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(71) Applicant: **Chevron Chemical S.A.**

92309 Levallois Perret Cédex (FR)

• **Cazin, Jacques**

76290 Saint Martin du Manoir (FR)

• **Vignerot, Daniel**

76700 Harfleur (FR)

• **Le Sausse, Christophe**

76290 Montvilliers (FR)

• **Batelier, Dominique**

76600 Le Havre (FR)

(72) Inventors:

• **Tequi, Pierre**

76430 Saint Romain de Colbosc (FR)

(74) Representative: **Beauchamps, Georges et al**

Cabinet Weinstein

20, avenue de Friedland

75008 Paris (FR)

(54) **Borate containing additive for manual transmission lubricant being stable to hydrolysis and providing high synchromesh durability**

(57) The high synchromesh durability performance and gear protection of a manual transmission gear box is provided by adding to gear box a lubricating oil composition having improved water stability and oxidation

control. That lubricating oil composition comprises a base oil of lubricating viscosity, an alkali-metal borate, an organic polysulfide, an alkyl succinic acid ester of a polyol, and an overbased sulfurized alkyl or alkenyl salicylate.

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Description

The present invention relates to extreme pressure (EP) additives for lubricating oils. Especially the invention relates to a lubricant additive (preferably phosphorus free) for a manual transmission gear box containing potassium triborate having very good gear distress prevention properties, high synchronesh durability performance, and good water stability performance.

BACKGROUND OF THE INVENTION

High-load conditions often occur in the gear sets used in automotive transmission differentials, pneumatic tools, gas compressors, high-pressure hydraulic systems, metal-working and similar devices as well as in many types of bearings. In order to avoid the undesirable effects which result when using an uncompounded oil under these high-load conditions, the lubricants for use in such service contain EP agents. For the most part, EP agents have been organic or metallo-organic compounds which are oil soluble or are easily incorporated as a stable dispersion in the oil.

Alkali metal borate is well known to the industry for its usefulness as a wear inhibitor and extreme pressure agent. In case of a contamination of the lubricant with water, additives containing alkali metal borate may not be stable to hydrolysis. Though alkali metal borate itself is slightly unstable in presence of water, the other components of the package such as friction modifiers, wear inhibitors, and metal deactivators deteriorate the hydrolysis stability of the lubricant. It is an object of the present invention to provide a lubricant having improved hydrolysis stability, while preventing gear distress, protecting the gear against fatigue, and having a high synchronesh durability. This last property is of paramount importance for manual transmission fluids.

SUMMARY OF THE INVENTION

The present invention provides an extreme pressure additive that improves the water stability, oxidation control, high synchronesh durability performance, and gear protection of a lubricating oil in a manual transmission gear box. That additive contains an alkali-metal borate, an organic polysulfide, an alkyl succinic acid ester of a polyol, and an overbased sulfurized alkyl or alkenyl salicylate.

The alkali-metal borate is present at a level of from 30% to 70%. Preferably, the alkali-metal borate is potassium triborate present at a level of from 40% to 66%.

The organic polysulfide is present at a level of from 10% to 30%. Preferably, the organic polysulfide is a di-tertiary-butyl-polysulfide present at a level of from 12% to 25%.

The alkyl succinic acid ester of a polyol is present at a level of from 1% to 20%. Preferably, the alkyl succinic acid ester is the reaction product of pentaerythritol and polyisobutenyl succinic anhydride, and the alkyl succinic acid ester is present at a level of from 5% to 15%.

The overbased sulfurized alkyl or alkenyl salicylate is present at a level of from 0.5% to 20%. Preferably, the overbased sulfurized alkyl or alkenyl salicylate is an overbased mixture of a sulfurized alkyl salicylate and a sulfurized alkyl phenate, present at a level of from 5% to 10%.

Preferably, the extreme pressure additive also has up to 20% of a fatty acid ester of a polyol, more preferably a pentaerythritol mono-oleate present at a level of from 5% to 10%.

In one embodiment, the extreme pressure additive also contains up to 20% of an alkyl substituted phenyl phosphate, up to 7% of at least one metal deactivator, and up to 0.1% foam inhibitor.

Preferably, the alkyl substituted phenyl phosphate is trixylenyl phosphate present at a level of from 5% to 10%.

Preferably, at least one metal deactivator is used, more preferably more than one metal deactivator. For example, both 2,5-dimercapto-1,3,4-thiadiazole and benzotriazole derivative can be used.

The extreme pressure additive can be used in a lubricating oil composition with a base oil of lubricating viscosity. That lubricating oil composition can also contain a viscosity index improver and a pour point depressant. The high synchronesh durability performance and gear protection of a manual transmission gear box can be improved by adding to the gear box that lubricating oil.

The extreme pressure additive can also be used in a concentrate comprising a compatible organic liquid diluent and the extreme pressure additive.

