which is at least difunctional with respect to hydroxyl groups. Although such polyoxyalkylene glycols may exhibit acceptable miscibility with HFC-134a, they often attract water and as a result tend to cause corrosion of the equipment and lose their insulation properties.

Lubricants comprising fatty acid esters of polyhydric alcohols have also been proposed for use with HFC-134a.

For example, EP-406479 A1 discloses a lubricant for hydrofluorocarbon refrigerants such as HFC-134a which comprises as the base oil an ester obtained by reacting at least one straight and/or branched chain monovalent fatty acid having a carbon number of 2 to 18 with at least one polyhydric alcohol having three or more hydroxyl groups. Although a large number of ester based lubricants are encompassed by the general disclosure in this publication, there is no specific disclosure of the lubricant with which the present invention is concerned and which has been found to provide a particularly good combination of properties.

EP-430657 A1 also discloses a lubricant for hydrofluorocarbon refrigerants such as HFC-134a which comprises a neopentyl polyol ester of a straight and/or branched chain fatty acid having 2 to 6 carbon atoms. However, there is no specific disclosure of the presently claimed lubricant which surprisingly has been found to provide a particularly good combination of properties.

The present inventors have now developed a lubricant which exhibits a good overall performance in heat transfer devices which use a hydrofluorocarbon, especially HFC-134a, as the refrigerant.

According to the present invention there is provided a lubricant comprising as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon

number of 6 and the branched chain fatty acid has a carbon number of at least 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6,

wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

With reciprocal or rotary type domestic refrigerators and small air conditioning systems (excluding car air conditioners) which use HFC-134a, a particularly desirable lubricant is one which simultaneously satisfies the following four criteria.

1) A mixture comprising HFC-134a and 10-15 % by weight, based on the weight of the HFC-134a, of the lubricant is compatible in at least the temperature range -30°C to +80°C.
2) The lubricant has a viscosity in the range of from 12-43 cSt at 40°C, and a viscosity in the range of from 3-7 cSt at 100°C.
3) The lubricant has a Falex failure load of 1000 pounds or more as measured in accordance with the procedure of ASTM D-3233.
4) The lubricant is stable under long term continuous operation, and even if it should absorb water, any hydrolysis products which are formed do not exhibit strong corrosive properties for the metal materials which contact with the lubricant.

The lubricant of the present invention can satisfy the above four criteria and, accordingly, may be usefully employed in reciprocal or rotary type domestic refrigerators and small air conditioning systems (excluding car air conditioners) which use HFC-134a as the refrigerant. Heat transfer devices of this type include those with a power source motor having an output of 0.5 horse power or less, and frequently 0.25 horse power or less.

In a heat transfer device, the lubricant will form part of a working fluid composition which also comprises a refrigerant.

Accordingly, the present invention also provides a working fluid composition which comprises:

(i) at least one hydrofluorocarbon; and

(ii) a lubricant comprising as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6,

wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

The refrigerant component (i) preferably comprises HFC-134a and more preferably will consist solely of HFC-134a.

The lubricant of the present invention comprises, as a base oil, an ester composition which comprises at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid having a specified carbon number. The pentaerythritol ester(s) must constitute at least 50 % by weight, i.e. from 50 to 100 % by weight, of the total weight of the base oil. The base oil may also comprise up to 50 % by weight, i.e. from 0 to 50 % by weight, of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid having a specified carbon number. Inclusion of a dipentaerythritol ester into the base oil increases the viscosity of the base oil and so the viscosity of the lubricant. Thus, a suitable amount of a dipentaerythritol ester may be and preferably is included in the base oil in order to adjust the viscosity thereof.

The fatty acid component of the ester composition must comprise at least 50 % by weight, i.e. from 50 to 100 % by weight, of caproic acid (i.e. hexanoic acid), and may comprise up to 50 % by weight, i.e. from 0 to 50 % by weight, of one or more branched chain, monovalent, saturated fatty acids having a carbon number of at least 6. This means that at least 50 % by weight, i.e. from 50 to 100 % by weight, of the fatty acid component used in the synthesis of the ester must consist of caproic acid. Preferably, the fatty acid component comprises at least 65 % by weight, i.e. from 65 to 100 % by weight, of caproic acid (i.e. hexanoic acid), and up to 35 % by weight, i.e. from 0 to 35 % by weight, of one or more branched chain, monovalent, saturated fatty acids having a carbon number of at least 6.

Preferably, any branched chain fatty acid which is used in the synthesis of the ester composition will also have a carbon number of 6.

Accordingly, in a preferred embodiment of the present invention there is provided a lubricant comprising as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid having a carbon number of 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid having a carbon number of 6,

wherein at least 50 % by weight of the C6 fatty acid component consists of caproic acid.

Suitable C_6 branched chain, monovalent, saturated fatty acids include, inter alia, methylvaleric acid, ethylbutyric acid, neohexanoic acid and isohexanoic acid. Mixtures of C_6 branched chain fatty acids may also be used.

Esterifiable derivatives of the fatty acids may also be used to prepare the ester composition, such as the acyl halides, anhydrides and lower alkyl esters thereof, and whenever reference is made herein to fatty acids, the esterifiable derivatives thereof are included. Suitable acyl halides are the acyl chlorides and suitable lower alkyl esters are the methyl esters.

The lubricant base oil may consist solely of the ester of pentaerythritol and caproic acid or it may be a mixed ester composition. Suitable mixed ester compositions include the following:

(A) A composition comprising the pentaerythritol esters of caproic acid and at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6.

(B) A composition comprising the pentaerythritol and dipentaerythritol esters of caproic acid.

(C) A composition comprising the pentaerythritol ester of caproic acid and the dipentaerythritol ester(s) of at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6.

(D) A composition comprising the pentaerythritol ester(s) of at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6 and the dipentaerythritol ester of caproic acid.

