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(54) Lubricant compositions and additives therefor.

(57) A product is formed by interacting either concurrently or in any sequence at a suitable elevated temperature above 30° C (i) one or more highly-active sulphur-containing extreme pressure or anti-wear agents, (ii) one or more amines, and (iii) one or more weak acids, in proportions such that the mole percentages of sulphur in (i) to amino nitrogen in (ii) used in forming the product is in the range of 100:1 to 5:1, and the proportion of component (iii) used in forming the product is such that there are from 0.2 to 2 chemical equivalents of acid per equivalent of amino nitrogen in component (ii). Lubricant compositions, especially suitable as gear oils, containing such products, confer extended life on gears operated in them.

This invention relates to lubricating fluid compositions, and in particular to gear oils and to additives therefor.

High performance gear oils usually consist of a major amount of mineral oil or synthetic base stock and a minor amount of suitable additives including in particular a sulphur-containing extreme pressure or antiwear agent. Such sulphur-containing materials are highly effective in promoting the extreme pressure and antiwear properties of the oil and may also have valuable anti-oxidant properties. However, such sulphur-containing materials are detrimental to the environment, may cause undesirable odour, and can lead to corrosion of the metal parts with which they come in contact, especially parts containing copper.

Gear oils, for example the oils used in the gear boxes and differentials of motor vehicles, and other mechanisms involving metal on metal, for example steel on steel or steel on bronze, acting parts, are required to protect the metal surfaces and particularly the teeth of the gears. Typically, such oils remain in use for long periods without being changed. In addition to providing general lubrication, the fluid protects the loaded metal parts such as the gear teeth from damage. Gear oils are customarily tested for their ability to protect gear teeth from damage such as wear and pitting for long periods. In one system for testing such oils a gear train is run under conditions of variable and very heavy stress until the gears fail. The length of time before such failure takes place, or the wear of the gear teeth (as measured by the iron content of the fluid) becomes excessive, provides a measure of the effectiveness of the gear oil. Some current gear oils provide a measure of protection in this respect, but still further improvement is desirable.

There is therefore a need for gear lubricating oils which provide better protection of the gears and/or which contain reduced sulphur content and a need for additive systems for such gear lubricating oils.

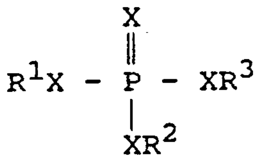
We have now discovered that by interacting a suitably high concentration of amino nitrogen (in the form of one or more amines) and a suitable quantity of acid (in the form of one or more weak acids) with one or more active sulphur-containing extreme pressure or antiwear agents at a suitably elevated temperature, significant improvements in gear oil performance can be achieved. In fact, the performance of typical compositions of this invention in a standard planetary spur gear test (described hereinafter) was found to surpass the performance of a widely-used commercially available gear oil additive package.

Accordingly, in one of its embodiments, this invention provides a product formed by interacting at a temperature above 30°C (i) one or more highly-active sulphur-containing extreme pressure or antiwear agents, (ii) one or more amines, and (iii) one or more weak acids, such interactions occurring either concurrently or in any sequence. The proportions of components (i), (ii) and (iii) used in forming the product can be varied over reasonably wide limits provided there is a sufficiently high amount of amino nitrogen present to interact both with at least a portion of the sulfur-containing material(s) and at least a portion of the weak acid(s) used. Usually the proportions of components (i) and (ii) are such that the mole percentages of sulphur in (i) to amino nitrogen in (ii) is in the range of 100:1 to 5:1 (preferably 40:1 to 5:1, and more preferably 25:1 to 5:1, and most preferably 20:1 to 25:1), and the proportion of component (iii) used in forming the product is usually such that there are from 0.2 to 2 chemical equivalents of acid per equivalent of amino nitrogen in component (ii).

Preferably, the proportions of component (iii) are such that there are from 0.2 to 0.9 (most preferably 0.4 to 0.8) chemical equivalents of acid per equivalent of amino nitrogen in component (ii). In other words, these preferred cases involve use of an amount of weak acid which theoretically is insufficient to neutralise all of the amine utilised in the combination.

