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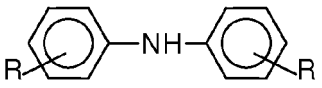
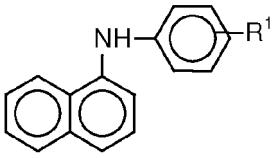
(54) **Lubricating oil composition**

(57) The present invention provides a lubricating oil composition comprising:
(a) a base oil;
(b) one or more diphenylamine (DPA) compounds having formula (I),



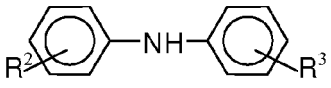
(I)

wherein each R is independently an alkyl group having from 1 to 16 carbon atoms, preferably from 3 to 14 carbon atoms, more preferably from 4 to 12 carbon atoms;
(c) one or more phenyl-α-naphthylamine (PANA) compounds having formula (II):



(II)

wherein R_1 is selected from the group consisting of H, an alkyl group containing from 3 to 15 carbon atoms and an alkylaryl group containing from 7 to 12 carbon atoms; and
(d) one or more substituted diphenylamine derivatives having formula (III)



(III)

wherein R_2 and R_3 are each independently an optionally substituted aryl or alkylaryl group, the one or more substituted diphenylamine derivatives having a number average molecular weight of from 321 to 700.

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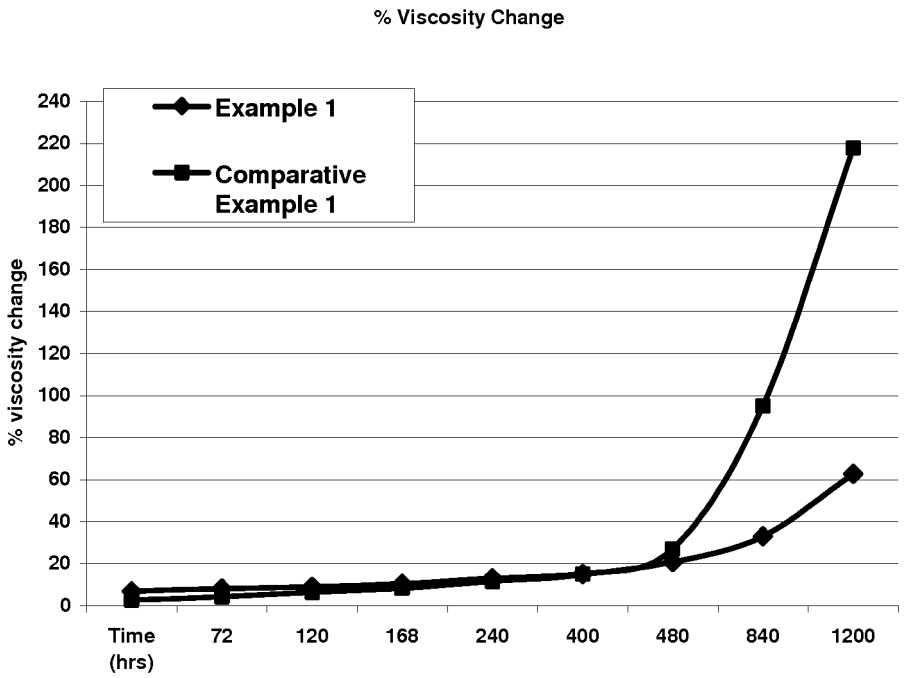
Fig. 1


% Viscosity Change
Example 1
Comparative Example 1
% viscosity change
240
220
200
180
160
140
120
100
80
60
40
20
0
Time (hrs)
72
120
168
240
400
480
840
1200

Description

[0001] The present invention relates to a lubricating oil composition for particular use as an aviation turbine oil.

[0002] In very high temperature applications, such as in jet engines for military and commercial aircrafts, organic compositions such as mineral lubricating oils are subject to such deterioration by oxidations that they may form significant insoluble deposits, which will foul engine parts, increase maintenance and decrease performance.

[0003] The use of synthetic base stocks such as polyol esters, for example prepared by reacting pentaerythritol and a mixture of fatty acids, combined with selected additives are well known for use in these aviation applications where bulk oil temperatures may be as low as -55°C to as high as 300°C and above.

[0004] In addition to the above, when used in aviation applications the lubricating oil may be exposed to high levels of oxygen and catalytically active metals, which encourage and exacerbate the oil degradation and additive depletion.

