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(54) Friction modification of synthetic gear oils

(57) Gear lubricant compositions having a kinematic viscosity at 100°C in the range of 4 to 32 $mm^2.s^{-1}$ (cSt), and comprise (a) a base oil having (i) more than 20% by volume of hydrogenated poly-α-olefin oil and (ii) less than 80% by volume of mineral oil or synthetic ester oil or a combination thereof; (b) an amount of an additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and (c) a friction improving amount in the range of 0.01 to 2 wt% based on the total weight of the lubricant of at least one overbased alkaline earth metal sulphurised phenate or salicylate, the lubricant being essentially free of any metal additive component other than said phenate or salicylate, and has on a weight basis a boron content, if any, of not more than 1,000 ppm.

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Description

This invention relates to improving the frictional characteristics of gear oils in which the base oil is, or contains a substantial quantity of a synthetic poly-alpha-olefin oil (PAO).

PAOs possess good thermal stability and viscometric properties. However attempts to formulate PAO-based gear oils especially transmission oils for use in large vehicles equipped with manual transmissions of the synchronizer type pose special problems. Even though such lubricants contain additives for wear protection, corrosion protection, and other property improvements, the lubricants afford unsuitably low frictional properties in synchronizer-based transmissions and thus cause poor synchronization of the gear changes. This negative aspect of such synthetic based gear oils is readily observed as low friction and noisy gear change in the Zahnradfabrik Friedrichshafen A.G. synchronizer test (described and referred to hereinafter as the "ZF Synchronizer test").

It has now been found possible to overcome this problem by means of small amounts of an additive which does not materially affect the other performance capabilities of the finished lubricant.

The additives used pursuant to this invention are overbased alkaline earth metal salts of oil-soluble sulfurized phenols or oil-soluble salicylic acids. The metals of such salts preferably are those which have low toxicity and which present little or no concern from the environmental standpoint, namely, magnesium and calcium. However, the overbased barium and strontium salts can be used, if desired.

In accordance with one embodiment of this invention, there is provided a lubricant having a kinematic viscosity at 100°C in the range of 4 to 32 $mm^2.s^{-1}$ (cSt), and preferably in the range of 8 to 20 $mm^2.s^{-1}$ (cSt), and comprising:

a) a base oil having (i) more than 20% by volume of hydrogenated poly-alpha-olefin oil and (ii) less than 80% by volume of mineral oil or synthetic ester oil or a combination thereof;
b) an amount of a gear oil additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and
c) a friction improving amount in the range of about 0.01 to about 2 wt % based on the total weight of the lubricant of at least one overbased alkaline earth metal sulfurized phenate or salicylate;

said lubricant being essentially free of any metal additive component (i.e., the lubricant contains at most 100 ppm and preferably no more than 50 ppm of metal as one or more additive components other than said phenate or salicylate), and having on a weight basis a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm. In one embodiment the lubricant has no boron additive content. In preferred embodiments the lubricant contains no metal additive component other than said phenate or salicylate.

Preferably the base oil of the above gear lubricant is composed of (i) at least 40%, and more preferably least 50%, by weight of hydrogenated poly-alpha-olefin oil; (ii) 5 to 25% by weight of synthetic ester oil, and (iii) 0 to 55%, and more preferably 0 to 50% by weight of mineral oil. It will be seen that the mineral oil is an optional component of the base oil.

Additional embodiments comprise use of the above lubricants in manual transmissions of the synchronizer type to improve the performance of the transmission during operation under service conditions. The lubricants can also be used to lubricate the axle or differential gearing system of the vehicle.

In the ZF Synchronizer test the beneficial increase in friction exhibited by finished gear lubricants of this invention manifests itself in a substantial increase in the number of cycles during which the test can be performed without poor synchronization of the gear changes and/or with the coefficient of friction being greater than 0.065.

In satisfying or exceeding the specification for API GL-4 service, the finished lubricant satisfies the requirements for other performance specifications such as API GL-5, and including specifications not yet in being (or even envisioned) such as MT-1, PG2, API GL-7, and MIL-L-2105E or specifications of other countries such as comparable JIS gear oil standards, or the like. In other words the specifications of API GL-4 are to be considered minimum performance levels which the gear oil additive package (b) imparts to the finished lubricant. For example, if the requirements of the API GL-7 specification are more stringent than API GL-4, an additive package that provides a lubricant which satisfies the API GL-7 requirements inherently satisfies the minimum performance requirements for use in the practice of this invention, whether or not the package has actually been subjected to the API GL-4 performance tests.