(E) A composition comprising the pentaerythritol esters of caproic acid and at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6 and the dipentaerythritol ester of caproic acid.

(F) A composition comprising the pentaerythritol ester of caproic acid and the dipentaerythritol esters of caproic acid and at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6.

(G) A composition comprising the pentaerythritol esters of caproic acid and at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6 and the dipentaerythritol esters of caproic acid and at least one branched chain, monovalent, saturated fatty acid having a carbon number of 6.

Of course, where the base oil is a mixed ester composition, it must contain the requisite amount of a pentaerythritol ester, i.e. at least 50 % by weight, e.g. from 50 to 99 % by weight, of the base oil must consist of a pentaerythritol ester(s). Moreover, the caproic acid must constitute at least 50 % by weight, e.g from 50 to 99 % by weight, of the fatty acid component used in the synthesis of the ester.

Mixed ester compositions comprising both pentaerythritol and dipentaerythritol esters are preferred and may be prepared by mixing together separately formed esters of pentaerythritol and dipentaerythritol. Alternatively, they may be prepared in a single step reaction in which a mixture of pentaerythritol and dipentaerythritol is reacted with caproic acid and optionally one or more branched chain, monovalent, saturated fatty acids having a carbon number of at least 6 and preferably 6.

The lubricants of the present invention were developed as a result of a number of important findings.

Firstly, as a result of the studies of the inventors, it was realised that the esters of pentaerythritol and dipentaerythritol are extremely stable to heat and importantly are appreciably more stable than the esters of glycols, such as ethylene glycol and propylene glycol, and trihydric alcohols, such as glycerol.

Secondly, as far as the fatty acids are concerned, esters of unsaturated fatty acids are susceptible to oxidation, cleavage, polymerisation and the like and cannot withstand the conditions to which they will be subjected in a heat transfer device, i.e. long term continuous operation. In consequence, only saturated fatty acids are used to prepare the lubricant base oil.

Of the esters of straight chain, saturated fatty acids, the following properties were observed as a result of experimental studies.

The esters of C_{2-5} straight chain, saturated fatty acids have excellent compatibility with HFC-134a, but exhibit poor lubricating properties. Furthermore, if C_{2-5} straight chain, saturated fatty acids are released, e.g. by hydrolysis of the ester, the acidity thereof is such that they may corrode the metal, for example copper and iron, which is contacted by the lubricant. Therefore, the lubricant base oil of the present invention does not comprise esters of straight chain, saturated fatty acids with a carbon number of 5 or less.

As far as the esters of straight chain, saturated fatty acids having a carbon number of 7 or more are concerned, it has been found that such esters exhibit poorer compatibility with HFC-134a than the C_6 fatty acid esters. Thus, in order to prepare the lubricant base oil of this invention, it is necessary to limit the chain length of the straight chain fatty acid to 6.

The esters of C_{2-5} branched chain, saturated fatty acids have excellent compatibility with HFC-134a, but have two major disadvantages. Firstly, they exhibit poor lubricating properties and, secondly, if C_{2-5}

branched chain, saturated fatty acids are released, e.g. by hydrolysis of the ester, they have a tendency to corrode the metal which is contacted by the lubricant. Therefore, the lubricant base oil of the present invention does not comprise esters of branched chain, saturated fatty acids with a carbon number of 5 or less.

As for the esters of branched chain, saturated fatty acids having a carbon number of 7 or more, these exhibit superior compatibility with HFC-134a than the esters of straight chain fatty acids having the same carbon number, but the lubricating properties are not ideal. Therefore, the preferred lubricant base oil of the present invention does not comprise esters of branched chain, saturated fatty acids with a carbon number of 7 or more.

As stated above, the viscosity of the lubricant can be increased by including a dipentaerythritol ester in the base oil. Thus, the viscosity of the lubricant can be adjusted to meet the viscosity requirements of a particular application by including a set amount of a dipentaerythritol ester in the base oil. For example, in cases where there is a high pressure on the rubbing and moving parts of the compressor or the compressor operates at high speed (for example, in a refrigerator having high refrigeration efficiency, a large refrigeration capacity or a refrigerator of the rotary type), the amount of the dipentaerythritol ester in the base oil can be increased in order to increase the viscosity of the lubricant. On the other hand, in cases where the pressure on the rubbing and moving parts of the compressor is low or the compressor operates at low speed, the amount of the pentaerythritol ester in the base oil can be increased in order to depress the viscosity and increase the energy efficiency of the heat transfer device.

The composition of the fatty acid component can also be adjusted within the range of 50 to 100 % by weight caproic acid and 0 to 50 % by weight of a C_6 or more branched chain, monovalent, saturated fatty acid(s) according to the required lubricating properties, the required viscosity, and the required compatibility.

The degree of esterification of the ester base oil used in this invention is preferably 100%, i.e. all the hydroxyl groups of the polyol component will preferably have been reacted in the esterification reaction. However, even if a reaction is carried out with a stoicheiometric excess of the fatty acid component, a long reaction time may be required to fully complete the reaction and consume all the hydroxyl groups in the reaction mixture. In fact, an ester base oil having a degree of esterification of 98% or more, i.e. 98 % or more of the hydroxyl groups provided by the polyol component have been esterified, is quite acceptable. However, as the degree of esterification is lowered, the compatibility with HFC-134a decreases, and we have found that the compatibility decreases suddenly if the degree of esterification of the base oil ester drops below about 90 %. Thereafter, the desirable properties of the present lubricant are lost, and, therefore, the lower limit of the degree of esterification of the ester base oil is about 90 %.

The lubricant of the present invention may comprise at least one additive selected from the group consisting of an antioxidant, a deacidifying agent and an extreme pressure agent.