DETAILED DESCRIPTION OF THE INVENTION

In its broadest aspect, the present invention involves an extreme pressure additive comprising an alkali-metal borate, an organic polysulfide, an alkyl succinic acid ester of a polyol, and an overbased sulfurized alkyl or alkenyl salicylate. Preferably, the additive can further comprise a fatty acid ester of a polyol. In one embodiment, the additive can further comprise an alkyl substituted phenyl phosphate, at least one metal deactivator, and a foam inhibitor.

The high synchromesh durability performance and gear protection of a manual transmission gear box can be provided by adding to the gear box a lubricating oil composition having improved water stability and oxidation control. That lubricating oil composition comprises a base oil of lubricating viscosity and the extreme pressure additive as described above.

Unless otherwise specified, all percentages are in weight percent of the total additive (calculated without diluent oil) and all ratios are molar ratios.

One method of producing the extreme pressure additive comprises blending together:

- (a) from 40% to 66% of potassium triborate;
- (b) from 12% to 25% of di-tertiary-butyl-trisulfide;
- (c) from 5% to 15% of the reaction product of pentaerythritol and polyisobutenyl succinic anhydride;
- (d) from 5% to 10% of an overbased mixture of a sulfurized alkylsalicylate and a sulfurized alkylphenate;
- (e) from 5% to 10% of pentaerythritol mono-oleate;
- (f) from 5% to 10% of trixylenyl phosphate;
- (g) from 1% to 3% of 2,5-dimercapto-1,3,4-thiadiazole;
- (h) from 0.5% to 1.5% of benzotriazole derivative; and
- (i) up to 0.1% of a foam inhibitor.

The additive produced by that method might have a slightly different composition than the initial mixture, because the components may interact. The components can be blended in any order and can be blended as combinations of components.

ALKALI-METAL BORATE

In the present invention, the additive contains from 30% to 70% of an alkali-metal borate, preferably from 40% to 66% potassium triborate.

The alkali-metal borates are well known in the art and are available commercially. Representative patents disclosing suitable borates and methods of manufacture include U.S. Patent Nos.: 3,313,727; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790. Particularly preferred are the hydrated potassium triborate microparticles having a boron-to-potassium molar ratio of about 2.5 to 4.5. At least 90% of the borate particles generally have a particle size lower than 0.39 μm .

Alkali metal borates are used for the protection of gears against wear (scoring, pitting, ridging, rippling), to provide an optimum friction coefficient, and to protect the synchronizer ring against wear.

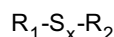
ORGANIC POLYSULFIDE

In the present invention, the additive contains from 10% to 30% of organic polysulfide, preferably from 12% to 25% di-tertiary-butyl-trisulfide.

The organic polysulfide is characterized as having sulfide linkages from at least 2 to about 10 sulfur atoms, preferably 2 to 6 sulfur atoms, more preferably 2 to 4 sulfur atoms. The organic polysulfides are generally di, tri, or tetrasulfide compositions with trisulfide compositions preferred.

Generally the organic polysulfides contain from 10% to 60% sulfur, preferably from 20% to 50% sulfur, and more preferably around 44% sulfur.

In its broadest sense, the organic polysulfide molecule may be defined by the formula:



with x being from 2 to 10. R_1 and R_2 may be olefinic compounds or alkyl groups having from 3 to 30 carbon atoms.

Preferably the organic polysulfide is di-tertiary-butyl-trisulfide which contains around 44% sulfur.

Organic polysulfides are introduced in the formulation to provide extreme pressure properties to protect gears against distress.

ALKYL SUCCINIC ACID ESTER OF A POLYOL

The alkyl succinic acid ester of a polyol is present at a level of from 1% to 20%. Preferably, the alkyl succinic acid ester is the reaction product of pentaerythritol and polyisobutenyl succinic anhydride, and the alkyl succinic acid ester is present at a level of from 5% to 15%.

The process for the preparation of alkenyl or alkyl substituted succinic anhydrides involving the reaction of a polyolefin and a maleic anhydride has been described in the art. In the case of the classes of compounds described in this invention, the alkenyl or alkyl group has a number average molecular weight (Mn) of from 500 to 2500 and a Mw/Mn ratio of from 1 to 500. The alkenyl or alkyl substituent of the succinic anhydride reactant is preferably polymerized isobutene having a Mn of 500 to 1500. Most preferably, it is a polymerized isobutene having a Mn of from 850 to 1200. The process for producing polyisobutenyl succinic anhydride has been described in the US Patent No. 3,381,022. The alkyl substituted succinic anhydride is reacted with polyhydric alcohol such as glycerol, pentaerythritol, and sorbitol. Preferably, the aliphatic polyhydric alcohol is pentaerythritol.