Another embodiment of this invention comprises the use of at least one overbased alkaline earth metal sulfurized phenate or salicylate in a gear lubricant composed of components a) and b) above -- especially a manual transmission lubricant for use in vehicles equipped with manual transmissions of the synchronizer type -- to improve the frictional properties of the lubricant without materially affecting the other performance capabilities of the finished lubricant, wherein, as described above, the lubricant is essentially free of any metal additive component other than the overbased phenate or salicylate, and has a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

Still another embodiment is a gear oil additive package which comprises (1) an oil-soluble phosphorus and sulfur-containing antiwear and/or extreme pressure additive complement and (2) at least one overbased alkaline earth metal sulfurized phenate or salicylate; said gear oil additive package being further characterized in that when blended with a base oil having a kinematic viscosity in the range of 4 to 32 cSt at 100°C and composed of a base oil as described above to form a lubricant containing from about 0.01 to about 2 wt % of said phenate or salicylate, the gear oil additive package provides a lubricant composition that:

A) satisfies or exceeds the specifications for API GL-4 service;
B) contains, if any, at most 100 ppm and preferably no more than 50 ppm of metal apart from the metal content of said phenate or salicylate; and
C) has a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

In another embodiment, a gear oil additive package (concentrate) or gear lubricant of this invention additionally contains at least one oil-soluble basic nitrogen-containing ashless dispersant, preferably a succinimide ashless dispersant and/or a succinic ester-amide ashless dispersant, and more preferably a Mannich base ashless dispersant. The oil-soluble phosphorus and sulfur-containing antiwear and/or extreme pressure additive complement of such compositions is preferably composed of (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulfur is bonded to carbon or to more sulfur, and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent. In these embodiments, the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of about 0.0005:1 to about 0.5:1, and preferably in the range of about 0.003:1 to about 0.2:1. Likewise the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of about 0.005:1 to about 5:1, and preferably in the range of about 0.01:1 to about 2:1. In each of these embodiments the gear oil additive package (concentrate) or gear lubricant preferably has a boron content such that the finished lubricant contains by weight up to 1,000 ppm, preferably up to 300 ppm, and most preferably not more than 25 ppm of boron. One preferred way of introducing at least a portion of such boron is to provide additive packages and finished lubricants compositions containing a borated basic nitrogen-containing ashless dispersant.

In additional embodiments, any of the above additive concentrates and finished lubricant compositions further comprise at least one oil-soluble demulsifying agent.

Preferably the lubricant compositions of this invention have a halogen content, if any, of no more than 100 ppm, and more preferably no more than 50 ppm on a weight basis.

Still another aspect of this invention is the method of beneficially modifying the frictional characteristics of a low-friction synthetic lubricant composition containing a gear oil additive package such that the lubricant composition satisfies or exceeds the specifications for API GL-4service, but does not exhibit satisfactory friction properties for use in manual transmissions, particularly those of the synchronizer type. The method comprises including in such lubricant composition an amount in the range of about 0.01 to about 2 wt % based on the total weight of the lubricant of at least overbased sulfurized phenate or salicylate such that the friction properties of the lubricant are improved for use in manual transmissions, particularly those of the synchronizer type.

In each of the embodiments of this invention, the overbased metal phenate or salicylate can be employed as a separate component (e.g., as a "top-treat" to the base oil with which the additive package has been or will be blended) or as a component of the additive package itself. Similarly, while use of additive packages is preferred, it is possible to blend the overbased metal sulfurized phenate and/or salicylate and the respective components of the additive package into the base oil individually or in various compatible sub-combinations.

Base Oils.

Most poly-alpha-olefin oils are formed by oligomerization or co-oligomerization of 1-alkene hydrocarbon having 6 to 20 and preferably 8 to 16 carbon atoms in the molecule and hydrogenation of the resultant oligomer. In some cases, a suitable poly-alpha-olefin oils can be co-oligomers of a short chain 1-olefin such as ethylene and one or more longer chain alpha-olefins, such as for example the product available from Mitsui Petrochemical Company, Ltd. under the LUCANT trademark. Hydrogenated poly-alpha-olefin oils formed from 1-decene are particularly preferred. Methods for the production of liquid 1-alkene hydrocarbon oils are known and reported in the literature. See for example U. S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822.