[0005] As new engines are developed the need for even more effective thermally and oxidatively stable lubricating oils is paramount.

[0006] In practice various lubricating oil compositions for use as an aviation turbine oil are known.

[0007] As an example, GB 2 384 245 discloses a turbine oil composition comprising: a major portion of a synthetic ester based base stock and a minor portion of an additive package comprising about 0.2 to about 5.0 wt.% of a specific DPA (diphenylamine) component, about 0.2 to about 5.0 wt.% of a specific PANA (phenyl-α-naphthylamine) component, and an oligomer formed by the reaction of a DPA component and a PANA component in the presence of at least one organic peroxide at an elevated temperature in the range of about 70 to 200°C.

[0008] A problem of the above and other lubricating oil compositions is that the stability thereof decreases over time resulting in a change in viscosity and an increase in TAN (total acid number).

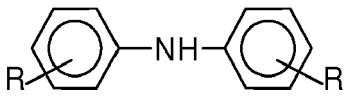
[0009] It is an object of the present invention to avoid the above or other problems.

[0010] It is another object of the present invention to provide an alternative lubricating oil composition.

[0011] To this end the present invention provides a lubricating oil composition comprising:

(a) a base oil;

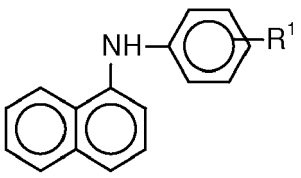
(b) one or more diphenylamine (DPA) compounds having formula (I),



(I)

wherein each R is independently an alkyl group having from 1 to 16 carbon atoms, preferably from 3 to 14 carbon atoms, more preferably from 4 to 12 carbon atoms;

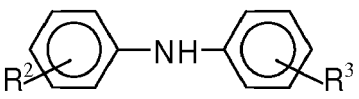
(c) one or more phenyl-α-naphthylamine (PANA) compounds having formula (II):



(II)

wherein R_1 is selected from the group consisting of H, an alkyl group containing from 3 to 15 carbon atoms and an alkylaryl group containing from 7 to 12 carbon atoms; and

(d) one or more substituted diphenylamine derivatives having formula (III)



(III)

wherein R_2 and R_3 are each independently an optionally substituted aryl or alkylaryl group, the one or more substituted

diphenylamine derivatives having a number average molecular weight of from 321 to 700.

[0012] It has been surprisingly found that the lubricating oil composition according to the present invention exhibits enhanced long-term stability. Further it has been found that the lubricating oil composition according to the present invention exhibits desirable resistance to sludge formation, which has been a problem in some commercial available aviation turbine oils.

[0013] A further advantage of the present invention is that it provides an alternative to the use of oligomers formed by the reaction of a DPA component and a PANA component such as for instance disclosed in GB 2 384 245.

[0014] There are no particular limitations regarding the base oil used in the present invention, and various conventional known mineral oils and synthetic oils may be conveniently used, provided that when the finished composition is used as an aviation turbine oil it can sufficiently withstand the often severe conditions it is exposed to during use. To this end specific additives may need to be added.

[0015] The base oil used in the lubricating oil composition of the present invention may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils.

[0016] Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

[0017] Suitable base oils for use in the lubricating oil composition of the present invention are Group I, Group II or Group III base oils, polyalphaolefins, Fischer-Tropsch derived base oils and mixtures thereof.

[0018] By "Group I" base oil, "Group II" base oil and "Group III" base oil in the present invention are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) categories I, II and III. Such API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

[0019] Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating oil composition of the present invention are those as for example disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

[0020] Synthetic oils include hydrocarbon oils such as olefin oligomers (PAOs), dibasic acid esters, polyol esters, and dewaxed waxy raffinate. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "XHVI" (trade mark) may be conveniently used.

[0021] Preferably, the base oil comprises a synthetic ester based base stock, in particular polyol ester-based base oils. Synthetic ester based base oils are well known in the art and are for example described in the above-mentioned GB 2 384 245. Ester based base oils (together with a selected additive package) are functional over a wide temperature range and exhibit good thermal and oxidative stability.

[0022] The preparation of esters from alcohols and carboxylic acids can be accomplished using conventional methods and techniques known and familiar to those skilled in the art, and form no part, per se, of the present invention. In general, technical pentaertythritol is heated with the desired carboxylic acid mixture, optionally in the presence of a catalyst. Generally, a slight excess of acid is employed to force the reaction to completion. Water is removed during the reaction and any excess acid is then stripped from the reaction mixture. The esters of technical pentaerythritol may be used without further purification or may be further purified using conventional techniques such as distillation.

