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(54) Use of bismuth compounds in extreme pressure grease lubricant compositions for rolling bearing application with extended service life.

(57) The invention relates to the use of bismuth-compounds in an extreme pressure grease lubricant composition for rolling bearing applications for extending the useful service life of rolling bearings. The bismuth can be used as an additive, preferably an EP additive, or as a soap or thickener. The invention further relates to a method for preparing an extreme pressure lubricant composition in which a bismuth containing soap or thickener is mixed with an oil and optionally one or more EP- or other additives.

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The invention relates to the use of bismuth-compounds in extreme pressure grease lubricant compositions for application in rolling bearings.

Generally, in cases wherein rolling bearings operate under extreme loading conditions and with long service intervals, extreme pressure grease lubricants are applied in order to make sure that an appropriate amount of lubricant film is always available within the bearing, in particular on the raceways and rolling elements thereof.

Such extreme pressure lubricant compositions generally contain an oil, a soap thickener, one or more EP additives and optionally further additives. The EP additives form a friction-reducing film on the metal surfaces of the bearing, usually due to a chemical reaction of the additives with the surface metals. The function of the supplied lubricant extreme-pressure additives is to minimize wear and to prevent scuffing and welding between contacting surfaces. As such, lead/sulfur-containing additives can be used.

However, these lead additives are not acceptable because of their toxicity and from an environmental viewpoint. Therefore, the lead/sulfur-containing additives are now usually replaced by sulfur/phosphorous EP additives. However, it has now been found that these sulfur/phosphorous additives reduce the service life of the bearings.

Extreme pressure lubricant compositions also contain a soap thickener, such as lithium 12-hydroxy stearate, which provides the grease with the desired physical and chemical structure. The grease should be able to maintain this structure in the bearing as long as possible under high temperature, vibratory and mechanical shearing action.

In this respect, it is necessary to maintain the mechanical stability of the soap or thickener of the grease during extended periods. As long as this soap structure can be maintained, the grease is able to hold in place the oil component which can regularly provide the lubricating properties.

In cases where the soap structure is damaged the grease is no longer able to hold the oil in place, which will then drain away out of the bearing. As a consequence the lubricating properties of the grease are lost and the bearing service life is reduced considerably if the grease is not replenished at short intervals. Furthermore, the grease should be chemically non-aggressive with respect to the metal parts of the bearing, in particular with the above environment with high temperatures and vibration.

In these respects the lead/sulfur- and sulfur/phosphorous EP additives containing grease lubricant compositions according to the state of the art are not satisfactory. The aim of the invention is therefore to obviate these disadvantages.

It has now been found that the use of bismuth compounds in extreme pressure grease lubricant compositions for rolling bearing applications extends the useful service life of rolling bearing applications.

According to the present invention a bismuth containing additive and especially an EP additive, a bismuth containing soap, or both can be used.

A grease containing a bismuth additive is known from NLGI SPOKESMAN, Vol. 57, Nr. 2, May 1993, O. ROHR "Bismuth, a new metallic but non-toxic replacement for lead as EP additive in greases", pages 6.50 - 13.57. In this article, it is described that a bismuth additive promotes the formation of a film on the rolling bearing metal surfaces and therefore could serve as a replacement for lead as extreme pressure additive in grease. The bismuth additive indeed appears to offer even better lubricating properties than a lead additive, in particular under high load, high temperature and high sliding speed conditions. Also it is mentioned that the organo-bismuth compound functions as a corrosion inhibitor and as an anti-oxidant.

However, this article is silent with respect to the field of the present invention, that is the provision of an extended useful service life of the greases and thus the bearing life. Whereas it is reported that the bismuth additive beneficially influences the lubricating properties of the oil component of the grease, no reference is made to any favourable effects on bearing service life.

The application of bismuth additives in a lubricant is also addressed in SU-A-1384603. Here, the bismuth is added to lubricating oil compounds for sliding contact surfaces. Although it is stated that the bismuth additives reduce the friction in a sliding contact, no reference is made to greases or to achieving an extended service life thereof.

The use of a bismuth-containing soap has not been described in the prior art.

In a first aspect, the invention therefore relates to the use of bismuth compounds in an extreme pressure lubricant for rolling bearing applications as an additive for extending the useful service life of rolling bearings.

In a second aspect, the invention relates to the use of a bismuth containing soap in an extreme pressure lubricant for rolling bearing applications for extending the useful service life of rolling bearings.