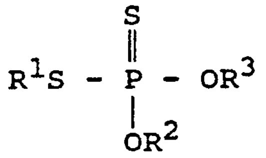
In accordance with this invention, a mixture which includes or comprises components (i), (ii) and (iii) is heated to a performance-enhancing temperature, that is, to a temperature at which the resultant product is more effective in the standard planetary spur gear test than it would be in the absence of such heating. While such temperatures may vary from case to case, generally speaking heating to temperatures in the range of 30 to 70°C and preferably in the range of 40 to 70°C and most preferably in the range of 50 to 60°C for periods in the range of 0.5 to 3 hours and preferably in the range of 0.5 to 2 hours are suitable. Components (i), (ii) and (iii) may be subjected to such heating when in undiluted form, when dissolved in an oleaginous solvent (preferably at a concentration above 20% of the total weight of the solution), or when in admixture with other conventional components used in gear oil additive concentrates, such as antioxidants, antifoamants, demulsification agents, dispersants, detergents, viscosity index improvers or pour point depressants, and inert diluents. Without desiring to be bound by theoretical considerations, it is believed that in addition to reaction between the amino nitrogen and weak acid, sulphur and/or sulphur-containing species also participate in one or more reactions taking place in the mixture. It is not presently known how these reactions or interactions proceed or what the chemical structure or structures of the resultant products may be. Nevertheless the resultant products exhibit improved performance capabilities as compared to the corresponding products which have not been subjected to such thermal treatment. It will thus be understood that the reactant mixture may be heated at any temperature above 30°C for any length of time which together yield a product that is more effective in the planetary spur gear test than the initial unheated mixture from which the product was made.

In another preferred embodiment of this invention the heating of the mixture of components (i), (ii) and (iii) is conducted in the presence of an ester of a pentavalent acid of phosphorus, such as the fully esterified or partially esterified phosphoric, phosphonic or pyrophosphoric acids or their sulphur-containing analogs. This heating process may be conducted in the presence of one or more compounds of the formula



$$R^1X - \overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle XR^2}{|}}{P}} - XR^3$$

wherein each of R^1, R^2 and R^3 is, independently, a hydrocarbyl group or a hydrogen atom, provided that at least one of R^1, R^2 and R^3 is hydrocarbyl, and each X is, independently, an oxygen atom or a sulphur atom. Most preferred are compounds of the formula



$$R^1S - \overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle OR^2}{|}}{P}} - OR^3$$

where at least 95 percent of the R^1 groups are hydrocarbyl groups, the balance, if any, being hydrogen atoms, and R^2 and R^3, when hydrocarbyl, can be aromatic, cycloaliphatic, and/or aliphatic hydrocarbon groups, or any combination of these. Preferably R^1, R^2 and R^3 are saturated or substantially saturated aliphatic, cycloaliphatic or polycycloaliphatic groups, such as alkyl, alkenyl, cycloalkyl, cycloalkenyl, cycloalkylalkyl, cycloalkylalkenyl, cycloalkenylalkyl, cycloalkenylalkenyl, and the like. As far as chain length or carbon atom content is concerned, the only requirement is that the hydrocarbyl groups are such that the compound is soluble in the base oil to at least the desired use concentration at ambient temperatures. The hydrocarbyl groups can contain functional substituents or non-hydrocarbon component groups which do not materially alter the predominantly hydrocarboneous character of the hydrocarbyl groups themselves.

To determine for the purpose of this invention whether a sulphur-containing extreme pressure or antiwear agent is or is not "active", use can be made of a copper coupon corrosion test which is conducted as follows: A copper coupon approximately 70 x 15 mm and about 1.25 mm in thickness is cleaned by use of steel wool (0000 grade), washed with heptane, and then with acetone, dried, and weighed to the nearest 0.1 mg. The cleaned coupon is placed in a test tube and covered completely with the composition to be tested, and the system is heated to 125° C, by means of an oil bath maintained at this temperature. After holding the system at 125° C for three hours, the copper coupon is removed from the test tube, rinsed with heptane and then with acetone. The dried coupon is then rubbed with a paper towel moistened with acetone to remove any surface flakes formed by copper corrosion. The coupon is then air-dried and weighed to the nearest 0.1 mg. The difference in weight as between the initial copper coupon and the coupon after the test represents the extent to which the copper was corroded under the test conditions. Therefore the larger the weight difference, the greater the copper corrosion, and thus the more active the sulphur compound.

For the purposes of this invention, if the coupon weight loss is 30 milligrams or more, the sulphur-containing agent is considered "active". A sulphur-containing extreme pressure or antiwear agent is deemed to be "highly-active" if the coupon weight loss in the above test is above 50 milligrams, and use of such "highly-active" sulphur-containing substances in forming the products of this invention is preferred. Unless the context indicates otherwise, the term "active" as used in this specification and in the claims encompasses "highly active" as well.