[0023] For further information with respect to the synthetic ester based base oil, reference is made to GB 2 384 245, EP 0 695 797, EP 1 323 815, US 4 826 633 and US 5 503 761, the teaching of which is hereby incorporated by reference.

[0024] Suitable synthetic polyol ester based base oils may be formed by the esterification of an aliphatic polyol with carboxylic acid. Preferably the aliphatic polyol contains from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Preferred examples are trimethylol propane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol and mixtures thereof.

[0025] The carboxylic acid reactant used to produce the synthetic polyol ester base oil may suitably be selected from aliphatic monocarboxylic acid or a mixture of aliphatic monocarboxylic acid and aliphatic dicarboxylic acid. The carboxylic acid may contains from 4 to 12 carbon atoms and includes the straight and branched chain aliphatic acids. Mixtures of monocarboxylic acids may also be used.

[0026] According to a preferred embodiment the polyol ester base oil comprises at least 80 wt.% monopentaerythritol.

[0027] Suitably, the polyol ester base oil may be a mixture of about 80 to 95 wt.% monopentaerythritol and 5 to 20 wt.% dipentaerythritol. This mixture is typically known as 'technical' pentaerythritol and may also contain some tri and tetra pentaerythritol, which are typically formed as by products during the production of technical pentaerythritol.

[0028] It is even more preferred that the polyol ester base oil comprises more than 90 wt.% monopentaerythritol, more preferably more than 95 wt.% monopentaerythritol. It is even more preferred that the polyol ester bas oil comprises about 100 wt.% monopentaerythritol.

[0029] The total amount of base oil incorporated in the lubricating oil composition of the present invention is preferably present in an amount in the range of from 60 to 99 wt.%, more preferably in an amount in the range of from 75 to 99 wt.% and most preferably in an amount in the range of from 88 to 95 wt.%, with respect to the total weight of the lubricating

oil composition.

[0030] The above-mentioned diphenylamine (DPA) compounds having formula (I) are known in the art and widely commercially available. They can be prepared as for example described in Tetrahedron Letters, 48(9), 1619-1623; 2007. Suitable, commercially available diphenylamine compounds include dioctyldiphenylamine (e.g. "RheinChemie RC7001", "Vanlube 81" or "Naugalube 438"), didecyldiphenylamine, didodecyldiphenylamine, dihexyldiphenylamine and similar compounds. Dioctyidiphenylamine (DODPA) is especially preferred.

[0031] Typically, the DPA compounds having formula (I) are present in an amount in the range of from 0.1 to 10.0 wt. %, preferably from 0.1 to 5.0 wt.%, more preferably from 0.2 to 4.0 wt.%, most preferably from 0.3 to 1.5 wt%, based on the total weight of the fully formulated lubricating oil composition.

[0032] The above-mentioned phenyl-α-naphthylamine (PANA) compounds having formula (II) are also known in the art and widely commercially available.

[0033] They can be prepared as for example described in Journal of Heterocyclic Chemistry, 28(2), 321-2, 1991. Suitable, commercially available diphenylamine compounds include phenyl-alpha-naphthylamine (e.g. "RheinChemie RC7130"), N-(para-tert.-octylphenyl)-alpha-naphthylamine (e.g. "Irganox L06"), N-(4-cumylphenyl)alpha-naphthylamine and the corresponding para-tert.-dodecylphenyl and para-tert.-butylphenyl alpha-naphthylamines.

[0034] Typically, the PANA compounds having formula (II) are present in an amount in the range of from 0.1 to 10.0 wt.%, more preferably from 0.1 to 5.0 wt.%, even more preferably from 0.5 to 4.0 wt.%, most preferably from 0.7 to 2.0 wt%, based on the total weight of the fully formulated lubricating oil composition.

[0035] The above-mentioned substituted DPA derivatives having formula (III) are also known in the art and widely commercially available. They can be prepared by reacting diphenylamine with a styrene-type component as for example described in WO 2004/069785 or by reacting 4-bromobiphenyl with benzylamine. Suitable, commercially available diphenylamine compounds include di(dimethylbenzyl)diphenylamine (e.g. "Naugalube AMS"), dibenzyldiphenylamine, bis(4-biphenylyl)amine, di(methylbenzyl)diphenylamine (e.g. "Naugalube 635") and similar components.