In a further aspect, the invention relates to a method for preparing an extreme pressure lubricant in which a bismuth containing soap is mixed with an oil and optionally one or more EP- or other additives. When a bismuth containing soap is used it is not strictly necessary to use Bi-containing or other EP-additives.

In all these aspects of the invention the presence of bismuth compounds has a favourable influence on the useful service life of rolling bearing applications.

When the bismuth compounds are used as EP additives, these compounds are in general bismuth carboxylates of the formula $(R\text{-}CO_2)_3Bi$, in which R is a branched, straight or cyclic alkyl group with 1-30 carbon atoms or an aryl, alkaryl or aralkyl group with 5-20 carbon atoms. Paraffinic bismuth carboxylates with 6-10 carbon atoms or naphthenic bismuth carboxylates are preferred, such as bismuth naphthenate and bismuth octoate. However, the use of bismuth compounds as EP additives according to the invention is not limited to the bismuth compounds mentioned above, and other organo bismuth compounds can be used, such as the bismuth containing additives known from the above prior art, or compounds analogous to known lead/sulfur-EP additives, in which the lead is replaced by bismuth.

The bismuth containing EP additives are used to partly or completely replace known EP additives, such as lead/sulfur additives or sulfur/phosphorous additives in extreme pressure lubricant compositions.

When the bismuth compound is used as an EP additive it can be added to the soap, the oil or to the already formed mixture of the oil and the soap thickener. Usually and preferably the additive is admixed with the oil.

The bismuth containing EP additives are used in the usual amounts, in general the amount of bismuth will be 0,1-5 % by weight of the total lubricant composition. Mixtures of one or more bismuth compounds can be used, optionally in admixture with one or more other EP additives. Further conventional additives for lubricant compositions can be used in usual amounts, if desired.

The bismuth containing EP additives can be soluble or non-soluble in the oil component of the lubricant composition.

The bismuth containing EP additives can also be used in extreme pressure lubricant compositions, which contain for instance non-soap thickeners, such as polyurea-based compounds, polytetrafluorethylene or silicone as a thickener instead of a soap.

When a bismuth containing soap according to the invention is used, this soap is usually a bismuth-salt of a fatty acid with 10-30 carbon atoms or a derivative thereof. Usually the bismuth analogues of known soap-thickeners are used, in which the bismuth replaces the metal, i.e. barium, aluminium, calcium, lithium, sodium, strontium etc. Examples are bismuth stearate, bismuth tristearate, bismuth tripalmetate, bismuth trioleate and derivatives thereof, such as bismuth 12-hydroxy stearate. The bismuth soap can contain the same or different fatty acid groups. Also mixtures of bismuth containing soaps can be used.

The bismuth containing soap is used in the usual amounts, depending upon the desired properties of the final lubricant composition. In general, this amount will vary between 5-14 % by weight of the total composition for a "soft" grease to 15-25 % by weight of the total composition for a "stiff" grease.

The bismuth containing soap can also be used in combination with known soaps containing other metals, such as lithium-soaps or calcium-soaps in a grease formulation. This will reduce the costs of the final extreme pressure lubricant composition.

The invention furthermore relates to a method for preparing an extreme pressure lubricant composition in which a bismuth containing soap or thickener is mixed with an oil and optionally one or more EP- or other additives. The mixing of the soap, the oil and the thickener can be carried out in a manner known per se for the preparation of EP greases from the prior art. Preferably, a bismuth containing EP additive as mentioned above is used. The bismuth containing soap, the oil and the EP additives and other additives are used in the usual amounts.

According to the invention it has been found that the favourable effect of the use of bismuth compounds on the useful service life is mostly due to the improved mechanical, physical and chemical stabilities of the grease (the oil/thickener composition). In contrast to the friction reducing "surface effects" mentioned above, this "bulk effect" has not been described in the prior art. The exact mechanism thereof is not known, however, the beneficial influence of the presence of bismuth compounds is obtained with both bismuth containing soaps and with bismuth containing EP additives.

The bearing service life is further increased by the favourable influence of the bismuth additive on stress corrosion and fatigue life.

Moreover, the replacement of lead by bismuth is an improvement having regard to the non-toxic properties of the latter.

The invention will now be illustrated by means of the following non-limiting example 1, in which the influence on the service life of rolling bearings of three bismuth containing lubricant compositions is compared with a sulfur/phosphorous containing lubricant composition according to the state of the art. Non-limiting example 2 illustrates the preparation of a bismuth-containing soap of the invention.