Generally speaking, sulphur-containing compounds which possess a linkage of two sulphur atoms (i.e., -S-S-) or four or more sulphur atoms (e.g., -S-S-S-S-, -S-S-S-S-S-, etc.) tend to be "active" or even "highly active" in the sense used herein. However, in some cases a product from one manufacturer -- for example sulphurised isobutene -- may have a much higher activity than a similar product from another manufacturer. Thus in cases where the activity of a given sulphur-containing extreme pressure or antiwear agent is not known with certainty, it is desirable to perform the above copper coupon corrosion test to ascertain whether it qualifies as an "active" material.

In proportioning components (i), (ii) and (iii), the total sulphur content of component (i) should be taken into account, even though some of the sulphur in the compound would not qualify as "active" within the meaning given above. It will also be understood that all of the sulphur present in the mixture (whether "active" or not) need not -- and in fact probably does not -- directly participate in the interaction(s) taking place in the mixture during the heating process. On the other hand, only free or very loosely complexed amino nitrogen should be taken into account with respect to proportioning of component (ii). For example, the amino nitrogen of any amine salt or amine complex with phosphorus acids such as dialkyl acid phosphates or phosphites is too tightly bound to be available for participation in the formation of the products of this invention, and thus although such amine salts or complexes may be present during the formation of the products of this invention, the amount of amino nitrogen in such amine salts or complexes should not be considered as amino nitrogen available for use in the formation of the products of this invention. In short, such tightly-bound amine salts or complexes with phosphorus acids form no part of component (ii).

Because of the toxicity of hydrogen sulphide (to say nothing of its disagreeable odour), it is desirable to utilise in the practise of this invention an active sulphur-containing extreme pressure or antiwear agent that yields less than 700 ppm, more preferably less than 500 ppm, of vapour space H_2S when heated by itself for one week at 65° C.

When conducting the heating process involving at least components (i), (ii) and (iii), it is particularly preferred to perform the process in at least two stages. Generally speaking, the performance of products made in a two-stage process tends to be even better than the performance exhibited by corresponding products made in a one stage operation. In the preferred two-stage process the product is produced by heating components (i) and (ii) in the first stage and then in the second stage heating component (iii) with the product formed from components (i) and (ii). Numerous variants of this two-stage process are, of course, possible, such as heating a portion of components (i) and (ii) in the first stage and then heating this mixture with the balance of components (i) and (ii) together with component (iii) in the second stage. This and other such variants are within the scope of this invention. The one-stage process of this invention involves heating components (i), (ii) and (iii) in the desired proportions all at the same time, or concurrently feeding all three components to the heated reaction in the desired proportions, either continuously or in incremental portions. Consequently, the reaction among components (i), (ii) and (iii) can be conducted in any sequence and in any number of reaction stages, although for the reasons already described, a two-stage process is preferred.

Both acids and amines have heretofore been used in lubricating oil compositions, but the known compositions do not achieve the advantages of the present invention. For example, United States Patent No. 3,398,095 discloses oils containing sulphurised carboxylic acid in combination with acids and amines as so-called "vapour space inhibitors". Such oils are stated to achieve excellent corrosion inhibition for ferrous metals. They are not however suitable as gear oils. United States Patent No. 4,615,818 discloses that lubricant compositions comprising an oil-soluble sulphurised organic compound may be improved, so as to reduce emission of volatile sulphur compounds, by inclusion of a hindered organic amine and preferably a carboxylic acid. There is, however, no suggestion that the performance of gear oils can be improved by inclusion of such compounds and the compositions disclosed in that patent would not achieve such a result.

The present invention accordingly further provides a lubricant composition containing a minor amount, for example 1 to 20% by weight, of a product resulting from interaction either concurrently or in any sequence at a suitably elevated temperature of (i) one or more active sulphur-containing extreme pressure or antiwear agents, (ii) one or more amines, and (iii) one or more weak acids, the proportions of components (i), (ii) and (iii) and the reaction conditions used in forming in the final product being as above-stated. Also provided by this invention are additive concentrates containing from 10 to 90% by weight (preferably from 20 to 80% by weight) of a pre-heated combination or product of this invention formed as described above.