This compound is used to improve the stability to hydrolysis and the compatibility/miscibility of the other parts of the additive.

OVERBASED SULFURIZED ALKYL OR ALKENYL SALICYLATE

The overbased sulfurized alkyl or alkenyl salicylate is present at a level of from 0.5% to 20%. Preferably it is an overbased mixture of a sulfurized alkylsalicylate and a sulfurized alkylphenate, and the mixture is present at a level of from 5% to 10%. Preferably, the salicylate part of that mixture is a single aromatic ring alkylsalicylate, as is described in the European Patent Application EP 0 786 448 A2.

The alkylphenols used to prepare the overbased sulfurized alkyl or alkenyl salicylate contain up to 85% of linear alkylphenol in mixture with at least 15% of branched alkylphenol in which the branched alkyl radical contains at least nine carbon atoms. Preferably, these alkylphenols contain from 35% to 85% of linear alkylphenol in mixture with from 15% to 65% of branched alkylphenol. The ratio of branched versus linear alkylphenol is given by weight. Preferably, the linear alkyl radical contains 12 to 40 carbon atoms, more preferably from 18 to 30 carbon atoms, and the branched alkyl radical contains at least 9 carbon atoms, preferably from 9 to 24 carbon atoms, more preferably 10 to 15 carbon atoms.

This compound is used to improve the stability to hydrolysis and to improve the thermal stability and the control of oxidation.

FATTY ACID ESTER OF POLYOL

If used, the fatty acid ester of a polyol is present at a level of up to 20%. Preferably it is pentaerythritol mono-oleate present at a level of from 5% to 10%.

The esters useful for this invention are oil-soluble and are preferably prepared from C₈ to C₂₂ fatty acids of the formula R-COOH wherein R is alkyl or alkenyl. The preferred esters are obtained from oleic acids: C₁₆₋₁₈ and C₁₈-unsaturated.

The ester is synthesized from the previously described fatty acids and polyols such as pentaerythritol, glycerol, sorbitol, etc.

This compound is used to have good friction properties, especially to provide good conditions for synchronization, and to improve the stability to hydrolysis.

ALKYL SUBSTITUTED PHENYL PHOSPHATE

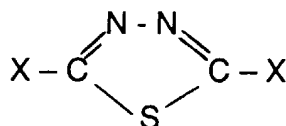
If used, the alkyl substituted phenyl phosphate is present at a level of up to 20%. Preferably it is trixylenyl phosphate present at a level of from 5% to 10%. The phenol derivative used to obtain this phosphate may be cresol, xylenol, or tri-butyl-phenol.

This compound is used for its wear inhibition properties, especially for the protection of the synchronizer ring.

METAL DEACTIVATOR

If used, the metal deactivator is present at a level of up to 7%. Preferably it is a mixture of a 2,5-dimercapto-1,3,4-thiadiazole derivative and a benzotriazole. The 2,5-dimercapto-1,3,4-thiadiazole derivative is present at a level of up to 3.5% (preferably from 1% to 3%). The benzotriazole is present at a level of up to 3.5% (preferably from 0.5 to 1.5%).

The 2,5 dimercapto-1,3,4,-thiadiazole derivative has the following formula



X may be an R - S or an R - S - S group with R being an alkyl group.

The 2,5 dimercapto-1,3,4,-thiadiazole derivative is used as a metal deactivator to prevent copper corrosion and as an extreme pressure agent.

The benzotriazole derivative is a mixture of the N,N-bis (2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methylamine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine. If desired, the benzotriazole derivative can be replaced with a tolutriazole derivative.

The benzotriazole derivative is used as a metal deactivator to prevent the corrosion of copper.

FOAM INHIBITOR

If used, the foam inhibitor is present at a level of up to 0.1%. Preferably the foam inhibitor contains about 3.5% silicon.

LUBRICATING OIL COMPOSITIONS

The additives produced by the process of this invention are useful for improving the water stability and oxidation control of lubricating oil compositions. When employed in this manner, the amount of the additive ranges from about 0.5% to 40% of the total lubricating oil composition, although preferably from about 1% to 25% of the total lubricating oil composition.

The lubricating oil composition comprises a base oil of lubricating viscosity and the extreme pressure additive of the present invention. The lubricating oil composition can also comprise viscosity index improvers and pour point depressants.

Examples of well-known viscosity index improvers include polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

An example of a well known pour point depressant is polymethyl methacrylate.