Synthetic ester oils are available in the marketplace. Typical synthetic ester oils include such materials as the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(1-ethylpropyl) adipate, di(1,3-dimethylbutyl) adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, di(1-methylpropyl) azelate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, mixed C_9 and C_{11} dialkyl phthalate, dibutyl sebacate, di(1-ethylpropyl) sebacate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Other synthetic esters which may be used as synthetic oils include those made from C_3-C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylol propane tripelargonate and pentaerythritol tetracaproate serve as examples.

The base oils may contain as optional blending components a mineral oil or other suitable oleaginous liquid of lubricating viscosity, provided the overall base lubricant satisfies the proportions and viscosity parameters given above, and is suitable for use in forming a finished gear lubricant that satisfies or exceeds the specifications for API GL-4 service, and provided further that the resultant finished oil remains amenable to friction improvement pursuant to this invention. Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, hydrotreated oils, partially hydrotreated oils, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques known to those skilled in the art. Suitable reprocessed or reclaimed mineral oil base stocks may also be used. Most gear oil packages contain diluent oils or solvents for certain active ingredients or components. However, since such diluent oils or solvents are added to the base oil along with the additive package or with one or more additive components blended separately or individually into the base oil, such diluent oils or solvents are to be omitted from consideration when assessing the makeup of the base oil of the compositions of this invention.

Overbased Phenate or Salicylate

Overbased alkaline earth metal sulfurized phenates are also known as overbased alkaline earth metal phenol sulfides. These materials as well as overbased alkaline earth metal salicylates are available as articles of commerce. Of the overbased alkaline earth phenates and salicylates, the magnesium compounds are a preferred group. The most preferred however are the overbased calcium phenates and salicylates. As between overbased phenates and overbased salicylates, the phenates are preferred. As is known, these overbased materials contain more than a stoichiometric amount of the metal. Methods for producing such materials have been reported in the patent literature. Test work has shown that the additive must be overbased, and for good performance the phenate should have a total base number (TBN) of at least 200 and preferably at least about 250. The salicylate should have a TBN of at least 150. TBN is measured using the ASTM D2896 procedure, and represents mg of KOH per gram of sample.

Quantities ranging from as little as 0.01 wt% up to as much as 2 wt% of the overbased metal phenate or salicylate (or combination thereof) based on the total weight of the finished lubricant can be employed. Ordinarily the amount used will not be greatly in excess of that amount needed to yield the friction performance desired in the particular finished gear oil lubricant in question. In most cases the amount will not be above 1 wt%, and often will not exceed 0.5 wt%. In the case of the friction-improved additive packages of this invention, the amount will be proportioned such that when the package is blended into the base oil at the recommended, or desired concentration, the resultant finished oil will contain the above-specified amount of the overbased phenate or salicylate. These proportions of the overbased metal phenate or salicylate are based on the active ingredient, and thus the weight of any solvent or diluent associated with the overbased phenate or salicylate as used should be subtracted from the additive weight when calculating the concentration of the overbased metal phenate or salicylate in the finished oil or in the friction-improved additive package. However the total weight of the finished oil or of the completed additive package will include the weight of such solvent or diluent.

Additive Packages

The specifications for API GL-4 and API GL-5 service are published in ASTM Publication STP-512A entitled "Laboratory Performance Tests for Automotive Gear Lubricants" (March 1987).

A number of gear oil additive packages (concentrates) that provide API GL-4 or API GL-5 performance are available in the marketplace. They generally contain at least a sulfur-phosphorus antiwear or extreme pressure additive system, one or more antioxidants, one or more corrosion inhibitors, and an antifoam additive and may, preferably do, contain a dispersant additive.

