

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 668 900 B2

(12)

NEW EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the opposition decision:

29.05.2002 Bulletin 2002/22

(45) Mention of the grant of the patent:

07.10.1998 Bulletin 1998/41

(21) Application number: **93924736.7**

(22) Date of filing: **10.11.1993**

(51) Int Cl.7: **C10M 169/06**

// (C10M169/06, 117:02,
117:04, 117:06, 135:02, 135:04,
135:06, 135:36, 135:18, 135:18,
137:02, 137:04, 137:10, 137:10,
137:12, 159:18), C10N10:04,
C10N10:12, C10N30:06,
C10N40:00

(86) International application number:

PCT/GB93/02313

(87) International publication number:

WO 94/11470 (26.05.1994 Gazette 1994/12)

(54) **GREASES**

SCHMIERFETTER

GRAISSES

(84) Designated Contracting States:

DE FR

(30) Priority: **14.11.1992 GB 9223945**

(43) Date of publication of application:

30.08.1995 Bulletin 1995/35

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EP 0 668 900 B2

Description

[0001] This invention relates to greases intended primarily but not exclusively for use in constant velocity joints.

[0002] Greases consist essentially of a base oil with a thickening agent and other additives may be included to promote specific properties, for example extreme pressure lubricants and anti-oxidants.

[0003] Whilst the object of such greases is to provide low friction between moving components, in practice the achievement of low friction does not necessarily lead to low wear since friction is only one factor which influences wear. In particular, wear may arise as a result of chemical interaction between one or more constituents of the grease and the materials from which the lubricated components are made.

[0004] The thickening agent employed is traditionally a soap, but greases formulated in this way cannot achieve the high performance as required by modern technological demands and more recently greases have been made using organic polymers as a thickening agent, particularly polyureas. However, such greases offer little advantage since whilst achieving lower friction, they promote greater wear than traditional soap greases.

[0005] US-A-4 536 308 discloses a simple lithium soap grease with an additive composition which consists of 4 to 8 wt % of sulphurised sperm oil substitute, 0.5 to 2.0 wt % of the reaction product of coconut oil and diethanolamine, 2.4 to 5.0 wt % of zinc dialkyldithiophosphate, 0.5 to 2.0 wt % of zinc diamyl-dithiocarbamate and 0.5 to 1.0 wt % of aromatic amine phosphate.

[0006] WO-A-9 113 955 discloses a complex lithium soap grease containing an organo-metallic compound such as a molybdenum dialkyldithiocarbamate.

[0007] GB-A-2 255 346 discloses a grease thickened with a diurea and additionally including 0.5 to 3 % by weight of molybdenum sulphide dialkyldithio-carbamate, 0.5 to 3 % by weight of a zinc dithiophosphate extreme pressure additive, 0.5 to 3 % by weight of a sulphur-phosphorus series extreme pressure additive containing no metallic element and having a sulphur content of 10-30 % by weight and a phosphorus content of 0.5-5 % by weight, and 0.5 to 3 % by weight of lead dialkyldithiocarbamate.

[0008] The object of the invention is to provide an improved grease offering low friction and low wear which is suitable for use in a constant velocity joint, but may also have other applications, and we have discovered that this can be achieved by utilising a lithium-based soap thickener in combination with other specific materials.

[0009] According to the invention we provide a grease consisting essentially of a base oil and a lithium-based soap thickener in combination with:-

(1) 2-5% by weight of an organo-molybdenum complex capable of functioning as a friction reducing additive and selected from the group comprising alkyl molybdenum dithiophosphates and alkyl molybdenum di-thiocarbamates and mixtures thereof;

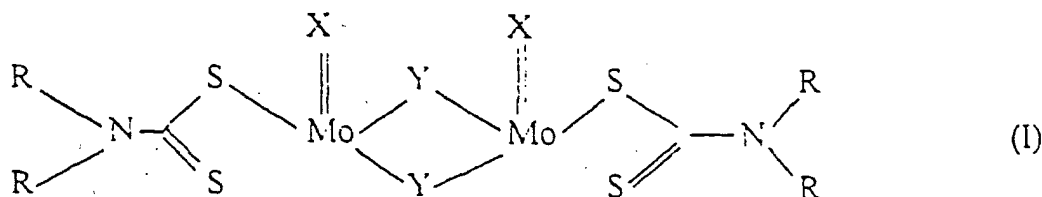
(2) 1-2% by weight of an anti-wear/anti-oxidant compound comprising a zinc di-thiophosphate;

(3) 1-2% by weight of an organo-sulphur compound extreme pressure additive selected from the group comprising sulphurised synthetic sperm oils, sulphurised fatty acid esters and mixtures thereof; and

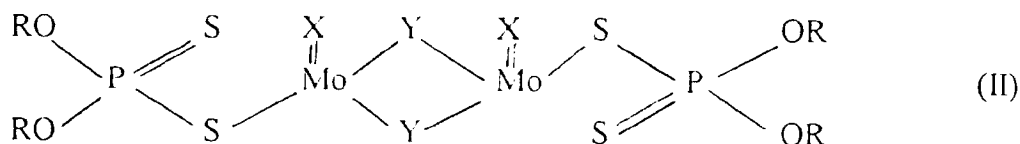
(4) 1-2% by weight of an organo-phosphorus compound extreme pressure additive comprising a tri-aryl phosphate.