The oil of lubricating viscosity in which the extreme pressure additive is dispersed can be any fluid of low dielectric constant which is inert under the reaction conditions (particularly nonsaponifiable) and of lubricating viscosity. Fluids of lubricating viscosity generally have viscosities of from 35 to 50,000 Saybolt Universal Seconds (SUS) at 100°F (38°C). The fluid medium or oil may be derived from either natural or synthetic sources. Included among the natural hydrocarbonaceous oils are paraffin base, naphthenic base and mixed base oils. Synthetic oils include polymers of various olefins (generally from 2 to 6 carbon atoms), alkylated aromatic hydrocarbons, etc. Nonhydrocarbon oils include polyalkylene oxides such as polyethylene oxide, aromatic ethers, silicone, etc. The preferred media are the hydrocarbonaceous oils, both natural and synthetic. Preferred among the hydrocarbonaceous oils are those having SAE viscosity numbers of 5W to 20W and 20W to 250W, and especially those having SAE viscosity numbers in the range 75W to 250W.

The content of the oil of lubricating viscosity in the lubricating oil composition will depend on the concentrations of the other components. The lubricating oil constitutes the balance of the composition after the concentrations of the borate, the antiwear agents and the organic sulfur compounds and any other desired additives have been specified.

ADDITIVE CONCENTRATES

Additive concentrates are also included within the scope of this invention. The concentrates of this invention comprise sufficient organic diluent to make them easy to handle during shipping and storage.

Suitable organic diluents which can be used include for example, solvent refined 100N, i.e., Cit-Con 100N, and hydrotreated 100N, i.e., RLOP 100N, and the like. The organic diluent preferably has a viscosity of from about 1 to about 20 cSt at 100°C.

Preferably, the organic diluent will constitute less than 10% of the concentrate.

EXAMPLES

The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

HYDROLYSIS STABILITY TEST:

The purpose of the hydrolysis stability tests is to assess the stability of a fully formulated lubricant to hydrolysis. Up to 3% water may be introduced by accident in the gear box during car wash. The additive has to be stable enough to avoid chemical reactions with water. Two tests have been developed to measure the hydrolysis stability.

For the first test, 3% water is mixed up manually with a fully formulated lubricant in a graduated cylinder. The cylinder containing the oil and water is stored at ambient temperature for ten days. After ten days, the mixture is visually inspected looking at the aspect of the oil, and at the part of the additive which has reacted with water. This part has to be 1 ml or lower, and the lubricant has to remain clear, without haze or gel formation.

For the second test, 0.5% of water is mixed up with a fully formulated lubricant with a mechanical stirring rod in a cylinder. The cylinder is stored at 60°C for one month. Then the mixture is visually inspected, looking at the aspect of the oil and at the deposit at the bottom of the cylinder. If the bottom of the cylinder is only covered by emulsion of oil and water, the result is acceptable. If more than 0.5 ml of deposit has been formed on the bottom of the cylinder, reactions between oil and water have occurred and the result is no longer acceptable.

EXAMPLE 1

The additive package contained the following compounds:

60.55%	potassium tri-borate,
15.14%	di-tertiary-butyl-trisulfide containing 44% sulfur,
6.06%	the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
8.48%	overbased sulfurized alkyl salicylate,
6.06%	pentaerythritol mono-oleate,
2.42 %	2,5 dimercapto-1,3,4,-thiadiazole derivative,
1.21%	benzotriazole derivative which is a mixture of N,N-bis (2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methyl-
	amine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine, and
0.08%	silicon-containing foam inhibitor.

The lubricant contained:

8.7%	of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,
9.0%	polymethacrylate type viscosity index improver,
0.2%	polymethacrylate type pour point depressant,
82.1%	mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.8 cSt, and the dynamic viscosity at -40°C was 45000 cP.

The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

In the first test (3% of water, oil stored at ambient temperature) the deposit was less than 1 ml, the free water was 2 ml, and the aspect of the oil was very clear.

In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

Protection against gear distress:

The described package provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following tests well known in the industry:

The FZG test rig (CEC L-07-A-95).

This protection remained effective even after oxidation (CEC L-48-A-95 oxidation procedure at 160°C during 192 hours).

The results were:

- CEC L-07-A-95: pass 12
- CEC L-07-A-95 double speed: pass 12
- CEC L-07-A-95 after oxidation CEC L-48-A-95 160°C 192 hour: damage load stage = 10.

The API L-37 procedure:

	API L-37	
Gear tooth surface condition	Pinion	Ring gear
Burnish	Medium-bright	Dull
Wear	Trace	Trace-light
Surface fatigue		
• Rippling	None	None
• Ridging	None	None
• Pitting	None	None
• Spalling	None	None
Scoring	None	None
Discoloration	Light	Light-medium
Corrosion	None	None
Deposits	Trace	Trace
Pass/Fail assessment	Pass 9.95	

Surface fatigue protection:

The described package has provided an effective protection of gears' teeth against surface fatigue (pitting). The protection against pitting was assessed through the FZG C pitting test run at 90°C. This test is well known in the industry.

The results of FZG C/8.3/90/1530 were:

first test: 231 hours

second test: 343 hours

third test: 196 hours.