[0036] Preferably, the substituted DPA derivatives having formula (III) contain only one N-atom. Also it is preferred that the one or more substituted diphenylamine derivatives have a number average molecular weight of from 321 to 653.

[0037] Typically, the substituted DPA derivatives having formula (III) are present in an amount in the range of from 0.1 to 10.0 wt.%, preferably from 0.1 to 5.0 wt.%, more preferably from 0.2 to 4.0 wt.%, most preferably from 0.3 to 1.5 wt%, based on the total weight of the fully formulated lubricating oil composition.

[0038] Further it is preferred that the total amount of the one or more diphenylamine compounds, the one or more phenyl-α-naphthylamine compounds and the one or more substituted diphenylamine derivatives is in the range of from 0.1 to 12.0 wt.%, based on the total weight of the lubricating oil composition.

[0039] Preferably, the molar ratio of the one or more diphenylamine (DPA) compounds having formula (I) to the substituted diphenylamine derivatives having formula (III) as used in the lubricating oil composition is in the range from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2.

[0040] The lubricating oil composition of the present invention may in addition to the above-mentioned additives, comprise further additives such as extreme pressure additives, pour point depressants, anti-oxidants, anti-foaming agents, hydrolytic stability agents, viscosity index improvers, corrosion inhibitors, load carrying agents, conductivity improvers, metal deactivators, acid scavengers and anti-wear agents.

[0041] In a further aspect the present invention provides the use of the lubricating oil composition according to the present invention as a turbine oil, in particular an aviation turbine oil.

[0042] Further the present inventions provides a method of improving the long term stability of a turbine oil, by using the lubricating oil composition according to the present inventions.

[0043] Also, the present invention provides an additive package suitable for a lubricating oil composition, the additive package comprising the above-mentioned components (b)-(d).

[0044] The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

EXAMPLES

Lubricating oil compositions

[0045] Aviation turbine oil formulations were blended using the base oil and additives specified in Table 1.

[0046] The amounts in Table 1 are in wt.%, based on the total weight of the fully formulated formulations.

[0047] The base oil as used in the formulations of Table 1 was a 5 cSt pentaerythritol ester further containing tricresyl phosphate antiwear additive, tolutriazole and dicarboxylic acid corrosion inhibitors and benzotriazole metal deactivators. The pentaerythritol ester had a viscosity of 5 mm^2/s at 100 °C and a maximum viscosity of 13,000 mm^2/s at -40 °C. In addition, the pentaerythritol ester has a maximum pour point of -54 °C and a minimum flash point of 246 °C.

[0048] The DPA component having formula (I) was dioctyl-diphenyl amine (DODPA) available from e.g. Vanderbilt

Company, Inc. (under the trade designation "Vanlube 81"), Ciba Specialty Chemicals Inc., Uniroyal Chemical Company Inc. and Rhein Chemie Ltd.

[0049] The PANA component having formula (II) was p-tert.-octylphenyl-alpha-naphthylamine available from e.g. Ciba Specialty Chemicals (under the trade designation "Irganox L06").

[0050] The DPA component having formula (III) was 4,4-di(dimethylbenzyl)diphenylamine available from e.g. Crompton Corporation (under the trade designation "Naugalube AMS") and DuPont de Nemours & Co.

[0051] The oligomeric antioxidant as used in Comparative Example 1 was the reaction product formed by the reaction of a DPA component and a PANA component in the presence of an organic peroxide. This oligomeric antioxidant is commercially available, e.g. from Vanderbilt Company, Inc (under the trade designation "Vanlube 9317".

TABLE 1

Component (wt.%)	Example 1	Comparative Example 1
Base oil + additive package	97	97
DPA having formula (I)	1	1
PANA having formula (II)	1	-
DPA having formula (III)	1	-
Oligomeric anti-oxidant	-	2
TOTAL	100	100

Long-term Stability Test

[0052] In order to show the long-term stability of the lubricating oil compositions according to the present invention, the following test was used.

[0053] The compositions were subjected to the Fed-Stan 791C, method 5308 Oxidation/Corrosion test. This test is a US Navy derived test method run for synthetic engine oils and is part of Mil-Spec-23699 and SAE AS 5780 specifications for aviation applications.