ZF Synchronizer Test

As is known in the art, the ZF Synchronizer test has been designed for the evaluation of oil performance in commercially available synchromesh units under endurance conditions with the bulk lubricant temperature controlled at a relatively high level. While it is important to simulate fairly closely the actual conditions met in service, the need to produce a test result in an acceptable period has to be taken into account. Briefly, two halves of a transmission synchromesh unit are repeatedly brought together under conditions of known force and speed differential until failure occurs. Failure may be defined in terms of synchromesh performance or overall wear. The test rig used in the procedure was designed with consideration of work done by Socin and Walters, SAE Paper Number 680008 entitled "Manual Transmission Synchronizers"; Fano, CEC TLPG4 Chairman's Final Report, 1985, entitled "Synchromesh Test Method With Proposed Synchro Test Rig"; and Brugen, Thies and Naurian of Zahnradfabrik Friedrichshafen A.G. in a paper entitled "Einfluss Des Schmierstoffes auf die Schaltelemente Von Fahrzeuggetrieben". The two synchromesh units are assembled in a gear box which forms the oil reservoir and facilitates splash lubrication of components. Drive may be transmitted along the main shaft or via the layshaft gears to give an increased ratio. The input speed is kept constant by means of a DC drive control system and a large flywheel simulating vehicle inertia. On changing gear, the output shaft accelerates and decelerates the small flywheel which simulates clutch inertia. A pivot linkage connected to a pneumatic cylinder provides the actuating force which is measured by means of a load ring strain gauge. A small heater is used to control oil temperature.

Torque transmitted through the output shaft can be measured to give an indication of the coefficient of friction between the synchronizing cones. The synchromesh units used are standard commercially available steel units with a molybdenum-based plasma spray coating on the inner surface of the outer synchro-ring. The synchromesh units are renewed before each test. Typically, when measured at a point of relatively high torque during a gear change, the coefficient of friction for satisfactory synchronizer performance in the test is at least 0.065.

Another performance criterion which may be used when performing the test for qualification purposes is excessive vibration of the gear box casing in the axial plane, a condition symptomatic of poor gear changes. For this purpose the control and monitoring of the rig is coordinated by a process controller. During a test the number of poor changes is recorded. The test is terminated prematurely if this number becomes unacceptable or the vibration becomes excessively harsh.

Test components may be evaluated by inspecting the friction surface of the inner synchronizer cone using a Perthometer stylus device both before and after test. Polishing of the metal surface or the build up of a glaze of decomposed lubricant or additive yields an unacceptably smooth surface finish. This in turn causes low frictional values during the gear change and can lead to clash of the sleeve and gear clutch teeth. Wear measurements are also made on the test components.

Performance

The following examples illustrate, inter alia, the dramatic improvements in performance that are made possible by the practice of this invention. These examples are not intended to limit, and should not be construed as limiting, this invention. In the examples, all percentages are by weight.

Example

ZF Synchronizer tests were performed under the same conditions using a lubricant of this invention and a control lubricant made from the same components with but one exception: the composition of this invention contained 0.5% (approximately 0.3% on an active ingredient basis) of an overbased calcium sulfurized alkyl phenate having a nominal TBN of 250 ("Phenate"), whereas the control contained no such component. The base oils were fully synthetic oil blends of two PAO fluids having nominal viscosities at 100°C of 8 and 40 cSt ($mm^2.s^{-1}$), and a synthetic ester, namely bis(tridecyl)-adipate ("DTDA"). Each lubricant contained the same quantity of the same metal-free and boron-free API GL-4 additive package (HiTEC 381, available from Ethyl Corporation). The proportions of these components are summarised in the following table:

Components	Control Composition, %	Invention Composition, %
PAO, 8 $mm^2.s^{-1}$	70.25	69.75
PAO, 40 $mm^2.s^{-1}$	16.00	16.00
DTDA	10.00	10.00
API GL-4 Package	3.75	3.75
Phenate	None	0.50

The control composition had a kinematic viscosity at 100°C of 9.53mm^2.s^{-1}. The composition of the invention had a kinematic viscosity at 100°C of 9.55mm^2.s^{-1}.

The control composition was able to complete only 792 cycles in the test. The test had to be shut down at that point because very harsh bad gear changes had occurred and the coefficient of friction had already fallen to below 0.05. In sharp contrast, the composition of this invention successfully completed 50,000 cycles, and during the entire test the coefficient of friction remained consistently above 0.065.

Claims

1. A lubricant having a kinematic viscosity at 100°C in the range of 4 to 32 mm^2.s^{-1} (cSt), and comprising:

a) a base oil comprising (i) more than 20% by volume of hydrogenated poly-α-olefin oil and (ii) less than 80% by volume of mineral oil and/or synthetic ester oil;
b) an amount of a gear oil additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and
c) a friction improving amount in the range of 0.01 to 2wt% based on the total weight of the lubricant of at least one overbased alkaline earth metal sulphurised phenate or salicylate;

the lubricant being essentially free of any metal additive component other than the phenate or salicylate, and having on a weight basis a boron content of not more 1,000 ppm.