Synchromesh durability:

The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the FZG SSP 180 procedure using Audi B80 brass synchronizer. This procedure was run at twice the normal duration. The protection of Mo/Steel synchronizer, often used in heavy duty trucks, was evaluated through the ZF synchromesh procedure.

FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass (x2) >100000 Axial wear 0.57 - 0.57 mm Axial wear 0.36 - 0.81mm Friction coefficient: Beginning:0.108/0.11 End: 0.099/0.095
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(continued)

5	FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig (200000 cycles)	Pass >200000 Axial wear: 0.42 - 0.88 mm Friction coefficient: Beginning: 0.11 100000: 0.095 End: 0.098
10		
15	ZF synchro test (Mo/steel synchronizer)	Pass >100000 Downshift: Friction coefficient: 0.079 - 0.085 Axial wear: 0.2 mm Ring wear: 0.1mm Upshift: Friction coefficient: 0.072 - 0.077 Axial wear: 0.25 mm Ring wear: 0.1mm
20		
25		

Oxidation stability:

The described package offered a very efficient protection of mineral lubricant against oxidation reactions. This fact was assessed through the CEC L-48-A-95 oxidation test run at 160°C during 192 hours, and through the API L-60-1 oxidation test.

35	Oxidation CEC L-48-A-95 192 hours at 160°C	Pass Viscosity Inc: 1.87 cSt TAN Inc: 1.4 mg KOH Deposit: none
40	API L-60-1	
	100°C Viscosity increase (%)	55.89
	Pentane insoluble (wt. %)	2.8
	Toluene insoluble (wt. %)	1.41
45	Carbon/varnish rating	9.20
	Sludge merit rating	9.50
	Pass/fail criteria	pass

EXAMPLE 2:

The additive package contained the following compounds:

43.92% potassium tri-borate,
28.54% di-tertiary-butyl-trisulfide containing 44% sulfur,
10.98% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
7.69% overbased sulfurized alkyl salicylate,
5.49% pentaerythritol mono-oleate,
3.29% 2,5 dimercapto-1,3,4,-thiadiazole derivative,

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0.09% a silicon-containing foam inhibitor.

The lubricant contained:

9.7% of a concentrate containing 94% of the above additive package and 6% of a 100N mineral oil,
9.0% polymethacrylate type viscosity index improver,
0.2% polymethacrylate type pour point depressant,
81.1% a mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.8 cSt, and the dynamic viscosity at -40°C is 45000 cP.

The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

In the first test (3% of water, oil stored at ambient temperature) the deposit was 1 ml, the free water was 2 ml, and the aspect of the oil was clear.

In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

Protection against gear distress:

The described package provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following tests well known in the industry:

The results of the FZG test rig CEC L-07-A-95: pass 12

Synchromesh durability:

The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the FZG SSP 180 procedure using Audi B80 brass synchronizer procedure.

FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass >100000 Axial wear 0.70 - 0.77 mm Friction coefficient: Beginning: 0.107 End: 0.08
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Oxidation stability:

The described package offered a very efficient protection of mineral lubricant against oxidation reactions. This fact was assessed through the CEC L-48-A-95 oxidation test run at 160°C during 192 hours, and through the API L-60-1 oxidation test.

Oxidation CEC L-48-A-95 192 hours at 160°C	Pass Viscosity Increase: 3.36 cSt TAN Increase: 2.7 mg KOH Deposit: none
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EXAMPLE 3:

The additive package contained the following compounds:

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65.72% potassium tri-borate,
16.44% di-tertiary-butyl-trisulfide containing 44% sulfur,
6.57% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
9.20% overbased sulfurized alkyl salicylate,
5 1.31% 2,5 dimercapto-1,3,4,-thiadiazole derivative,
0.66% benzotriazole derivative which is a mixture of N,N-bis (2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methyl-amine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine, and
0.10% silicon-containing foam inhibitor.

10 The lubricant contained:

8.0% of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,
9.0% polymethacrylate type viscosity index improver,
0.2% polymethacrylate type pour point depressant,
15 82.8% a mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.8 cSt, and the dynamic viscosity at -40°C is 45000 cP.

20 The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

In the first test (3% of water, oil stored at ambient temperature) the deposit was 1 ml, the free water was 2 ml, and the aspect of the oil was very clear.

25 In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

EXAMPLE 4:

30 The additive package contained the following compounds:

56.45% potassium tri-borate,
22.58% di-tertiary-butyl-trisulfide containing 44% sulfur,
5.65% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
35 7.90% overbased sulfurized alkyl salicylate,
5.65% pentaerythritol mono-oleate
1.13% 2,5 dimercapto-1,3,4,-thiadiazole derivative,
0.57% benzotriazole derivative which is a mixture of N,N-bis (2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methyl-amine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine, and
40 0.07% silicon-containing foam inhibitor.