Particularly preferred lubricants are those which contain a product formed from components (i), (ii) and (iii) in accordance with this invention and wherein the product and the concentration thereof enable the lubricant to give at least 60 and more preferably at least 75 hours of running time in the planetary spur gear test (in the form referred to hereinafter) before a substantial increase in iron content in the oil (an increase which usually occurs relatively rapidly) is observed or before gear tooth breakage occurs.

The lubricant may be a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil. 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.

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid alpha-olefin polymers of appropriate viscosity. Especially useful are hydrogenated or unhydrogenated liquid oligomers of C_6-C_{16} alpha-olefins, such as hydrogenated or unhydrogenated alpha-decene trimer. Alkyl benzenes of appropriate viscosity, e.g. didodecylbenzene, can also be used.

Useful synthetic esters include the esters of monocarboxylic and polycarboxylic acids with monohydroxy alcohols and polyols. Typical examples are didodecyl adipate, trimethylolpropane tripelargonate, pentaerythritol tetracaproate, di(2-ethylhexyl) adipate, and dilauryl sebacate. Complex esters made from mixtures of mono- and di-carboxylic acids and mono- and/or polyhydric alkanols can also be used.

Typical natural oils that may be used include castor oil, olive oil, peanut oil, rape oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired. Viscosity index improvers may or may not be included in the natural oils in order to achieve the viscosity properties deemed necessary or desirable.

The additives or additive concentrates of this invention can be blended into any such lubricant base stocks when forming the finished lubricants of this invention. The base oils for such use are generally mineral oil base stocks such as for example conventional and solvent-refined paraffinic neutrals and bright stocks, hydro-treated paraffinic neutrals and bright stocks, naphthenic oils, cylinder oils, etc., including straight run and blended oils. As noted above, synthetic base stocks such as for example poly-alpha-olefins with synthetic diesters in weight proportions (PAO:ester) ranging from about 95:5 to about 50:50, typically about 75:25 can be treated. The product of this invention is also particularly suitable for use in PAO which contains little or no ester. Generally speaking, the base stocks used in automotive gear oils range in viscosity grades from SAE 50 to 250 and preferably from 70 to 140. Suitable automotive gear oils also include cross-grades such as 75W-140, 80W-90, 85W-140, 85W-90, and the like. In general, the base stocks used in industrial gear oils will have a viscosity in the range of from about ISO grade 32 to ISO grade 680 and preferably from ISO grade 68 to ISO grade 460.

The new lubricant compositions may be supplied either as finished lubricants ready for use or in the form of an additive package, i.e. a concentrate, which requires dilution with base lubricating fluid before use. As described in more detail below, the lubricant compositions of the invention may contain, in addition to the substances already mentioned, any usual additive for inclusion in such lubricants which is compatible with the product of this invention formed from a highly-active sulphur-containing agent, weak acid, and amine. Examples of such additives are given below.

A very wide variety of active sulphur-containing oil-soluble extreme pressure or antiwear agents may be used in forming the compositions of the invention, and any known such agents may in principle be used. Examples of such agents are included within the categories of sulphurised olefins, sulphurised esters, sulphurised fatty acids, dialkylpolysulphides, diaryl polysulphides, diaralkyl polysulphides, sulphur, and sulphurised oils.

In the preferred compositions of the invention the sulphur atoms in the active sulphur containing species are bound directly to carbon or to more sulphur.

One preferred class of such agents is made by reacting an olefin such as isobutene with sulphur. The product, e.g. sulphurised isobutene, typically has a sulphur content of about 10 to about 50%, preferably 30 to 50% by weight. A wide variety of other olefins or saturated hydrocarbons may be used in place of the isobutene. As noted above, the candidate product should be subjected to the coupon corrosion test to ascertain that it qualifies as an "active" compound.

Other examples of preferred sulphur-containing extreme pressure agents which, if "active", may be used in the compositions of the invention are sulphur and the sulphurised fatty esters and oils already mentioned, such as sulphurised sperm oil and sulphurised lard oil.

The proportion of interacted product of this invention included in the lubricant compositions of the invention is typically 1 to 20% by weight, usually 1.7 to 10% by weight, and preferably 2-4%, based on the weight of the lubricant.