The figures further illustrate the invention and show:

Fig. 1: the influence of bismuth additives on bearing life;
Fig. 2: the bearing condition monitoring of DGBB test;
Fig. 3: a plot of overall trend value versus test time;
Fig. 4: a plot of temperature versus test time.

Example 1

Several tests have been carried out in order to demonstrate the effect of a bismuth additive. In these tests, the following samples were used:

Sample 1: Lithium base grease, antioxidant (0.5 wt%) + organo-bismuth and sulphur additive (0.5 wt% Bi) from Miracema, Brazil.

Sample 2: Lithium base grease, antioxidant (0.1 wt%), anti-rust (3.2 wt%), organo-bismuth (0.5 wt% Bi) from Miracema, Brazil or from Pharmacie Centrale de France.

Sample 3: Mineral base oil + antioxidant + (0.5-2 wt% Bi) bismuth carboxylate e.g. Liovac 3024 from Miracema, Brazil.

Sample 4: Fully formulated commercially Litium soap extreme pressure (E/P) grease containing sulphur/phosphorous (S/P) EP additive package.

The grease samples 1, 2 and 4 are further described in Table 2.

Grease samples 1, 2 and 4 above were subsequently applied for bearing life tests under high load and high temperature conditions as listed below in Table 1:

TABLE 1

Bearing type	Deep groove ball bearing (DGBB 6206 2RS1)
Speed	2500 rpm
Radial load	6000 N
Test temperature	120 ± 2 ° C (outer ring)
Grease filling	2,4 g
Strategy	sudden death factor group of 2, in which sets of two bearings are run simultaneously until one of the bearings fails.
Type of failure	Bearing noise (fatigue related) Temperature rise (grease failure)
C/P	3,25
Kappa	0,75 (calculated on the base oil rheology and assuming fully flooded conditions).
Grease Relubrication	none

In figure 1 the test results are shown. It is clear that the statistical values for L10 and L50 bearing life (which includes both grease life and fatigue life) of grease samples 1 and 2 according to the invention are significantly better than that of sample 4. (L10 = time until failure of 10% of the samples in hrs; L50 = time until failure of 50% of the samples in hrs).

Further DGBB tests were conducted for a range of greases containing bismuth additives. A bearing sample size of 10 bearings/grease was employed in 5 subgroups. Bearing test performance was compared between SKF LGEP2 and two experimental formulated greases containing bismuth additives shown in Table 2.

Table 3 shows the bearing life test results of SKF LGEP2 (sample 4) and the two Bi-greases (samples 1 and 2). It shows that the observed L10 life of both bismuth greases is about 2 times longer than the reference grease LGEP2. Based on the statistical hypothesis test procedures, the comparison of L10 life between LGEP2 and the bismuth greases is classed as weakly significant i.e. the probability of significance is greater than 80%, but less than 90%. The test comparison of the L50 life between LGEP2 and sample 3 is statistically significant (i.e. >90% probability).

TABLE 2

Lubricant	Soap Type	Base Oil Viscosity, cSt 40°C	100°C	NLGI Grade	Remarks
Sample 1* (EP grease containing bismuth additive)	Li-soap	195	15	2	experimental grease (LGEP2 grease without additives) + 0.52 wt% antioxidant + 0.47 wt% Bi additives (L-3089)
Sample 2* (EP grease containing bismuth additive)	Li-soap	195	15	2	experimental grease (LGEP2 grease without additives) + 0.12 wt% antioxidant + 3.21 wt% anti-rust + 0.5 wt% Bi-additives (L-3016)
Sample 4 SKF LGEP2 (F11607)	Li-soap	195	15	2	commercial EP grease containing S/P additives

Note: * special batch prepared by AB Axel Christiernsson

TABLE 3

Grease sample	Calculated LIFE (hours) (90% confidence interval)		Weibull slope, β	Number of related failure	
	L10	L50		Fatigue	Grease
Sample 1	487.6 (279.7-620.7)	750.0 (628.5-967.9)	4.4	5 (either inner ring/ball/outer ring)	-
Sample 2	512.3 (192.7-734.2)	918.1 (690.9-1436.0)	3.2	1 (inner ring)	3
SKF LGEP2 (Sample 4)	244.7 (86.8-383.8)	546.2 (392.9-878.8)	2.4	2 (inner ring)	3