The lubricant contained:

9.3% of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,
45 9.0% polymethacrylate type viscosity index improver,
0.2% polymethacrylate type pour point depressant,
81.5% a mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

50 The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.8 cSt, and the dynamic viscosity at -40°C is 45000 cP.

The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

55 In the first test (3% of water, oil stored at ambient temperature) the deposit was less than 1 ml, the free water was 2 ml, and the aspect of the oil was clear.

In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

Protection against gear distress:

The described packages provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following test well known in the industry:

The results of the FZG test rig CEC L-07-A-95: pass 12.

Surface fatigue protection:

The described package has provided an effective protection of gears' teeth against surface fatigue (pitting). The protection against pitting was assessed through the FZG C pitting test run at 90°C. This test is well known in the industry.

The results of FZG C/8.3/90/1530 were:

first test: 266 hours

second test: 343 hours

third test: 175 hours.

Synchromesh durability:

The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the FZG SSP 180 procedure using Audi B80 brass synchronizer. This procedure was run at twice the normal duration. The protection of Mo/Steel synchronizer, often used in heavy duty trucks, was evaluated through the ZF synchromesh procedure.

FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass >100000 Axial wear 0.34 - 0.8 mm Friction coefficient: Beginning: 0.102 End: 0.111
ZF synchro test (Mo/steel synchronizer)	Pass >100000 Downshift: Friction coefficient: 0.082 - 0.085 Axial wear: 0.15 mm Ring wear: 0.1mm Upshift: Friction coefficient: 0.085 - 0.076 Axial wear: 0.2 mm Ring wear: 0.15mm

Oxidation stability:

The described package offered a very efficient protection of mineral lubricant against oxidation reactions. This fact was assessed through the CEC L-48-A-95 oxidation test run at 160°C during 192 hours.

Oxidation CEC L-48-A-95 192 hours at 160°C	Pass Viscosity Increase: 2.02 cSt TAN Increase: 1.87 mg KOH Deposit: none
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EXAMPLE 5:

The additive package contained the following compounds:

- 5 60.55% potassium tri-borate,
- 15.14% di-tertiary-butyl-trisulfide containing 44% sulfur,
- 6.06% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
- 8.48% overbased sulfurized alkyl salicylate,
- 6.06% trixylenyl phosphate
- 10 2.42% 2,5 dimercapto-1,3,4,-thiadiazole derivative,
- 1.21% benzotriazole derivative which is a mixture of N,N-bis (2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methyl-amine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine, and
- 0.08% silicon-containing foam inhibitor.

15 The lubricant contained:

- 8.7% of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,
- 9.0% polymethacrylate type viscosity index improver,
- 0.2% polymethacrylate type pour point depressant,
- 20 82.1% a mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.8 cSt, and the dynamic viscosity at -40°C is 45000 cP.

25 The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

In the first test (3% of water, oil stored at ambient temperature) the deposit was less than 1 ml, the free water was 2 ml, and the aspect of the oil was very clear.

30 In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

Protection against gear distress:

35 The described package provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following test well known in the industry:

The results of the FZG test rig CEC L-07-A-95, double speed: pass 12.

Synchromesh durability:

40 The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the FZG SSP 180 procedure using Audi B80 brass synchronizer. This procedure was run at twice the normal duration.

45	FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass (x2)
		>100000
		Axial wear 0.2 - 0.46 mm
50		Axial wear 0.2 - 0.52 mm
		Friction coefficient:
		Beginning: 0.11/0.11
55		End: 0.100/0.106

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(continued)

FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass >200000 Axial wear: 0.23 - 0.52 mm Friction coefficient: Beginning: 0.11 100000: 0.106 End: 0.101
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Oxidation stability:

The described package offered a very efficient protection of mineral lubricant against oxidation reactions. This fact was assessed through the CEC L-48-A-95 oxidation test run at 160°C during 192 hours.

Oxidation CEC L-48-A-95 192hours at 160°C	Pass Viscosity Increase: 1.64 cSt TAN Increase: 0.9 mg KOH Deposit: none
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EXAMPLE 6:

The additive package contained the following compounds:

59.94% potassium tri-borate,
13.32% di-tertiary-butyl-trisulfide containing 44% sulfur,
13.32% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
6.66% overbased sulfurized alkyl salicylate,
6.66% pentaerythritol mono-oleate, and
0.10% silicon-containing foam inhibitor.

The lubricant contained:

8.0% of a concentrate containing 94% of the above additive package and 6% of a 100N mineral oil,
5.0% polymethacrylate type viscosity index improver,
0.2% polymethacrylate type pour point depressant,
86.8% a mixture of 65% of a 90N mineral base oil and 35% of a 600N mineral base oil.

The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.2 cSt, and the dynamic viscosity at -40°C is 60000 cP.