The new compositions preferably contain a phosphorus-containing extreme pressure or anti-wear agent. Such phosphorus-containing agents include derivatives of phosphorus oxyacids, of phosphorus thioacids, of polyphosphorus oxyacids and of polyphosphorus thioacids, such as phosphites; mono-, di- and trithiophosphites; phosphates; mono-, di- and trithiophosphates and their corresponding phosphorothioates; and pyrophosphates and thiophosphates; and especially their oil-soluble esters, acid esters, and amine salts. Preferably a mono- or dihydrocarbyl phosphite, thiophosphite, phosphate, thiophosphate or thiophosphorothioate or a mixture thereof is used, where the hydrocarbyl groups may be alkyl, alkenyl, phenyl, alkylphenyl or dialkylphenyl. Examples of suitable esters are mono-methyl, dimethyl, mono-n-butyl, di-n-butyl, mono-isobutyl, di-isobutyl, monoamyl, diamyl, di-n-octyl, di-(2-ethyl-n-hexyl), monooleyl, dioleyl, monophenyl, diphenyl and di(do-decylphenyl) phosphite and phosphate, their sulphur analogs, and the amine salts of any of the foregoing. Such phosphorus-containing agents are usually included in the new compositions in a proportion of 0.01 to 3.5% based on the weight of the lubricant.

The compositions of the invention may also contain an alkali metal borate, e.g. sodium or potassium borate, e.g. in a proportion of 0.5 to 8% by weight of the lubricant.

The acid used in forming the new compositions is a weak acid, preferably one having a pKa of greater than about 2.0, and is usually a carboxylic acid in which one or more carboxyl groups are attached to a hydrocarbon radical of 1 to 100, preferably 2 to 50 carbon atoms, preferably an acyclic hydrocarbon radical, and most preferably 6 to 36 arbon atoms. Other weak acids, e.g. a boric acid such as H_3BO_3 or metaboric acid, may also be used. Examples of suitable acids are alkanoic and alkenoic mono-, di- or polycarboxylic acids of 1 to 100, preferably 2 to 54, carbon atoms, e.g. acetic acid, n-octanoic acid, decanoic acid, myristic acid, oleic acid, linolenic acid, tetrapropenylsuccinic acid, aselaic acid or dimerised or trimerised linoleic acid. The acid used must be such as to form an oil-soluble salt with the amine used in forming the products of this invention. The most preferred acids are acyclic monocarboxylic acids in which the hydrocarbon group is a primary hydrocarbon group which is either saturated or mono- or polyethylenically unsaturated and contains from 12 to 36 carbon atoms. Examples of such preferred acids include lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, ricinoleic acid, palmitoleic acid, petroselenic acid, vaccenic acid, and erucic acid, among others.

Any amine may potentially be used in forming the compositions of the present invention. Preferred amines are aliphatic mono- and polyamines containing 2 to 40 carbon atoms per molecule. Primary, secondary and tertiary amines are suitable and these are preferably linear or branched aliphatic, cycloaliphatic or ethylenically unsaturated aliphatic amines of 6 to 22 carbon atoms, e.g. n-octylamine, oleylamine, cyclohexylamine, polyethylene polyamines such as triethylene tetramine, and the tertiary alkyl primary amines sold under the trade name Primene 81-R and Primene JM-T. As already noted, the amine must be capable of forming an oil-soluble salt with the acid used. The most preferred amines are acyclic primary monoamines in which the hydrocarbon group is a primary hydrocarbon group which is either saturated or mono- or polyethylenically unsaturated and contains from 8 to 22 carbon atoms. Examples of such preferred amines include n-octylamine, n-nonylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-pentadecylamine, n-octadecylamine and oleylamine, among others.

Instead of a mixture of acid and amine, an amino-acid may be used in an amount satisfying the proportions of amine and weak acid specified hereinabove. Suitable amino-acids include glycine, alanine, and phenylalanine. Similarly, one or more amino-acids may be used in combination with (i) one or more amino-free weak acids, (ii) one or more non-carboxylic amines, or (iii) one or more amino-free weak acids and one or more non-carboxylic amines.

One measure for determining that the correct proportion of amine and acid have been used in forming the new products of this invention is a determination of the pH of the reaction product. Since the product compositions consist essentially of a solution of various organic compounds usually in an oil which is usually a hydrocarbon oil, the compositions have, in a strict sense, no pH. However, it has been found that if a sample of the product is diluted in a mixture of methanol and toluene and then assayed with a conventional pH probe as used in aqueous systems, a measurement is obtained with provides a useful measure of the relative proportions of basic and acidic materials present in the composition. Measured in this way, the pH of the compositions of the invention should be in the range of 3 to 10 or preferably of 7 to 9.