[0010] We have shown that greases according to such a formulation may be used as a base grease, together with other conventional additives, such as molybdenum disulphide, in the preparation of a grease composition which in testing and when used in a constant velocity joint provides both low friction and low wear in a manner not achievable by other known grease formulations or other trial formulations differing from the above formulation. It is thought that this combination of properties arises from a synergistic effect obtained by the use of the combination of the organo-sulphur and organo-phosphorus compounds in conjunction with the organo-molybdenum complex and the lithium-based soap.

[0011] The organo-molybdenum complex may comprise a molybdenum di-thiocarbamate in accordance with the formula



or a molybdenum di-thiophosphate according to the formula



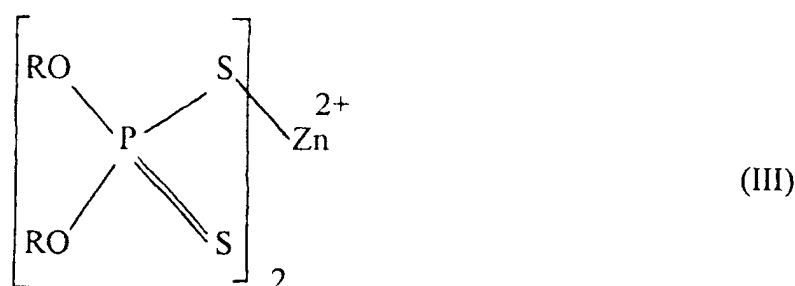
wherein in both cases

X or Y = S or O

R = primary or secondary alkyl group

or a mixture of such compounds.

[0012] The anti-wear/anti-oxidant compound may comprise a zinc dithiophosphate according to the formula



[0013] The thickener may comprise a simple lithium soap formed from stearic acid or from 12-hydroxystearic acid or from other similar fatty acids, or a lithium complex soap formed from a mixture of such acids. More particularly, the lithium complex soap may comprise a mixture of hydroxy fatty acids and di-acid salts, such as lithium 12-hydroxystearate and lithium azelate.

[0014] Simple lithium soaps and complex lithium soaps when used in formulations in accordance with the invention appear to behave in substantially the same way, except that where the simple soap is employed the grease will operate only up to temperatures of about 120°C, whereas the complex soaps enable temperatures of up to about 180°C to be sustained.

[0015] The base oil may comprise a mineral oil or a synthetic oil or a mixture of such oils.

[0016] The invention also resides in a method of lubricating a constant velocity joint characterised by the use of such a grease, and further in a constant velocity joint packed with such a grease.

[0017] The invention will now be described by reference to the following Examples which illustrate various grease formulations comprising lithium-based thickeners, some of which are in accordance with the invention and others for the purposes of comparison.

[0018] In Examples 1 to 10 the base grease comprised a polyalphaolefin containing 10% lithium complex soap thickener consisting of a 60:40 mixture of 12-hydroxystearate and azelate, with the addition of conventional additives such as tackiness agents, corrosion inhibitors and viscosity index improvers.

EXAMPLE 1

[0019] A lithium soap grease in accordance with the invention was made by using the above-mentioned base grease and adding thereto:-

2% of an organo-molybdenum complex comprising 2-ethylhexyl-molybdenum di-thiophosphate.

2% of an organometallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate.

2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil.

1% of an organo-phosphorus compound comprising tritolylphosphate.

EXAMPLE 2

[0020] A comparative lithium soap grease not in accordance with the invention was made by using the above-mentioned lithium complex base grease and adding thereto:-

- 5 5% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiophosphate.
- 2% of an organo-metallic anti-wear/anti-oxidant comprising antimony di-amyldithiocarbamate.
- 2% of an organo-sulphur compound comprising a sulphurised fatty acid and ester. (but no organo-phosphorus compound)

EXAMPLE 3

[0021] A further comparison lithium soap grease not in accordance with the invention was made up using the same lithium complex base grease and adding thereto: -

- 15 4% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiocarbamate.
- 2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10) (but no organo-sulphur or organo-phosphorus compound).

[0022] These three greases were tested in an Optimol SRV reciprocating sliding friction and wear machine and compared with a typical calcium complex, low cost, low performance grease (A) and a typical polyurea, low friction, high wear, grease (B) and the results are illustrated in Figure 1 which shows the co-efficient of friction as measured over a period of one hour at 80°C with a 1.5 mm stroke at 40 Hz and a moderate 200 N load.