The described package demonstrated a good oil and water separation with very limited reaction with water at ambient temperature (22°C and at 60°C), even when 3% of water is added into the package. There was slight deposit at the interface between water and oil which was essentially due to water and oil emulsion. This performance was evaluated with the previously described in-house procedures.

In the first test (3% of water, oil stored at ambient temperature) the deposit was 1 ml, the free water was 2 ml, and the aspect of the oil was very clear.

In the second test (0.5% of water, oil stored at 60°C) the bottom was covered by oil/water emulsion and the aspect of the oil was clear.

Protection against gear distress:

The described package provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following test well known in the industry:

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	API L-37	
Gear tooth surface condition	Pinion	Ring gear
Burnish	Medium-bright	Dull
Wear	Trace	Trace
Surface fatigue		
• Rippling	None	None
• Ridging	None	None
• Pitting	None	Medium
• Spalling	None	None
Scoring	None	None
Discoloration	Light	Medium
Corrosion	None	None
Deposits	None	None
Pass/Fail assessment	Pass 9.89	

Synchromesh durability:

The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the ZF synchromesh procedure.

ZF synchro test (Mo/steel synchronizer)	Pass >1 00000 Downshift: Friction coefficient: 0.090 - 0.074 Axial wear: 0.25 mm Ring wear: 0.15mm Upshift: Friction coefficient: 0.087 - 0.072 Axial wear: 0.30 mm Ring wear: 0.15mm
---	--

Oxidation stability:

The described package offered a very efficient protection of mineral lubricant against oxidation reactions. This fact was assessed through the CEC L-48-A-95 oxidation test run at 160°C during 192 hours, and through the API L-60-1 oxidation test.

Oxidation CEC L-48-A-95 192 hours at 160°C	Pass Viscosity Increase: 1.47 cSt TAN Inc: 1.4 mg KOH Deposit: none
API L-60-1 100°C Viscosity increase (%) Pentane insoluble (wt. %) Toluene insoluble (wt. %) Carbon/varnish rating Sludge merit rating	40.50 2.18 1.60% 9.40 9.75

(continued)

Pass/fail criteria	Pass
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5 The previously described examples showed an improvement compared to the following:

Comparative Example A:

The additive package contained the following compounds:

10

57.09% potassium tri-borate,
 21.40% di-tertiary-butyl-trisulfide containing 44% sulfur,
 4.28% primary alcohol zinc dithiophosphate,
 7.14% high molecular weight substituted imidazoline,
 15 9.99% low over-based alkyl calcium sulfonate, and
 0.10% silicon-containing foam inhibitor.

The lubricant contained:

20

7.4% of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,
 5.0% polymethacrylate type viscosity index improver,
 0.2% polymethacrylate type pour point depressant,
 87.4% a mixture of 55% of a 90N mineral base oil and 45% of a 600N mineral base oil.

25

The SAE grade is 75W-80W, the kinematic viscosity at 100°C is around 7.2 cSt, and the dynamic viscosity at -40°C is 60000 cP.

Hydrolytic stability:

30

The described package has demonstrated a poor oil and water separation with important reaction with water at ambient temperature 22°C and at 60°C. There was a lot of deposit at the interface between water and oil which was essentially due to the reaction of some compounds of the additive with water. This performance was evaluated with the previously described in-house procedures.

35

In the first test (3% of water, oil stored at ambient temperature) the deposit was 4 ml, the free water was 0 ml, and the aspect of the oil was very hazy.

In the second test (0.5% of water, oil stored at 60°C) the deposit was 50 ml.

Protection against gear distress:

40

The described packages provided a very effective protection of gears' teeth against adhesive wear and abrasive. This protection against gear distress has been assessed through the following test well known in the industry:

The FZG test rig CEC L-07-A-95: pass 12.

Comparative Example B:

45

The additive package contained the following compounds:

50

50.59% potassium tri-borate,
 18.97% di-tertiary-butyl-trisulfide containing 44% sulfur,
 12.65% the reaction product of a 950 Mw polyisobutene, succinic anhydride and pentaerythritol,
 2.53% primary alcohol zinc dithiophosphate
 6.32% high molecular weight substituted imidazoline,
 8.85% high over-based alkyl calcium sulfonate, and
 0.09% silicon-containing foam inhibitor.

55

The lubricant contained:

8.3% of a concentrate containing 95% of the above additive package and 5% of a 100N mineral oil,

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5.0% polymethacrylate type viscosity index improver,
0.2% polymethacrylate type pour point depressant,
86.5% a mixture of 55% of a 90N mineral base oil and 45% of a 600N mineral base oil.

5 The SAE grade was 75W-80W, the kinematic viscosity at 100°C was around 7.2 cSt and the dynamic viscosity at -40°C was 60000 cP.