In case of bearing test with DGBB's, a complex bearing failure is observed. Some bearings failed due to grease degradation, and some failed due to pitting of ball/inner ring/outer ring (see Table 3). Figure 2 shows the spectrum plot of a test bearing (#22). It can be seen that the frequency at 205 Hz is due to a ball defect, outer ring defect frequency is at 157 Hz, and the 230 Hz frequency is attributed to inner ring defect. Post investigation of the failed bearing confirmed the spectrum data. In general, all the failed bearings due to rolling contact fatigue were detected and recorded by the SKF CoMo monitoring system. Figure 3 shows a time trend versus the overall spectrum energy value plot for a bearing (#23). This was the criterion used to terminate the test automatically when the overall value increase to a set alarm level (A2) as shown.

Bearings primarily failing due to "dry-running" can be detected with the continuous temperature measuring system. Figure 4 illustrates a plot of temperature recorded versus time. The machine of a test group bearings (#3 and #4) stopped due to a sudden increase in temperature of bearing #3 after approximately 680 hours of running.

The difference in grease life observed between LGEP2 and Bi-greases can not solely be attributed to the presence of different additive systems because of many variables which could not be controlled accurately under test conditions e.g. lubricant starvation, amount of "active" grease in bearing after initial grease, channelling etc. It must be noted that thermal and mechanical stress, lubrication oxidation and degradation, oil separation and migration can also greatly influence the grease life and performance.

Post analysis of the failed DGBBs reveals that bearing failure is due to a combination of grease failure (dry-running) and contact fatigue. Interestingly, all bearings tested with Bi-grease sample 1 failed due to spalling, and the bearings tested with the other Bi-grease (sample 2) failed predominantly due to the "dry-running". This suggests that the presenbce of 'active' sulphur additive in grease can induce problems by reducing thermal/oxidation and mechanical stability as well as promoting rolling contact fatigue.

Grease samples 1 and 2 have also been shown to give better shear stability than grease sample 4 containing S/P additive. The poor results for sample 4 are due to the softening of grease structure, resulting an excessive oil leakage from the grease.

The mechanical stability of Bi-greases was evaluated using the SHELL roll stability tester. The results show that under test conditions at 80 °C for 50 hrs, the SKF LGEP2 grease consistency changes from 2 to a fluid-like lubricant softer than '00'. This poor inherent property of the grease is primarily due to the nature of the soap thickener, and, to some extent, of the S/P EP additive package used in the grease. Bi-EP greases showed a significant improvement in the mechanical stability.

To determine the flange-roller wear prevention of bismuth containing lubricant compositions an oil containing an organo-bismuth additive, sample 3, was tested in a SKF R3 test machine. The test conditions are tabulated in Table 4.

TABLE 4

Flange-Roller Contact Test Conditions:	
Bearing type	taper roller bearing (580/572);
Speed	2500 rpm
Test temperature	75 ± 2 °C (outer ring)
C/P	2
Kappa	1.2
Rate of oil supply	at equilibrium 1 litre/min

Under these conditions, it was shown that sample 3 prolonges the roller bearing life of flange-roller bearings and avoids the possible adverse effect of an S/P EP additive on fatigue life.

<u>Example 2</u>

Preparation of bismuth soaps:

The bismuth soap is prepared as other metal soaps such as lead soap. This preparation can be carried out in either an open vessel or an autoclave. Normal bismuth base grease can be prepared by:

1. saponification - reaction of bismuth compounds such as bismuth oxides and bismuth hydroxide with chosen acid such as fatty acids or glycerides. Commonly used metal soap types such as bismuth soap of 12-hydroxy stearic acid, bismuth stearate, bismuth oleate are then produced. The soap at this stage contains about 25-50 portentage of bismuth;
2. dispersion of soap in oil - this is done by adding an oil or oils to the bismuth concentrate at about 150-160 °C, after which is cooled (normally while being agitated and for further addition of other additive types) to room temperature;
3. the cooled lubricating grease is then passed through a mill and a filtering system.

The mixed complex bismuth base lubricating greases can also be prepared according to the preparation technology of other metal soaps such as lead or lithium.

Claims

1. Use of bismuth compounds, in an extreme pressure grease lubricant composition for rolling bearing applications for extending the useful service life of rolling bearings.

2. Use of bismuth compounds according to claim 1, for extending the fatigue life of rolling bearings.

3. Use of bismuth compounds according to claim 1, for extending the oxidation life at elevate temperatures of rolling bearings.