The compositions of the invention may contain other additives suitable for use in gear oils, for example:

Antioxidants
Zinc dihydrocarbyldithiophosphates such as zinc dialkyldithiophosphates, zinc dicycloalkyldithiophosphates and zinc diaryldithiophosphates; hindered phenols; amines and various organic compounds containing nitrogen, sulphur or phosphorus.

Antifoamants and demulsification agents
Silicone-based fluids, ethylene glycol-propylene glycol condensation products, alkylpolyacrylates.

Dispersants
Polyalkenyl succinimides, succinate esters, N-vinylpyrrolidone-methacrylate ester copolymers, fatty acid esters and fatty acid amides, and carboxylic acid derivative compositions (e.g., succinimides, succinic acid esters, succinic acid ester-amides, etc.) that have been post-treated by reaction with one or more post-

treating reagents such as boron oxide, boron oxide hydrate, boron halides, boron acids, esters of boron acids, carbon disulphide, hydrogen sulphide, sulphur, sulphur chloride, alkenyl cyanides, carboxylic acid acylating agents (e.g., maleic anhydride, maleic acid, fumaric acid, malic acid, azelaic acid, adipic acid, C1 to C30 alkenylsuccinic acids, C1 to C30 alkenylsuccinic anhydrides, etc.), aldehydes, ketones, urea, thiourea, guanidine, dicyanodiamide, hydrocarbyl phosphates, hydrocarbyl phosphites, hydrocarbyl thiophosphates, hydrocarbyl thiophosphites, phosphorus sulphides, phosphorus oxides, phosphoric acid, phosphorous acid, hydrocarbyl thiocyanates, hydrocarbyl isocyanates, hydrocarbyl isothiocyanates, epoxides, episulphides, formaldehyde or formaldehyde producing compounds plus phenols, and sulphur plus phenols.

Detergents
Metal salts of organic naphthenates, salicylates, sulphonates, phenates or phosphonates.

Viscosity index improvers or pour point depressants
Alkylpolymethacrylates or olefin copolymers.

Friction Modifiers
Alkyl or alkenyl fatty acid amides, alkyl or alkenyl succinimides, or alkyl or alkenyl phosphonates.

Dispersnt viscosity index improvers
Olefin polymers grafted with a nitrogen-containing moiety such as described in U.S. Pat. No. 4,519,929

The invention includes within its scope lubricant additive concentrates comprising 5 to 95% of (a) one or more products formed by interacting (i) at least one highly-active sulphur-containing extreme pressure or anti-wear agent, (ii) at least one amine, and (iii) at least one weak acid, and 95 to 5% of (b) a diluent oil, the said percentages being by weight based on the total weight of the concentrate. Such concentrates may also contain 1 to 50% of one or more phosphorus-containing extreme pressure or anti-wear agents.

The following Examples illustrate the invention. The sulphurised isobutylenes used in the examples are commercially available products which contain 45 ± 3% sulphur and which are "active" within the meaning of this disclosure.

EXAMPLE 1

The ingredients listed below are pre-mixed in the relative proportions specified, heated to 60° C for 1.5 hours, and the resultant mixture is incorporated in an SAE 80W-90 mineral oil of North Sea origin at a concentration of 5.5% w/w.

Sulphurised Isobutylene	3.9
Octyl Amine	0.6
Oleyl Amine	0.163
Octanoic Acid	0.5
2-Ethylhexyl-Acid Phosphate	0.196
Copper Deactivator	0.07
Antifoam	0.06

Apart from the amino-nitrogen which is tied up as amine salt of 2-ethylhexyl acid phosphate, this oil blend contains approximately 12.1 mole % sulphur per mole % of amino nitrogen, and approximately 0.77 chemical equivalents of weak acid per equivalent of amino nitrogen.