Thus, in accordance with a further aspect of the present invention, there is provided a lubricant comprising:

(A) as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6,

wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6; and

(B) at least one additive selected from the group consisting of an antioxidant, a deacidifying agent and an extreme pressure agent.

Preferred antioxidants are the compounds containing a hindered phenol in the molecule, preferred deacidifying agents are the compounds containing an epoxy group in the molecule, and the preferred extreme pressure agents are the phosphate esters of phenol which may be substituted by a lower alkyl group, or the phosphate esters of monovalent, saturated, aliphatic alcohols.

The following compounds are representative of the preferred antioxidants, deacidifying agents and extreme pressure agents.

Antioxidants: 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-hydroxyphenol, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 2,2'-butylidenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene and the like.

Deacidifying agents: Phenyl glycidyl ether, butylglycidyl ether, bisphenol A epichlorohydrin condensate, vinylcyclohexene dioxide, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxycyclohexane)-meta-dioxane, 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexane carboxylate, polypropylene glycol diglycidyl ether, resorcin diglycidyl ether, polyethylene glycol diglycidyl ether and the like.

Extreme pressure agents: Tricresyl phosphate, trisnonylphenylphosphite, distearyl phosphate, tributylphosphate, trilaurylphosphate, trilaurylphosphite, mono-di-mixed-lauryl phosphite, mono-di-mixed-tridecyl phosphate, mono-2-ethylhexyl-2-ethylhexylphosphate, di-2-ethylhexyl phosphate and the like.

The present invention is now illustrated, but not limited, by the following examples.

EXAMPLES

Synthesis 1

Synthesis of base oil A1 - a pentaerythritol ester of caproic acid (degree of esterification 99.1 %)

108.9 g (0.8 moles) of pentaerythritol and 557.8 g (4.8 moles) of caproic acid were charged to a 2-litre round-bottomed flask and then mixed together. To the resulting mixture were added 1 g of active carbon (powdered form, Katayama Kagaku) and 3 drops of sulphuric acid as catalysts. The reactant mixture was then heated at 180 °C under reflux in an atmosphere of nitrogen. The water formed during the esterification reaction was removed and collected in a quantitative water receiver (a Dean and Stark Column). When the theoretical quantity of water (57.7 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 3 hours. The active carbon was removed from the viscous liquid remaining in the flask by filtration, and the crude ester was then purified by passing through a column filled with alumina (chromatography grade, Katayama Kagaku). 381.9 g of the pure ester with a total acid value of 0.01 mg KOH/g or less was obtained. The degree of esterification of the purified ester was calculated from the hydroxy group value obtained using the method of JIS K0070 and was found to be 99.1 %. The yield of pure ester was 90.9 % (the yield on pentaerythritol taking into account the degree of esterification).

The reagents used in this synthesis and the following syntheses were Special Grade or Grade 1 reagents manufactured by Katayama Kagaku unless otherwise stated.

Synthesis 2

Synthesis of base oil A2 - a pentaerythritol ester of caproic acid (degree of esterification 98.4 %)

136.2 g (1.0 mole) of pentaerythritol and 488.0 g (4.2 moles) of caproic acid were mixed together and to this mixture 1 g of active carbon and 3 drops of sulphuric acid were added as catalysts. The reaction was then carried out using the same method as described in Synthesis 1. When the theoretical quantity of water (72.1 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 3 hours. The ester was purified, the degree of esterification measured and the yield determined using the techniques described in Synthesis 1.

Synthesis 3

Synthesis of base oil A3 - a pentaerythritol ester of caproic acid (degree of esterification 94.6 %)

136.2 g (1.0 mole) of pentaerythritol and 464.8 g (4.0 moles) of caproic acid were mixed together and to this mixture 1 g of active carbon and 3 drops of sulphuric acid were added as catalysts. The reaction was then carried out using the same method as described in Synthesis 1. When the theoretical quantity of water (72.1 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 3 hours. The ester was purified, the degree of esterification measured and the yield determined using the techniques described in Synthesis 1.

Comparative Synthesis 1

Synthesis of comparative base oil E1 - a pentaerythritol ester of caproic acid (degree of esterification 87.5 %)

136.2 g (1.0 mole) of pentaerythritol and 429.9 g (3.7 moles) of caproic acid were mixed together and to this mixture 1 g of active carbon and 3 drops of sulphuric acid were added as catalysts. The reaction was then carried out using the same method as described in Synthesis 1. When the theoretical quantity of water (66.7 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 3 hours. The ester was purified, the degree of esterification measured and the yield determined using the techniques described in Synthesis 1.

The results for Syntheses 2 and 3 and Comparative Synthesis 1 are shown in Table 1.

Table 1

Base oil	Yield (g)	Degree of Esterification	Yield (%)
A2	472.1	98.4	90.4
A3	444.8	94.6	87.6
E1	421.8	87.5	87.9

The base oils A1, A2 and A3 prepared above were each pentaerythritol caproic acid esters. Each of these oils can be used alone as a base oil in the lubricant of the present invention, or they can be blended with additive esters of dipentaerythritol to form a mixed ester composition which can also serve as a base oil in the lubricant of the invention. Similarly, the "A" series oils which are prepared hereinafter can be used as base oils in the lubricant of the present invention.

The esters B1 and B2 prepared in the following Syntheses 5 and 6 are dipentaerythritol esters and cannot be used alone as a base oil in the lubricant of the present invention. Thus, where the lubricant comprises only ester B1 or ester B2 as a base oil it is a comparative lubricant. However, the esters B1 and B2 can be formulated with a pentaerythritol ester, e.g. one of the "A" series base oils, to form a mixed ester composition which is useful as a base oil in the lubricant of the present invention. Therefore, the esters B1 and B2 are hereinafter termed additive oils.

Comparative base oil E1, with a degree of esterification of less than 90%, did not have the required compatibility with HFC-134a and, therefore, could not be used as a base oil in the lubricant of the present invention.