[0054] This test can be run at various temperatures but for the purpose of the above quoted specifications are typically 175°C, 204°C and 218°C for 72 hours (h).

[0055] For the purpose of the present invention, the tests on the compositions of Example 1 and Comparative Example 1 were conducted in accordance with the above Fed-Stan 791C, method 5308 Oxidation/Corrosion test at 175°C, but extending the typical test duration from 72 h up to 1560 h.

[0056] In the test the lubricating oil composition to be tested and metal catalysts were placed in a test tube, a condenser placed on top and then immersed in a heating block. Air was blown through the sample at a rate of 5 l/h.

[0057] At the end of each time period a tube was removed from the heating block, weighed to calculate volatility loss and then the used (tested) oil viscosity and total acid number (TAN) was measured. In addition, the used (test) oil was filtered to determine any sludge formation.

Results

[0058] The amount of viscosity change (in %) obtained for Example 1 and Comparative Example 1 is indicated in Table 2 below. Furthermore, the TAN change (in mgKOH/g) is shown in Table 3. The amount of sludge formation is shown in Table 4. For ease of comparison, the results of Tables 2-4 are also displayed in Figures 1-3 respectively.

TABLE 2

	Viscosity change [%]								
Time [h]	72	120	168	240	400	480	840	1200	1560
Example 1	6.8	8.0	8.9	10.4	12.9	14.9	20.8	32.9	62.7
Comparative Example 1	2.6	4.1	6.4	8.2	11.6	15.0	26.8	95.0	217.7

TABLE 3

	TAN change [mgKOH/g]								
Time [h]	72	120	168	240	400	480	840	1200	1560
Example 1	0.09	0.13	0.08	0.14	0.51	0.67	0.72	1.20	3.04
Comparative Example 1	0.00	0.03	0.05	0.11	0.62	0.77	1.44	3.13	7.36

TABLE 4

	Sludge formation [mg]								
Time [h]	72	120	168	240	400	480	840	1200	1560
Example 1	0.2	0.3	0.2	0.3	0.6	0.3	0.4	0.6	0.5
Comparative Example 1	0.4	0.3	0.3	0.3	0.6	0.4	0.4	0.5	0.5

Discussion

[0059] In typical Aviation Turbine Engine applications the assessment level for oil change is at a TAN rise of 1.0 mgKOH/g.

[0060] As can be seen in Table 3 above and the attached Fig. 2, the composition of Example 1 reached this level of 1.0 mgKOH/g at a much later stage (after about 1150 hours) than the composition of Comparative Example 1 (after about 650 hours), giving a clear performance benefit.

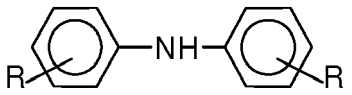
[0061] Table 2 and Fig. 1 show comparable performance up to 480 hours after which the composition of Example 1 maintained resistance to viscosity increase more extensively than the composition of Comparative Example 1.

[0062] The results in Table 4 and Fig. 3 show that the compositions of Example 1 and Comparative Example 1 performed similar with respect to sludge formation. In this respect it is noted that the sludge formation has been a problem in many commercial available aviation turbine oils.

Claims

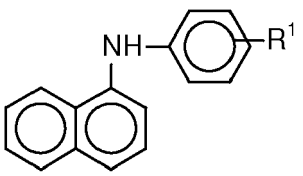
1. A lubricating oil composition comprising:

(a) a base oil;
(b) one or more diphenylamine (DPA) compounds having formula (I),



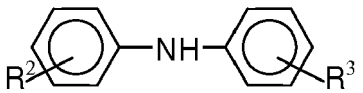
(I)

wherein each R is independently an alkyl group having from 1 to 16 carbon atoms, preferably from 3 to 14 carbon atoms, more preferably from 4 to 12 carbon atoms;
(c) one or more phenyl-α-naphthylamine (PANA) compounds having formula (II):



(II)

wherein R_1 is selected from the group consisting of H, an alkyl group containing from 3 to 15 carbon atoms and an alkylaryl group containing from 7 to 12 carbon atoms; and
(d) one or more substituted diphenylamine derivatives having formula (III)



(III)

wherein R_2 and R_3 are each independently an optionally substituted aryl or alkylaryl group, the one or more substituted diphenylamine derivatives having a number average molecular weight of from 321 to 700.