EXAMPLE 2

A gear oil additive concentrate of this invention is formed by heating at 50° C for one hour a mixture of sulphurised isobutylene, trihydrocarbyl ester of dithiophosphoric acid, octyl amine, bis-2-ethylhexyl-phosphate, oleylamine, alkyl acid phosphite, a friction modifier and a succinimide type dispersant. In the second stage of the procedure, oleic acid, antifoam agent, and process oil are added to the hot mixture produced in the first stage. The resultant concentrate is then allowed to cool to about 35° when metal deactivator is added. The resultant concentrate contains (apart from amine tied up with phosphorus acids) approximately 21 mole % of sulphur per mole of amino nitrogen and approximately 0.56 chemical equivalent of weak acid (oleic acid) per equivalent of amino nitrogen. A gear oil is formed by blending this additive concentrate to a level of 6.5% w/w in an SAE 90 base oil (equivalent to a concentration of 2.27 weight % of sulphurised isobutylene). An oil formulated in this manner gave trouble-free performance of over 100 hours in the planetary spur gear test. In this test a system of spur-type gears is driven under variable and very heavy loads. The lubricating fluid is circulated around the system by a pump and is maintained at between 95° C and 130° C. Samples of the lubricating fluid are removed periodically and analysed for iron content. The test is terminated when excessive wear is recorded either by high iron levels in the oil, or by gear tooth breakage.

EXAMPLE 3

A mixture is formed from sulphurized isobutylene, oleylamine, octanoic acid, trihydrocarbyl dithiophosphate, a succinimide dispersant and a friction modifier in weight proportions of approximately 11.7:2.8:0.7:5.5:1:1 respectively. This mixture is heated at 60° C for one hour. To this hot mixture in a second stage are added octylamine, bis-2-ethylhexyl phosphate, an amine salt of a dihydrocarbyl thiophosphate and antifoam agent in weight proportions of approximately 0.2:0.4:3.3:0.2, respectively. Thereafter a mineral oil and a metal deactivator are added so that the resultant concentrate contains approximately 35% of the initial sulphurized isobutylene and approximately 18.3% of the mineral oil diluent. Excluding amine that is tied up with phosphorus acids, the additive concentrate contains approximately 18 mole % of sulphur per mole of amino nitrogen and approximately 0.6 equivalent of weak acid per equivalent of amino nitrogen. An SAE 90 base oil containing 6.5% of this additive concentrate gives over 90 hours of trouble-free performance in the planetary spur gear test.

EXAMPLE 4

The procedure of Example 3 is repeated with the following modifications: the bis-2-ethylhexyl phosphate, the octylamine and the antifoam agent are included in the first stage, the oleyl amine, the dispersant and the friction modifier are introduced into the second stage reaction mixture, and the second stage reaction mixture is held at 50° C for 30 minutes. An SAE 90 mineral oil containing 6.5% w/w of this additive concentrate exhibited a period of over 60 hours of satisfactory performance in the planetary spur gear test.

EXAMPLE 5

The procedure of Example 4 is repeated except that the first stage reaction mixture is heated to 50° C for 20 minutes and the second stage reaction mixture is held at 50° C for one hour. Similar results are obtained in the planetary spur gear test.

EXAMPLE 6

The proceudre of Example 3 is repeated except that the octylamine is added in the first stage reaction, the octanoic acid is added in the second stage reaction mixture, the first stage reaction mixture is maintained at 50° C for one hour, and the amine salt of a dihydrocarbyl thiophosphate is added in a final stage along with the mineral oil and metal deactivator. Satisfactory planetary spur gear performance for 75 hours was achieved using a gear oil containing 6.5% w/w of this additive concentrate.

EXAMPLE 7

The procedure of Example 3 is repeated with the following modifications: the octylamine and the trihydrocarbyl dithiophosphate are introduced into the first stage reaction mixture, and the octanoic acid is introduced into the second stage reaction mixture. Performance in excess of 100 hours in the planetary spur gear test was achieved with a lubricating oil containing 6.5% w/w of such an additive concentrate.

EXAMPLE 8

A commercially available gear oil additive formulation was found to be substantially insoluble in PAO (poly-alpha-olefin synthetic lubricating oil). Such a blend formed a very cloudy mixture which partially separated over a period of several days at ambient temperature. In contrast, a blend of the concentrate produced as in Example 2 at GL-5 dosage was found to be fully soluble in the PAO yielding a stable SAE 80W-90 GL-5 gear lubricating oil formulation.

The products of the invention may be used in a wide variety of automotive and industrial gear applications. Examples of such applications include use in hypoid axles and in mechanical steering drives in passenger cars and in cross-country vehicles. Further examples include use in hypoid axles, planetary hub reduction axles, mechanical steering and transfer gear boxes in utility vehicles such as trucks.

Systems in which the products of the invention may additionally be used include pinion and planetary hub reduction gear boxes, synchromesh gear boxes, power take-off gears and limited slip rear axles; they are especially useful in synchroniser type gear boxes. The thermal stability and oxidative stability of the products of the invention make them particularly suitable for use in transmission systems which may be operating at high temperatures.