4. Use of bismuth compounds according to claim 1, for extending the wear life of rollers and flanges of axial bearings under axial load.

5. Use of bismuth compounds according to claim 1, for protecting rolling bearing metal components against stress corrosion.

6. Use of bismuth compounds according to claim 1, for protecting rolling bearing metal surfaces against chemical attack.

7. Use of bismuth compounds according to claim 1, for extending the useful life of an extreme pressure lubricant composition for rolling bearing applications.

8. Use of bismuth compounds according to claim 1 and/or 7, for improving the extreme pressure characteristics of the soap or thickener constituent in the extreme pressure lubricant composition.

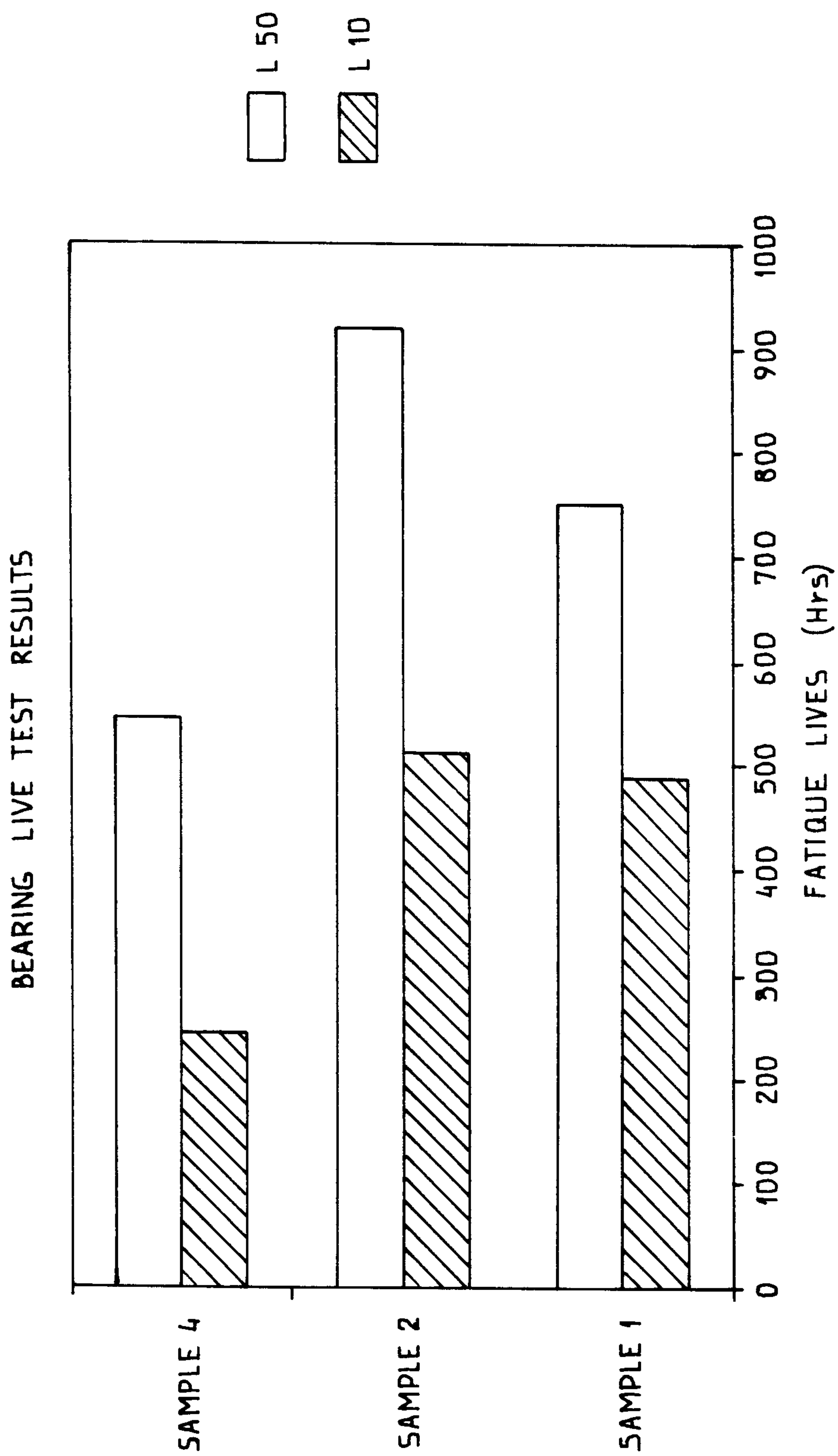
9. Use of bismuth compounds according to claim 1, 7 and/or 8, for increasing the shear stability of the soap or thickener constituent in the grease.