Synthesis 4

Synthesis of base oil A4 - a pentaerythritol ester of caproic acid and 2-ethylbutyric acid (weight ratio of acids 1:1)

136.2 g (1.0 mole) of pentaerythritol and 348.6 g (3.0 moles) of each of caproic acid and 2-ethylbutyric acid were charged to a 2-litre round-bottomed flask and then mixed together. To the resulting mixture were added the active carbon and sulphuric acid catalysts and an esterification reaction was then carried out using the method described in Synthesis 1.
When the theoretical quantity of water (72.1 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 3 hours. Purification of the ester was carried out as in Synthesis 1. 470.2 g of the ester with a degree of esterification of 98.1% was finally recovered. The yield was 90.0%.

Synthesis 5

Synthesis of additive oil B1 - a dipentaerythritol ester of caproic acid and 2-ethylbutyric acid (weight ratio of acids 1:1)

127.2 g (0.5 moles) of dipentaerythritol and 261.5 g (2.25 moles) of each of caproic acid and 2-ethylbutyric acid were charged to a 2-litre round-bottomed flask and then mixed together. To the resulting mixture were added the active carbon and sulphuric acid catalysts and an esterification reaction was then carried out using the method described in

Synthesis 1. When the theoretical quantity of water (54.1 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 6 hours. Purification of the ester was carried out as in Synthesis 1. 337.3 g of the ester with a degree of esterification of 92.0 % was finally recovered. The yield was 84.7%.

Synthesis 6

Synthesis of additive oil B2 - a dipentaerythritol ester of 2-ethylbutyric acid

127.5 g (0.5 moles) of dipentaerythritol and 523.0 g (4.5 moles) of 2-ethylbutyric acid were charged to a 2-litre round-bottomed flask and then mixed together. To the resulting mixture were added the active carbon and sulphuric acid catalysts and an esterification reaction was then carried out using the method described in Synthesis 1. When the theoretical quantity of water (54.1 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 7 hours. Purification of the ester was carried out as in Synthesis 1. 330.0 g of the ester with a degree of esterification of 93.5 % was finally recovered. The yield was 82.0 %.

Synthesis 7

Synthesis of base oil A5 - a pentaerythritol/ dipentaerythritol ester of caproic acid and 2-ethylbutyric acid (weight ratio of polyols 1:1; weight ratio of acids 1:1)

50.0 g (0.37 moles) of pentaerythritol, 50.0 g (0.20 moles) of dipentaerythritol and 231.2 g (1.99 moles) of each of caproic acid and 2-ethylbutyric acid were charged to a 2-litre round-bottomed flask and then mixed together. To the resulting mixture were added the active carbon and sulphuric acid catalysts and an esterification reaction was then carried out using the method described in Synthesis 1. When the theoretical quantity of water (49.8 ml) had been formed, the reaction was deemed to be completed and was then terminated. The necessary reaction time was about 5 hours. Purification of the ester was carried out as in Synthesis 1. 298.6 g of the ester with a degree of esterification of 97.5 % was finally recovered. The yield was 84.4%. Analysis of the ester by liquid chromatography showed that the weight ratio of pentaerythritol ester to dipentaerythritol ester was 54:46 and that caproic acid comprised 54.8 % by weight of the acid component in the ester composition.

Comparative Syntheses 2-10

Synthesis of comparative base oils E2 to E9 and comparative additive oil E13

The selected polyol was reacted with an excess quantity of the selected fatty acid in accordance with

Synthesis 1. The reaction was terminated when the theoretical quantity of water was observed to have been formed. The comparative base oils E2 to E9 were obtained after alumina purification. The polyols and monovalent fatty acids which were used and the combined proportions of the fatty acids on a weight basis are shown in Table 2.

Table 2

	Polyvalent alcohol (weight ratio)		Monovalent fatty acid (weight ratio)
E2	pentaerythritol	-	valeric acid
E3	pentaerythritol	-	valeric acid (50) 2-methylbutyric acid (50)
E4	dipentaerythritol	-	valeric acid (50) 2-methylbutyric acid (50)
E5	pentaerythritol	-	caproic acid (50) enanthic acid (50)
E6	pentaerythritol		enanthic acid
E7	pentaerythritol		2-ethylcaproic acid
E8	pentaerythritol		branched C_7 (33) branched C_8 (67)
E9	pentaerythritol		branched C_9
E13	dipentaerythritol		enanthic acid

Preparation of mixed ester base oils:

In the following preparations, the mixed ester base oils C1 to C7 are base oils of the invention whereas the mixed ester base oils E10 to E12, and E14 are comparative base oils.

<u>Preparation of base oil C1 - a 1:1 mixture (on a weight basis) of base oil A1 (the pentaerythritol ester of caproic acid) and additive oil B1 (the dipentaerythritol ester of caproic acid and 2-ethylbutyric acid)</u>

25.0 g of base oil A1 and 25.0 g of additive oil B1 were weighed into a 100 ml beaker and then stirred for 30 minutes with a magnetic stirrer. The viscosity of the obtained base oil (C1) was determined at 40°C and 100°C with an Ubbelohde viscometer in accordance with the method of JIS K2283.

<u>Preparation of base oils C2 and C3 and comparative base oils E10 and E11 by mixing varying proportions of base oil A1 and additive oil B1.</u>

The prescribed weights of base oil A1 and additive oil B1 were placed into a 1 litre round-bottomed flask equipped with a stirrer. The mixture was then heated to 60°C and stirred for about 30 minutes. 500 g each of the base oils C2 and C3 and the comparative base oils E10 and E11 were obtained.

The composition of the base oils C1 to C3 and comparative base oils E10 and E11 are shown in Table 3.