2. Lubricating oil composition according to claim 1, wherein the base oil comprises a synthetic ester based base oil.

3. Lubricating oil composition according to claim 2, wherein the base oil comprises at least 80 wt.% monopentaerythritol, preferably at least 90 wt.%.

4. Lubricating oil composition according to any one of claims 1 to 3, wherein the one or more diphenylamine compounds, the one or more phenyl-α-naphthylamine compounds and the one or more substituted diphenylamine derivatives each are present in an amount in the range of from 0.1 to 10.0 wt.%, preferably from 0.1 to 5.0 wt.%, based on the total weight of the lubricating oil composition.

5. Lubricating oil composition according to any one of claims 1 to 4, wherein the total amount of the one or more diphenylamine compounds, the one or more phenyl-α-naphthylamine compounds and the one or more substituted diphenylamine derivatives is in the range of from 0.1 to 12.0 wt.%, based on the total weight of the lubricating oil composition.

6. Lubricating oil composition according to any one of claims 1 to 5, wherein the molar ratio of the one or more diphenylamine (DPA) compounds having formula (I) to the substituted diphenylamine derivatives having formula (III) as used in the lubricating oil composition is in the range from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2.

7. Use of the lubricating oil composition according to any of claims 1 to 6 as a turbine oil.

8. Method of improving the long term stability of a turbine oil, by using the lubricating oil composition according to any of claims 1 to 6.

9. Additive package for a lubricating oil composition, the additive package comprising components (b)-(d) as described in claim 1.

Fig. 1

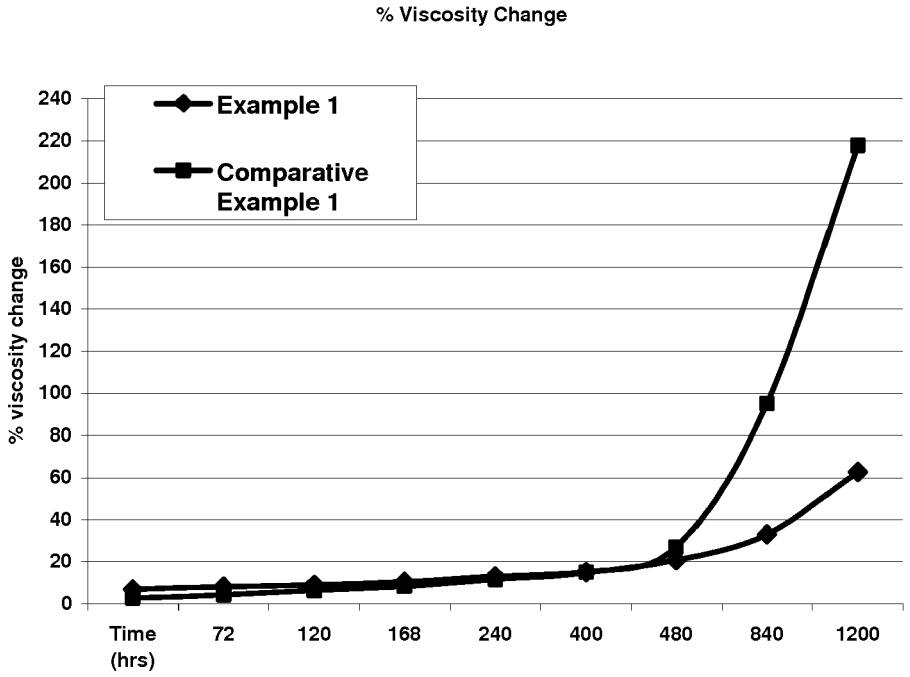

% Viscosity Change
Example 1
Comparative Example 1
% viscosity change
240
220
200
180
160
140
120
100
80
60
40
20
0
Time (hrs)
72
120
168
240
400
480
840
1200