10. Use of bismuth compounds according to claims 1-9, in which the bismuth compound is used as an additive, preferably an EP additive.

11. Use of bismuth compounds according to claims 1-9, in which the bismuth compound is used as a soap or thickener.

12. Method for preparing an extreme pressure lubricant composition in which a bismuth containing soap or thickener is mixed with an oil and optionally one or more EP- or other additives.

fig-1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L 50
L 10
SAMPLE 4
SAMPLE 2
SAMPLE 1
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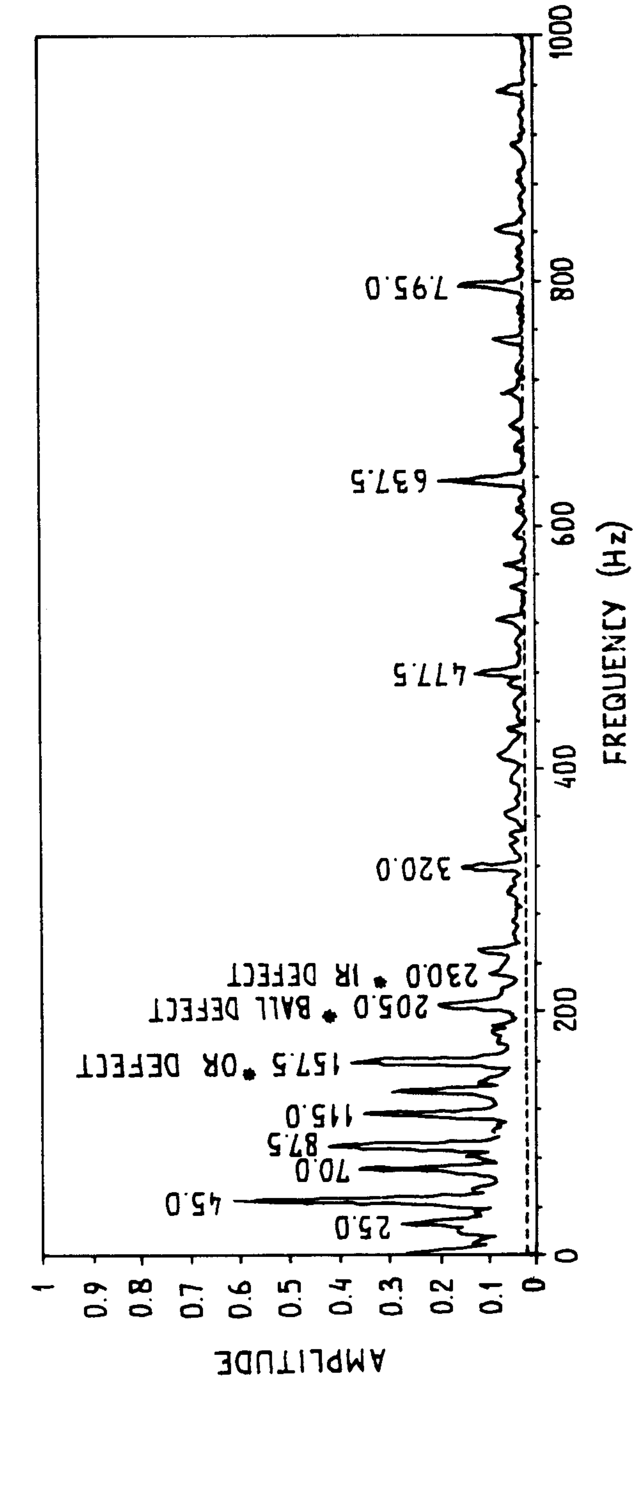
100
200
300
400
500
600
700
800
900
1000
FATIQUE LIVES (Hrs)