Table 3

Base oils C and comparative base oils E	Composition Amount of base oil A1 - wt. %	 Amount of additive oil B1 wt. %
C1	50	50
C2	70	30
C3	55	45
E10	30	70
E11	18	82

Preparation of base oils C4 and C5 and comparative base oil E12 by mixing varying proportions of base oil A4 and additive oil B1.

The prescribed weights of base oil A4 and additive oil B1 were placed into a 1 litre round-bottomed flask equipped with a stirrer. The mixture was then heated to 60°C and stirred for about 30 minutes.

The composition of the base oils C4 and C5 and comparative base oil E12 are shown in Table 4.

Table 4

Base oils C and comparative base oil E	Composition Amount of base oil A4 - wt. %	 Amount of additive oil B1 wt. %
C4	70	30
C5	50	50
E12	30	70

Preparation of base oils C6 and C7 and comparative base oil E14 by mixing varying proportions of base oil A1 and additive oil B2.

The prescribed weights of base oil A1 and additive oil B2 were placed into a 1 litre round-bottomed flask equipped with a stirrer. The mixture was then heated to 60°C and stirred for about 30 minutes.

The composition of the base oils C6 and C7 and comparative base oil E14 are shown in Table 5.

Table 5

Base oils C and comparative base oil E	Composition	
	Amount of base oil A1 - wt. %	Amount of additive oil B2 wt. %
C6	75	25
C7	70	30
E14	25	75

Formulated lubricants D1 to D12 comprising base oil A1 and various additives:

Examples of formulated lubricants of this invention are shown in Table 6.

Table 6

Lubricant	D1	D2	D3	D4	D5	D6
Additive						
Antioxidant 1	-	-	-	-	-	1.0
Antioxidant 2	0.5	-	0.5	-	0.5	-
Deacidifying Agent 1	-	1.0	1.0	-	1.0	-
Deacidifying Agent 2	-	-	-	-	-	-
Extreme Pressure Agent 1	-	-	-	-	-	-
Extreme Pressure Agent 2	-	-	-	-	-	-
Extreme Pressure Agent 3	-	-	-	2.0	2.0	-

Table 6 continued

Lubricant	D7	D8	D9	D10	D11	D12
Additive						
Antioxidant 1	-	-	-	-	-	-
Antioxidant 2	-	-	-	-	-	-
Deacidifying Agent 1	-	-	-	-	-	-
Deacidifying Agent 2	1.2	-	-	-	-	-
Extreme Pressure Agent 1	-	0.05	0.06	-	-	-
Extreme Pressure Agent 2	-	-	-	1.0	2.0	-
Extreme Pressure Agent 3	-	-	-	-	-	2.0

The numbers in Table 6 represent the weight in grammes (g) of each additive added to 100 g of the base oil A1. The additives are as follows:

Antioxidant 1

1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)-butane (Topanol CA, a product manufactured by ICI, England).

Antioxidant 2

2,6-di-t-butyl-4-methylphenol.

Deacidifying Agent 1

Polypropylene glycol diglycidyl ether (DER736, a product manufactured by Dow Chemicals, USA.)

Deacidifying Agent 2

3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexane-carboxylate (ERL-4221, a product manufactured by Union Carbide, USA)

Extreme Pressure Agent 1

Mono-di mixed lauryl phosphate (Phoslex A12, a product manufacture by Sakai Kagaku Kogyo)

Extreme Pressure Agent 2

Trilaurylphosphate (a product manufactured by Daihachi Kagaku Kogyo).

Extreme Pressure Agent 3

Tricresylphosphate (a product manufactured by Akzo Japan)

Example 1

Accelerated tests were carried out to determine the hydrolytic stability of various oils and the iron dissolution properties of the hydrolysed oils. The oils tested were A1 (the pentaerythritol ester of caproic acid), E3 (the pentaerythritol ester of valeric acid and 2-methyl butyric acid and E4 (the dipentaerythritol ester of valeric acid and 2-methyl butyric acid.

The total acid value and water content of the test oil were adjusted to 0.01 mgKOH/g or less and 2000 ppm respectively before the test. 600 g of the test oil was charged to a 1 litre iron autoclave together with 80 g HFC-134a. The autoclave was sealed and maintained at a temperature of 175°C for 30 days. After cooling the autoclave to room temperature, the oil was removed. The total acid value of the oil was measured and the concentration of the iron which had dissolved into the oil determined by fluorescent X-ray spectroscopy. The results are shown in Table 7.

Table 7

Test Oil	Total acid value (mgKOH/g)	Iron concentration (ppm)
A1	1.12	5.6
E3	2.30	231
E4	2.15	155

From the above results, it is apparent that the esters of fatty acids with a carbon number of 5, namely E3 and E4, readily hydrolyse, and elute large quantities of iron during the accelerated tests.

Example 2

Investigations were carried out to determine the viscosity at 40°C and 100°C, the compatibility with HFC-134a, the thermal stability and the lubricating properties of lubricants comprising only base oils A and C and the formulated lubricants D (all of which are lubricants of this invention). By way of comparison, the same investigations were carried out for lubricants comprising the additive oils B or comparative base oils E which are outside the scope of this invention. The experimental methods which were used are described below.

Viscosity Determination Test

The viscosities were determined at 40°C and 100°C for each test lubricant using a Ubbelohde viscometer in accordance with the method of JIS K2283.

Compatibility Test

Into a glass autoclave were introduced and sealed 5.1 g of the refrigerant HFC-134a and 0.9 g of the lubricant to be tested. The refrigerant and lubricant were then thoroughly mixed by shaking. In order to determine the compatibility (miscibility) of the lubricant/refrigerant mixture at low temperatures, the mixture was gradually cooled in a freezer down to -50°C and visually examined during the cooling for evidence of phase separation (the mixture turns cloudy). On the high temperature side, the mixture was gradually heated to 80°C and observed in the same way for evidence of phase separation.