2. A lubricant according to claim 1 which does not contain any metal-containing additive component other than the phenate or salicylate, and which has on a weight basis a boron content of not more than 300 ppm.

3. A lubricant according to claim 1 or 2 which has a boron content not more than 25 ppm.

4. A lubricant according to any one of claims 1 to 3 which does not contain boron.

5. A lubricant according to any one of claims 1 to 4 wherein component c) is at least one overbased alkaline earth metal sulphurised phenate having a TBN of at least 200.

6. A lubricant according to claim 5 wherein the phenate is an overbased calcium sulphurised phenate having a nominal TBN of 250.

7. A lubricant according to any one of claims 1 to 6 wherein the base oil a) comprises (i) at least 40% by weight of hydrogenated poly-α-olefin oil; (ii) 5 to 25% by weight of synthetic ester oil, and (iii) 0 to 55% by weight of mineral oil.

8. A lubricant according to any one of claims 1 to 7 wherein the gear oil additive package b) comprises at least one oil-soluble basic nitrogen-containing ashless dispersant and an oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement comprising (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulphur is bonded to carbon or to more sulphur and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent, wherein the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of 0.0005:1 to 0.5:1, and the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of 0.005:1 to 5:1.

9. A lubricant according to any one of claims 1 to 8 having on a weight basis a halogen content of no more than 100ppm.

10. Use in a manual transmission of the synchronizer type of a lubricant according to any one of claims 1 to 9 to improve transmission performance during operation under service conditions.

11. Use of at least one overbased alkaline earth metal sulphurised phenate or salicylate to improve the frictional properties of a lubricant comprising a) a base oil as defined in claim 1 or 7 and b) a gear oil additive package as defined in claim 1, the lubricant being essentially free of any metal additive component other than the phenate or salicylate and having on a weight basis a boron content of not more than 1,000 ppm.

12. Use according to claim 11, wherein the lubricant comprises from 0.01 to 2 wt% based on the total weight of the lubricant of overbased sulphurised phenate or salicylate.

13. A gear oil additive concentrate which comprises (1) an oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement and (2) at least one overbased alkaline earth metal sulphurised phenate or salicylate wherein, when blended with a base oil as defined in claim 1 or 7 to form a lubricant containing from 0.01 to 2 wt% of said phenate or salicylate, the gear oil additive concentrate provides a lubricant which has a kinematic viscosity at 100°C in the range of 4 to $32 mm^2.s^{-1}$ (cSt), which satisfies or exceeds the specifications for API GL-4 service, which contains up to 100 ppm of metal additive component other than the phenate or salicylate, and which has a boron content of not more than 1,000 ppm.

14. A gear oil additive concentrate according to claim 13 which when blended with base oil provides a lubricant which contains no metal additive other than the phenate or salicylate, and which has a boron content of not more than 300 ppm.

15. A gear oil additive concentrate according to claim 13 or 14 additionally comprising at least one oil-soluble basic nitrogen-containing ashless dispersant and in which the oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement of the concentrate comprises (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulphur is bonded to carbon or to more sulphur, and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent wherein the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of 0.0005:1 to 0.5:1, and the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of 0.005:1 to 5:1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 0983

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.6)
X	US-A-5 250 122 (UCHIDA ET AL.) * examples 3,4; table 1 *	1-6,9	C10M169/04
Y	EP-A-0 578 435 (ETHYL) * the whole document *	1-15	
Y	EP-A-0 501 527 (LUBRIZOL) * page 9, line 1 - line 20; claims 11,12 * * page 17, line 40 - line 45 *	1-15	
Y	EP-A-0 620 268 (ETHYL) * page 2 * * page 3, line 34 - line 40 *	1-15	
A	EP-A-0 531 585 (ETHYL) * the whole document *	1-15	
A	WO-A-87 05927 (LUBRIZOL) * page 5, line 1 - line 10; claims 1,3,6 *	1	
A	US-A-5 089 156 (CHRISOPE ET AL.) * examples 1-47 *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 October 1996	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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T : theory or principle underlying the invention
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L : document cited for other reasons
& : member of the same patent family, corresponding document