fig-2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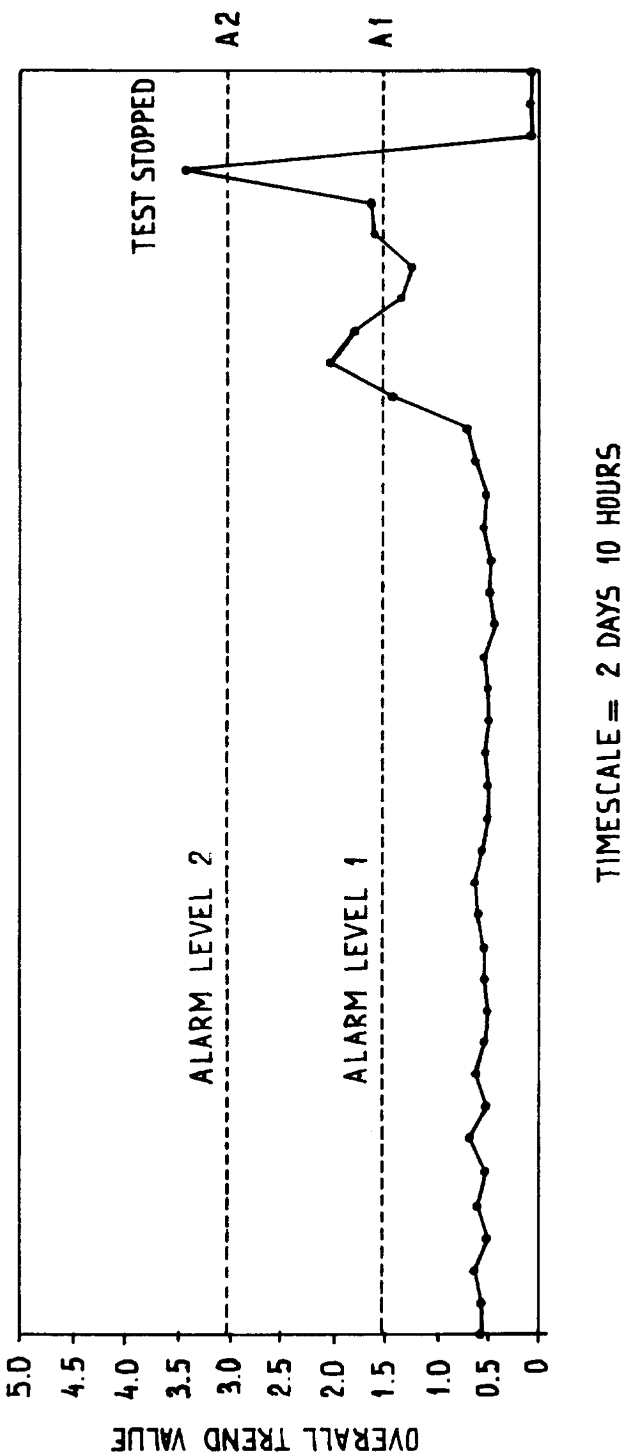
45.0
70.0
87.5
115.0
157.5 * OR DEFECT
205.0 * BALL DEFECT
230.0 * IR DEFECT
320.0
477.5
637.5
795.0