In addition, the products of the invention may be used to formulate a single oil meeting the specifications of lubricants for use in both gear boxes and in rear axles, whereas hitherto two different oils were required to meet the specifications for these two uses. A product serving both such uses is referred to as a total drive line product.

Examples of the performance criteria which may be met by lubricants of this invention and by lubricants containing the additive concentrates of this invention are exemplified in the following specifications:

Automotive

- Mercedes-Benz Specifications DB 235.0 and DB 235.1.
- Zahnradfabrik Friedrichshafen Specifications ZF TE ML 02 and ZF TE ML 05.
- American Petroleum Institute Gear Oil Specifications API GL5 (published in ASTM STP 512A, March 1987) and API GL4.
- Peugeot S.A. Specifications PRS SAE 75W 80W (transmission) and PRS SAE 75W 80W (manual).
- Renault Specification 03-80-100 B.V.M.
- UK Military Specification CS 3000B.
- Mack Specification GO-G and GO-H.
- Volkswagen Specification VW 501.50.
- Ford Specification M2C-175A.

Industrial

- U.S. Steel Specification No. 224.
- AGMA Specification 250.04.
- David Brown Specification No. 51.53101 Type E.
- DIN 51517.

Claims

1. A product formed by interacting at a temperature above 30° C either concurrently or in any sequence (i) one or more active sulphur-containing extreme pressure or anti-wear agents, (ii) one or more amines, and (iii) one or more weak acids, the proportions of components (i) and (ii) being such that the mole percentages of sulphur in (i) to amino nitrogen in (ii) used in forming the product is in the range of 100:1 to 5:1, and the proportion of component (iii) used in forming the product being such that there are from 0.2 to 2 chemical equivalents of acid per equivalent of amino nitrogen in component (ii).

2. A product as claimed in Claim 1 when produced in at least two stages, one stage involving the interaction of at least a portion of components (i) and (ii), and a following stage involving the interaction of at least a portion of component (iii) with product formed form components (i) and (ii).

3. A product as claimed in either of Claims 1 and 2 when produced in the presence of at least one partial ester or full ester of an acid of pentavalent phosphorus.

4. A product as claimed in any one of Claims 1 to 3 when produced using proportions of components (i) and (ii) such that the mole percentages of sulphur in (i) to amino nitrogen in (ii) is in the range of 40:1 to 5:1.

5. A product as claimed in any one of Claims 1 to 4 when produced using one or more sulphurised olefins as component (i).

6. A product as claimed in any one of Claims 1 to 5 when produced using one or more acyclic monoamines as component (ii).

7. A product as claimed in any one of Claims 1 to 6 when produced using one or more aliphatic carboxylic acids as component (iii).

8. A product as claimed in any one of Claims 1 to 7 when produced using an amount of component (iii) theoretically insufficient to completely neutralise the amino nitrogen of component (ii).

9. A lubricant composition containing a minor amount of a product as claimed in any one of Claims 1 to 8.

10. A lubricant additive concentrate containing a product as claimed in any one of Claims 1 to 8.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 3536

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)
A	US-A-4 317 739 (J.R. SPERCE) * Column 1, lines 59-62; column 2, lines 3-9; column 2, lines 40-47; column 2, line 65 - column 3, line 5; column 5, lines 12-26 *	1,2,5,6,9, 10	C 10 M 159/12 // (C 10 M 159/12 C 10 M 129:28 C 10 M 133:06 C 10 M 135:02 C 10 M 139:00)
A	US-A-4 744 912 (A.B. CARDIS) * Claims 1,2; example 1 *	1,3-6,9, 10	
A	WO-A-8 605 508 (THE LUBRIZOL CORP.) * Claims 17,18,30,31; page 21, table II * & US-A-4 615 818 (S.A. DIBIASE) (Cat. D)	1,5-7,9, 10	
D,Y	US-A-3 398 095 (C.W. JUDD) * Claim 1; column 3, lines 55-59 *	1,6,7,9	
A	WO-A-8 503 709 (THE LUBRIZOL CORP.) * Page 6, lines 5-9; page 16, lines 24-29; page 31, lines 6-11; page 31, line 31 - page 32, line 6; page 39, example 9; page 34, lines 21-28 *	1,3,6-8	
A	US-A-2 475 410 (H.G. SMITH) * Claim 1; column 3, lines 11-65 *	1,6,7,9,10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	28 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 catagory
A : technological background
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