Fig. 2

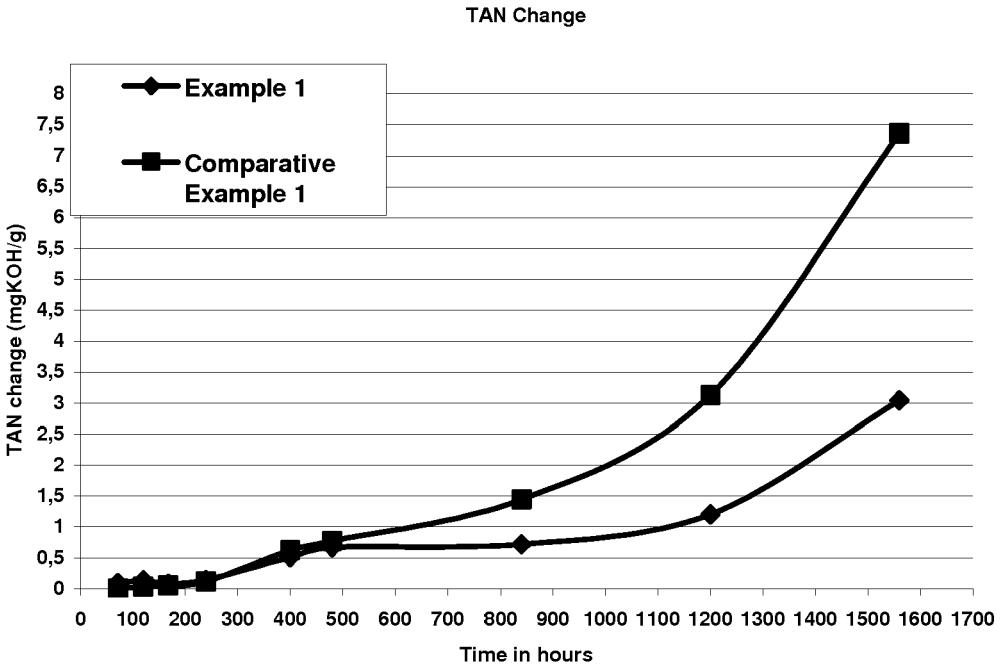
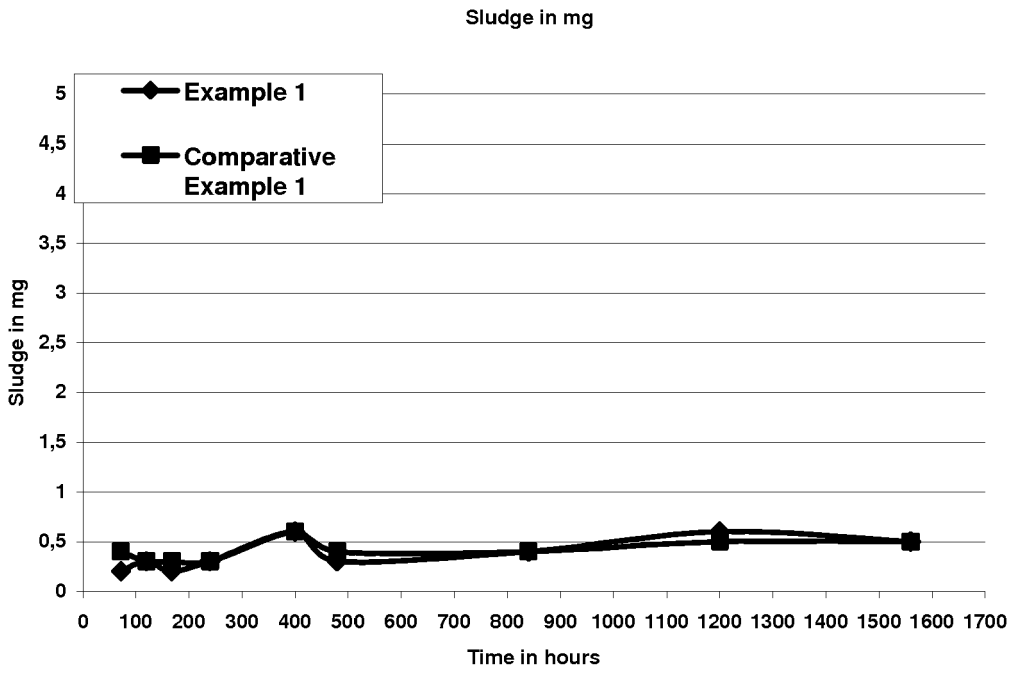

TAN Change
Example 1
Comparative Example 1
TAN change (mgKOH/g)
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
5,5
6
6,5
7
7,5
8
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700
Time in hours

Fig. 3


Sludge in mg
Example 1
Comparative Example 1
Sludge in mg
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700
Time in hours

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 11 9062

DOCUMENTS CONSIDERED TO BE RELEVANT

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Place of search	Date of completion of the search	Examiner
Munich	7 December 2007	Pöllmann, Klaus

CATEGORY OF CITED DOCUMENTS

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