Hydrolytic stability:

10 The described package had demonstrated a poor oil and water separation with important reaction with water at ambient temperature 22°C and at 60°C. There is a lot of deposit at the inter-face between water and oil which is essentially due to the reaction of some compounds of the additive with water. This performance was evaluated with the previously described in-house procedures.

15 In the first test (3% of water, oil stored at ambient temperature) the deposit was 1.5 ml, the free water was 0 ml, and the aspect of the oil was very hazy.

In the second test (0.5% of water, oil stored at 60°C) the deposit was 8 ml and the aspect of the oil was very hazy.

Synchromesh durability:

20 The described package provided an effective protection of synchronizer's ring against wear. The synchromesh durability performance of the described packages was measured with the FZG SSP 180 procedure using Audi B80 brass synchronizer. This procedure was run at twice the normal duration. The protection of Mo/Steel synchronizer, often used in heavy duty trucks, was evaluated through the ZF synchromesh procedure.

25	FZG SSP 180 (Audi B80 brass synchronizer) Hürth test rig	Pass (x2) >100000 Axial wear 0.1 - 0.1 mm
30		>100000 Axial wear 0.40 - 0.90 mm
35	ZF synchro test (Mo/steel synchronizer)	pass >100000 Downshift: Friction coefficient: 0.078 - 0.091 Axial wear: 0.15 mm
40		Ring wear: 0.1mm Upshift: Friction coefficient: 0.071 - 0.085 Axial wear: 0.2 mm
45		Ring wear: 0.15mm

50 While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Claims

55 1. An extreme pressure additive comprising:

- (a) from 30% to 70% of an alkali-metal borate, preferably from 40% to 66% of potassium triborate;
- (b) from 10% to 30% of an organic polysulfide, preferably from 12% to 25% of a di-tertiary-butyl-trisulfide;

(c) from 1% to 20% of an alkyl succinic acid ester of a polyol, preferably from 5% to 15% of the reaction product of pentaerythritol and poly-isobutenyl succinic anhydride; and
 (d) from 0.5% to 20% of an overbased sulfurized alkyl or alkenyl salicylate, preferably from 5% to 10% of an overbased mixture of a sulfurized alkylsalicylate and a sulfurized alkylphenate.

- 5
2. An extreme pressure additive according to Claim 1 further comprising:
 (e) up to 20% of a fatty acid ester of a polyol, preferably from 5% to 10% of pentaerythritol mono-oleate.
- 10
3. An extreme pressure additive according to Claim 1 or 2 further comprising:
 (f) up to 20% of an alkyl substituted phenyl phosphate, preferably 5 to 10% of trixylenyl phosphate;
 (g) up to 7% of at least one metal deactivator, preferably from 1% to 3% of 2,5-dimercapto-1,3,4-thiadiazole derivative and from 0.5% to 1.5% of a benzotriazole; and
 (h) up to 0.1% of a foam inhibitor.
- 15
4. Application of the extreme pressure additive as claimed in any of Claims 1 to 3 to improve water stability, to improve oxidation control, to provide high synchromesh durability performance, and to provide gear protection of a lubricating oil in a manual transmission gear box.
- 20
5. A lubricating oil composition comprising a base oil of lubricating viscosity and the extreme pressure additive as claimed in any of Claims 1 to 3.
- 25
6. A lubricating oil composition according to Claim 5 further comprising a viscosity index improver and a pour point depressant.
- 30
7. A concentrate comprising a compatible organic liquid diluent and the extreme pressure additive as claimed in any of Claims 1 to 3.
- 35
8. A method of providing high synchromesh durability performance and providing gear protection of a manual transmission gear box, said method comprising adding to said gear box a lubricating oil composition having improved water stability and oxidation control, said lubricating oil composition comprising a base oil of lubricating viscosity and the extreme pressure additive as claimed in any of Claims 1 to 3.
- 40
9. A method of producing an extreme pressure additive comprising blending together:
 (a) from 40% to 66% of potassium triborate;
 (b) from 12% to 25% of a di-tertiary-butyl-trisulfide;
 (c) from 5 to 15% of the reaction product of pentaerythritol and polyisobutenyl succinic anhydride;
 (d) from 5% to 10% of an overbased mixture of a sulfurized alkylsalicylate and a sulfurized alkylphenate;
 (e) from 5% to 10% of pentaerythritol mono-oleate;
 (f) from 5% to 10% of trixylenyl phosphate;
 (g) from 1% to 3% of 2,5-dimercapto-1,3,4-thiadiazole;
 (h) from 0.5% to 1.5% of benzotriazole derivative; and
 (a) up to 0.1% of a foam inhibitor.
- 45
10. An extreme pressure additive produced by the method as claimed in Claim 9.
- 50
- 55



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 40 1967

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 December 1998	Examiner Hilgenga, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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