Thermal Stability Test

Into a stainless steel autoclave were introduced and sealed 50 g of the lubricant to be tested, 25 g of the refrigerant HFC-134a and 3.7 g of metal pieces (copper, iron and aluminium). The mixture was heated at 175°C for 14 days and then cooled. The lubricant was removed from the autoclave and the hues thereof determined in accordance with JIS K2580. Furthermore, the total acid value of the lubricant was measured in accordance with JIS K2501.

Falex Failure Load Test

The failure load (in pounds) of each lubricant was determined in accordance with the method of ASTM D-3233 using a Falex experimental apparatus.

Table 8 shows the measured values for the viscosity, compatibility, thermal stability and Falex failure load for lubricants of this invention comprising base oils C1 to C7 and A1 to A5 and, as a comparison, for lubricants comprising the additive oils B1 and B2 and lubricants comprising comparative base oils E1 to E14.

Table 8

	Viscosity (cSt)		Phase separation temperature (°C)		Failure Load (lb)	Heat Test
	40°C	100°C	Low Temp.	High Temp.		
A1	18.5	4.1	-50 or less	80 or more	1200	L 0.5
A2	18.4	4.1	-46	80 or more	1050	L 0.5
A3	19.3	4.2	-40	80 or more	1100	L 0.5
A4	24.2	4.6	-50 or less	80 or more	1100	L 0.5
A5	37.0	6.8	-50 or less	80 or more	1050	L 0.5
C1	35.7	6.3	-50 or less	80 or more	1100	L 0.5
C2	27.1	5.3	-50 or less	80 or more	1050	L 0.5
C3	32.0	5.7	-50 or less	80 or more	1100	L 0.5
C4	33.7	5.7	-50 or less	80 or more	1000	L 0.5
C5	42.8	6.8	-50 or less	80 or more	1000	L 0.5
C6	27.5	5.3	-50 or less	80 or more	1000	L 0.5
C7	30.1	5.6	-50 or less	80 or more	1000	L 0.5
B1	83.0	10.8	-50 or less	80 or more	900	L 0.5
B2	208.1	16.1	-50 or less	80 or more	800	L 0.5
E1	21.0	4.3	-23	80 or more	1000	L 0.5
E2	15.5	3.7	-50 or less	80 or more	800	L 0.5
E3	17.9	3.8	-50 or less	80 or more	1050	L 0.5
E4	64.5	9.5	-50 or less	80 or more	750	L 0.5
E5	20.5	4.4	-20	80 or more	1100	L 0.5
E6	23.8	4.9	+ 5	80 or more	1050	L 0.5
E7	32.5	5.6	-37	80 or more	800	L 0.5
E8	45.3	6.6	-26	80 or more	800	L 0.5
E9	122.3	16.7	+25 or more	-	750	L 0.5
E10	48.4	7.7	-50 or less	80 or more	1000	L 0.5
E11	56.0	8.3	-50 or less	80 or more	950	L 0.5
E12	55.3	8.1	-50 or less	80 or more	900	L 0.5
E13	44.4	7.6	+25 or more	-	950	L 0.5
E14	85.6	10.1	-50 or less	80 or more	800	L 0.5

From the results of the viscosity measurements on the lubricants of this invention, it is confirmed that they meet the desired viscosity requirements (i.e. a viscosity of from 12-43 cSt at 40°C and a viscosity of from 3-7 cSt at 100°C).

As far as the compatibility with HFC-134a is concerned, it was found that the phase separation temperature at the low temperature end for a blend of HFC-134a and the pentaerythritol ester E6 of enanthic acid (a straight chain, monovalent, saturated fatty acid having carbon number 7) was 5°C which is well above the desired value of -30°C or less. Furthermore, with a pentaerythritol ester of branched chain, monovalent fatty acids with carbon numbers of 7 and 8 (see comparative base oil ester E8), the phase separation temperature on the low side of -26 °C is also above the desired value of -30°C. In addition, with the pentaerythritol ester E9 of a branched chain fatty acid with a carbon number of 9, the phase separation temperature was remarkably high at +25° C or more. It is therefore confirmed that lubricants comprising these base oils are not satisfactory. Moreover, the dipentaerythritol ester E13 of enanthic acid is unsatisfactory, because, in the same way, the phase separation temperature was 25°C or more which means that phase separation will result at room temperatures.

As far as the Falex failure load is concerned, the lubricant base oil A1 (i.e. the pentaerythritol ester of caproic acid) showed a high value of 1200 lb. When the proportion of branched chain, saturated fatty acid was increased in the ester (see lubricant base oils C4 and C5 for example), although lower lubricating properties were observed, it was confirmed that esters having the required proportion of acyl groups derived from caproic acid are useful base oils in the lubricant of this invention, since the failure load was 1000 lb or more. When the pentaerythritol ester was formed exclusively with branched chain, saturated fatty acids (see comparative base oils E7, E8 and E9 where the branched acids have a carbon number of 8, 7+8, and 9 respectively), the lubricating properties were remarkably depressed and thus lubricants containing these esters as the base oil are not satisfactory.

As far as the results of the thermal stability tests are concerned, for all the esters the ASTM colours were within L 0.5, and it was confirmed that the fatty acid esters of polyols having a neopentyl skeleton are stable with respect to heat.

Table 9 below shows the total acid values (which were measured in the thermal stability test) for the formulated lubricants D1 to D7 of this invention and, by way of comparison, for a lubricant of this invention comprising only the base oil A1.

Table 10 below shows the measured failure loads for the formulated lubricants D8 to D12 of this invention and, by way of comparison, for a lubricant of this invention comprising only the base oil A1.