Fig-3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A1
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ALARM LEVEL 1
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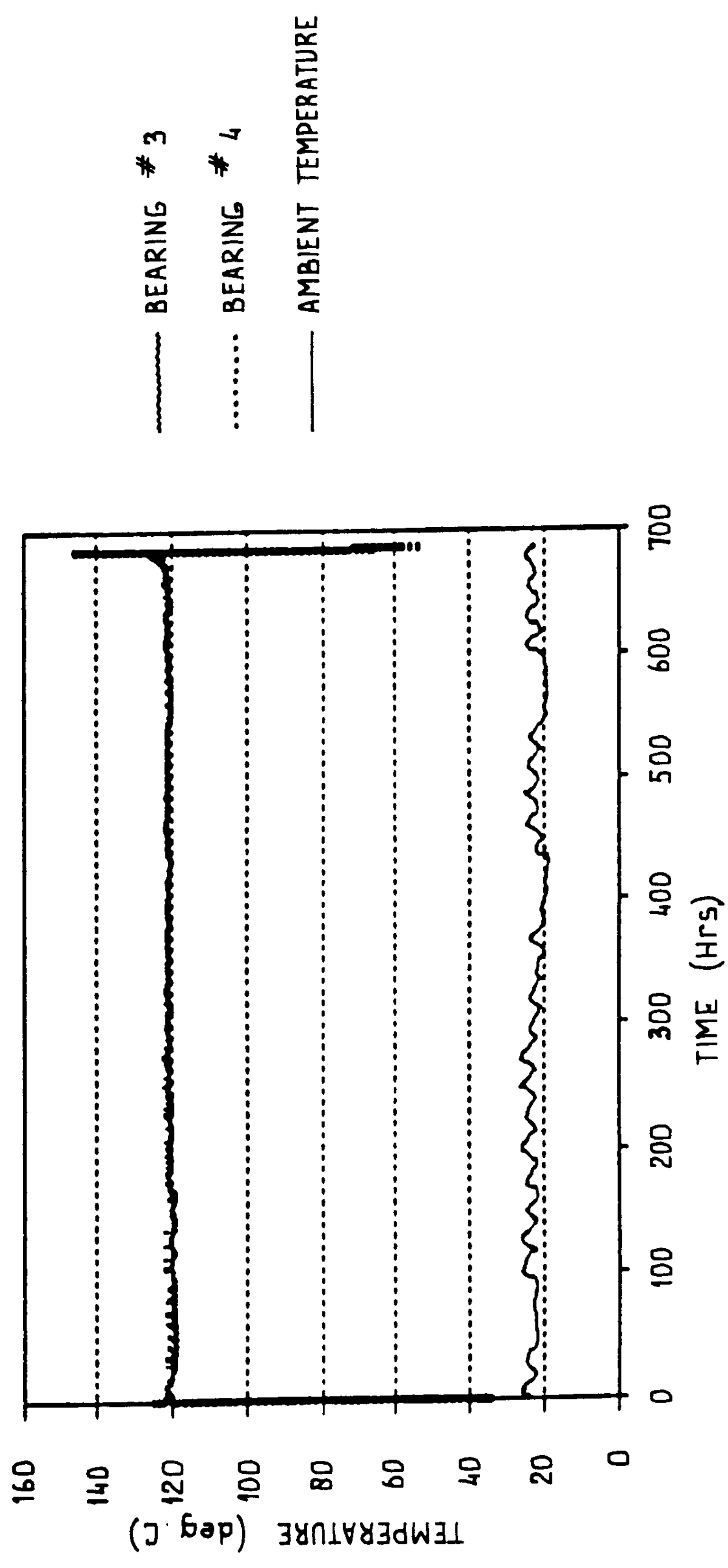
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

fig-4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BEARING # 4
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TEMPERATURE (deg. C)
TIME (Hrs)
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20
40
60
80
100
120
140
160
100
200
300
400
500
600
700

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0782

DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	CHEMICAL ABSTRACTS, vol. 101, no. 21, 19 November 1984 Columbus, Ohio, US; abstract no. 194779h, KUSOCHKIN, V. YA. ET AL 'Effect of lubricating grease on operating characteristics of enclosed roller bearings' * abstract * & TRENIE IZNOS (1984), 5(5), 882-8 CODEN: TRIZD6, 1984	1-3,5-7, 10,11	C10M117/02 C10M117/04 C10M129/32 C10M129/40 C10M129/50 //C10N10:10, C10N30:06, C10N30:10, C10N30:12, C10N40:02, C10N50:10
D,Y	NLGI SPOKESMAN, vol. 57, no. 2, May 1993 pages 50-57, O.ROHR 'BISMUTH ...,A NEW METALLIC BUT NON-TOXIC REPLACEMENT FOR LEAD AS EP-ADDITIVE IN GREASES' * page 9-53, left column, line 39 - line 42 * * page 10-54, right column, line 1 - line 4 *	1-3,5-7, 10,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C10M
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X A	US-A-3 028 334 (E.V. WILSON) 3 April 1962 * column 1, line 11 - line 15 * * column 2, line 19 - line 24 * * column 5; example III *	12 7,11	
X	US-A-5 266 225 (D.HALL) * column 1, line 44 - line 47 * * column 4; example 3 *	12	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 July 1995	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0782

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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A	GB-A-795 811 (WAKEFIELD) 28 May 1958 * page 4; examples 21,22 * * page 7, line 6 - line 10 *	1,3,7	
A	EP-A-0 556 404 (TONEN CORPORATION) 25 August 1993 * page 3, line 31 * * page 14, line 3 - line 5 *	1,3,10	
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A	US-A-3 839 209 (SOCIETE FRANCAISE DES COUSSINETS) 1 October 1974 * abstract; claim 1 *		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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D,A	DATABASE WPI Week 8842 Derwent Publications Ltd., London, GB; AN 88-298267 & SU-A-1 384 603 (GOMEL UNIV) , 30 March 1988 * abstract *		

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