Table 9

Lubricant	Total acid value mgKOH/g
D1	0.39
D2	0.02
D3	0.02
D4	0.41
D5	0.02
D6	0.30
D7	0.02
A1	0.39

Table 10

Lubricant	Failure load (lb)
D8	1350
D9	1800
D10	1200
D11	2100
D12	1200
A1	1200

From the results shown in Table 9, it is apparent that the total acid values measured in the thermal stability tests were markedly better for the formulated lubricants D2, D3, D5 and D7 which comprise a deacidifying agent or a deacidifying agent and an antioxidant.

Furthermore, the addition of an extreme pressure agent to the base oil results in a marked improvement in failure load; see, in particular, formulated lubricant D11 which comprises Extreme Pressure Agent 2 and formulated lubricant D9 which comprises Extreme Pressure Agent 1.

Example 3

The additive oil B1 and base oil A1 were mixed together in varying proportions to give mixed ester oils having differing viscosities. The effect of varying the relative proportions of oils A1 and B1 on the viscosity (in cSt) of the mixed ester oil at 40°C and 100°C is shown in Table 11. Curves formed by plotting these results are shown in Figures 1 and 2.

Thus, Figure 1 shows the relationship between the viscosity at 40°C and the proportion of base oil A1 (in weight %) in the mixed ester oil, and Figure 2 shows the relationship between the viscosity at 100°C and the proportion of base oil A1 (in weight %) in the mixed ester oil.

Table 11

Oil type	Wt. % of A1 in the oil	Dynamic viscosity (cSt)	
		40°C	100°C
A1	100	18.5	4.1
C2	70	27.1	5.3
C3	55	32.0	5.7
C1	50	35.7	6.3
E10	30	48.4	7.7
E11	18	56.0	8.3
B1	0	83.0	10.8

Example 4 - Compressor Test

Test oils A1, C2 and E2 (250 ml) to which no extreme pressure additive had been added were charged to a Japanese made hermetic type reciprocating compressor system (130W) together with HFC-134a. The outlet and inlet pressures were set to 25 kg/cm^2 and 1 kg/cm^2 (gauge pressures) respectively. The compressor was run continuously for 1000 hours within a room held at 30°C.

After completion of each test, the compressor was dismantled and the roundness of the front end of the piston measured in accordance with the method of JIS B0621 using a roundness meter (made by Tokyo Seimitsu, the Ronocom 3A model). The results are shown in Table 12.

Table 12

	Test Oil	Roundness (µm)
Invention	A1	2.4
Invention	C2	3.8
Comparison	E2	9.8

The test results show that the lubricants of the invention (base oil A1 and base oil C2) had excellent lubricating properties, and a good roundness was maintained even after a prolonged period of operation. In contrast, when the comparative base oil E2, which is outside the scope of this invention, was used as the lubricant, the lubricating properties were inferior and after the test there was severe unsymmetrical wear of the piston head.

The lubricant of this invention has good compatibility with HFC-134a, can fulfil the viscosity requirements of reciprocal or rotary type domestic refrigerators and small air conditioning systems, and has an acceptable lubricating performance. Moreover, if the lubricant comes into contact with water, hydrolysis of the ester and acid formation occurs with difficulty even over a long period of operation, and even if hydrolysis is caused the acid which is formed does not exhibit strong corrosive properties for the metallic materials of the machinery internal parts. Furthermore, the lubricant of this invention has good lubricating properties at the time of start up of the heat transfer device, and any increase in the total acid value during operation can be well controlled with the use of deacidifying agents.

Claims:

1. A lubricant comprising as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain, monovalent, saturated fatty acid, wherein the straight chain fatty acid has a carbon number of 6 and the branched chain fatty acid has a carbon number of at least 6,

wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

2. A lubricant as claimed in claim 1 comprising as a base oil an ester composition consisting essentially of:

(1) at least 50 % by weight of at least one pentaerythritol ester of a straight and/or branched chain monovalent saturated fatty acid having a carbon number of 6; and optionally

(2) up to 50 % by weight of at least one dipentaerythritol ester of a straight and/or branched chain monovalent saturated fatty acid having a carbon number of 6,

wherein at least 50 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

3. A lubricant as claimed in claim 1 or claim 2 wherein at least 65 % by weight of the fatty acid component consists of a straight chain fatty acid having a carbon number of 6.

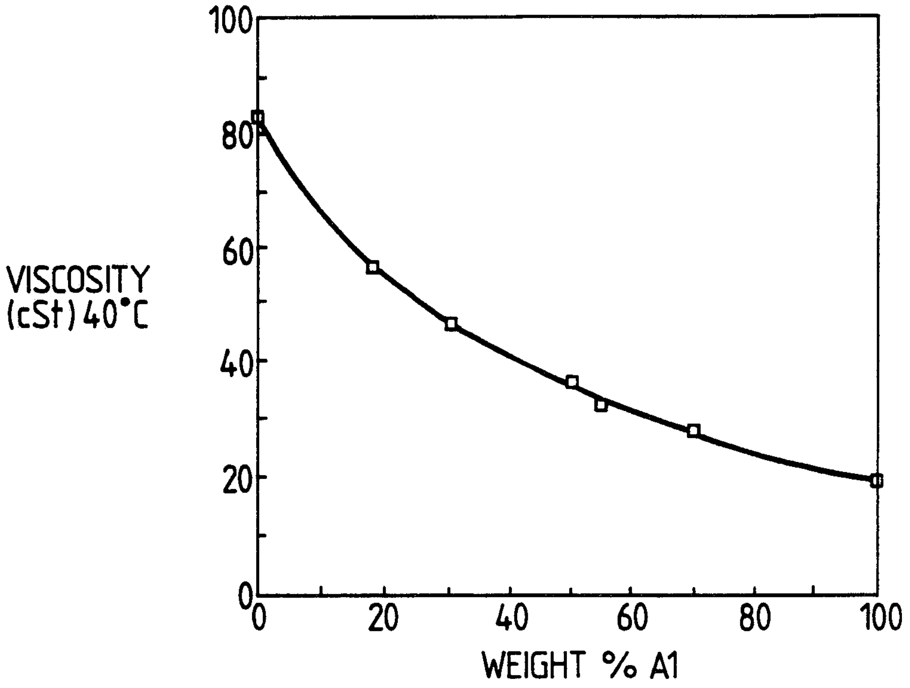
4. A lubricant as claimed in any one of claims 1 to 3 which additionally comprises at least one additive selected from the group consisting of an antioxidant, a deacidifying agent and an extreme pressure agent.

5. A lubricant as claimed in claim 4 wherein the antioxidant is a compound containing a hindered phenol in the molecule, the deacidifying agent is a compound containing an epoxy group in the molecule, and the extreme pressure agent is a phosphate ester of phenol which may be substituted by a lower alkyl group, or a phosphate ester of a monovalent, saturated, aliphatic alcohol.

6. A working fluid composition which comprises:
(i) at least one hydrofluorocarbon; and
(ii) a lubricant as claimed in any one of claims 1 to 5.

7. A working fluid composition as claimed in claim 6 wherein the hydrofluorocarbon component (i) comprises HFC-134a.

Fig.1.


VISCOSITY
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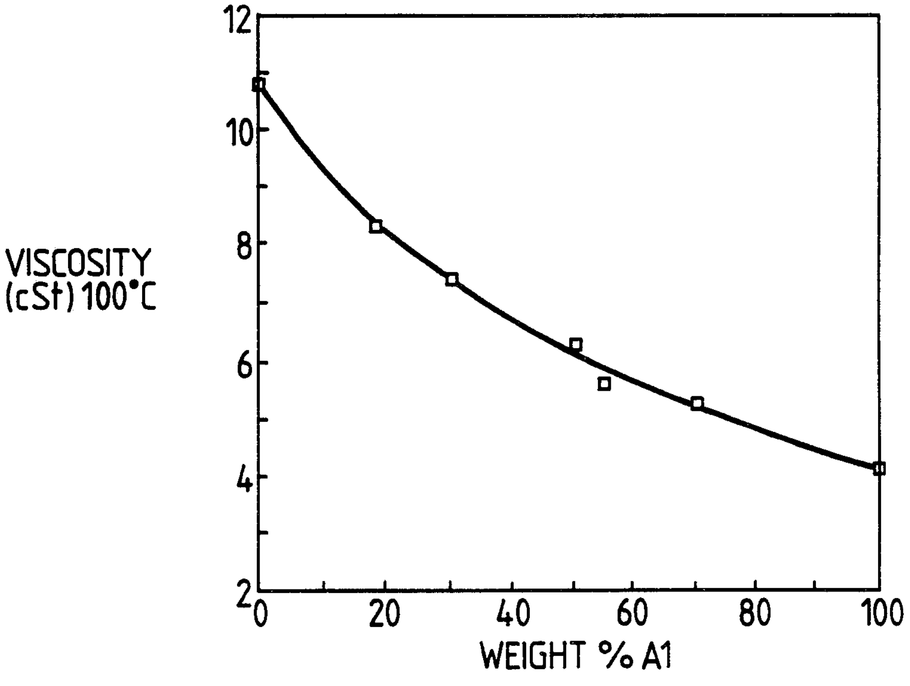
80
60
40
20
0
0
20
40
60
80
100
WEIGHT % A1

Fig.2.


VISCOSITY
(cSt) 100°C
12
10
8
6
4
2
0
20
40
60
80
100
WEIGHT % A1

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/02045

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10M105/38; C10M169/04; C10M171/00; //(C10M169/04, 105:38,129:10,129:18,129:66,137:04,145:36)(C10N40:30)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,2 815 327 (L.M BRENTWOOD) 3 December 1957 see column 2, line 5 see column 2, line 7 see claim 1 ---	1-4
X	PATENT ABSTRACTS OF JAPAN vol. 5, no. 031 (C-045)25 February 1981 & JP,A,55 155 093 (NIPPON OIL LTD) 3 December 1980 see abstract ---	1-5
X	GB,A,967 592 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) 26 August 1964 see page 1, line 82 see page 2, line 21 see page 3; table 1 --- -/--	1-5

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

IV. CERTIFICATION

Date of the Actual Completion of the International Search 17 DECEMBER 1992	Date of Mailing of this International Search Report 18. 01. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer HILGENGA K.J.

International Application No PCT/GB 92/02045

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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X	EP,A,0 448 402 (ASAHI DENKA KOGYO KABUSHIKI KAISHA) 25 September 1991 see page 3, line 6 see page 3, line 25 - line 26 see claim 1 ---	1-7
P,X	EP,A,0 485 979 (HITACHI LTD) 20 May 1992 see page 15; example 11 see claims 16,18-21 see column 4, line 6 - line 8 ---	1-7
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A	EP,A,0 435 253 (NIPPON OIL CO) 3 July 1991 see page 3, line 57 see page 9; example 4 see claims 1,7,19 ---	1-7
X	DATABASE WPIL Week 9027, Derwent Publications Ltd., London, GB; AN 90-207255 [27] & JP,A,2 140 297 (KAO CORP) 29 May 1990 see abstract -----	1-3,6,7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9202045
SA 66392

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/12/92
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GB-A-967592		AT-A- 229465 BE-A- 604945 CH-A- 391161 DE-B- 1148683 DE-B- 1160967 FR-A- 1292599 FR-A- 1303182 GB-A- 978354 NL-C- 134508 NL-A- 265906 NL-A- 266093 US-A- 3112267 US-A- 3160657	
US-A-4234497	18-11-80	None	
US-A-4175045	20-11-79	None	
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82