[0023] Wear in the SRV test was determined by microscopic inspection to obtain a measurement of scar diameter, and a Rank Taylor Hobson Surtronic surface finish measuring machine was employed to determine the depth and cross-section of any scarring. These two measurements were used to calculate wear rate. The term "low wear" as used herein generally indicates that no scar depth was measurable.

[0024] As can be seen, the grease of Example 3 performed only a little better in terms of co-efficient of friction than prior art grease (A) and not as well as prior art grease (B) and it also did not exhibit the required low wear characteristic. The grease of Example 2 performed somewhat better than prior grease (B) but again did not exhibit the required low wear characteristics. By contrast the grease in accordance with Example 1, i.e. in accordance with the invention, not only had an improved co-efficient of friction relative to the other greases tested, but also exhibited low wear characteristics, as illustrated in Figure 2 which shows the surface profile of test samples from the SRV tests using the grease of Examples 1 and 2 at moderate load. As can be seen the grease of Example 1 in accordance with the invention shows no significant scarring, whereas that of Example 2 shows some scarring.

[0025] Three of these greases were compared with a further prior art low friction clay grease (C) in a test similar to that described above and the results are illustrated in Figure 3 which shows the co-efficient to friction as measured over a period of 30 minutes at 50°C with a 3 mm stroke at 30 Hz and a light 80N load.

[0026] Again, only the grease of Example 1, in accordance with the invention, gave a suitably low co-efficient of friction in combination with low wear characteristics.

EXAMPLE 4

[0027] A further lithium soap grease in accordance with the invention was made up using the above-mentioned lithium complex base grease and adding thereto:-

- 5 5% of an organo-molybdenum complex comprising 2-ethyl hexyl molybdenum di-thiocarbamate.
- 2% of an organo-metallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate.
- 2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil.
- 50 2% of an organo-phosphorus compound comprising tritolylphosphate and with the further addition of 5% superfine molybdenum disulphide.

EXAMPLE 5

[0028] A further comparative lithium soap grease not in accordance with the invention was made up as in Example 4 but omitting the tritolylphosphate and substituting half of the stated organo-molybdenum complex by a primary alkyl molybdenum di-thiocarbamate.

EXAMPLE 6

[0029] A further comparative lithium soap grease not in accordance with the invention was made up as in Example 4 but omitting the tritolylphosphate.

[0030] These three greases were compared in a SRV test similar to that described above and following which the wear was determined in the same manner. The friction results are illustrated in Figure 4 which shows the co-efficient of friction as measured over a period of 1 hr at 80°C. with a 3 mm stroke at 40 Hz and a heavy 500 N load.

[0031] As can be seen, the greases of Examples 4 and 6 performed significantly better in terms of co-efficient of friction than the grease of Example 5, but only the grease of Example 4 had the required low wear characteristics, as illustrated in Figure 5 which shows the surface profile of test Samples from the SRV tests using greases of Examples 4 and 6 at high load. As can be seen the grease of Example 6, which is not in accordance with the invention, shows very significant scarring whereas that of Example 4 shows much less scarring.

EXAMPLE 7

[0032] A still further lithium soap grease in accordance with the invention was prepared as in Example 1 but using a sulphurised fatty acid ester instead of the sulphurised synthetic sperm oil. Another blend also substituted trixylenyl-phosphate for the tritolylphosphate, giving similar results.

EXAMPLE 8

[0033] A still further comparative lithium soap grease not in accordance with the invention was prepared as in Example 2 but replacing half of the stated molybdenum di-thiophosphate by 2-ethylhexyl molybdenum di-thiocarbamate.

EXAMPLE 9

[0034] A still further comparative lithium soap grease not in accordance with the invention was prepared using the above-mentioned lithium complex base grease and adding thereto:-

4% of an organo-molybdenum complex comprising an equal mixture of 2-ethylhexyl molybdenum di-thiocarbamate and a primary alkyl molybdenum di-thiocarbamate.

2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10).

2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil (no organo-phosphorus compound).

EXAMPLE 10

[0035] A still further comparative lithium soap grease not in accordance with the invention was prepared using the above-mentioned lithium complex base grease and adding thereto:-

2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10).

3% of an organo-sulphur compound comprising sulphurised synthetic sperm oil

(but no organo-molybdenum complex and no organo-phosphorus compound)

[0036] These four greases were compared in a further SRV test similar to that described above and again the wear was determined in the same manner. The friction results are illustrated in Figure 6 which shows the co-efficient of friction as measured over 1 hr at 80°C, with a 3 mm stroke at 40 Hz and a moderate 200 N load.

[0037] The greases of Examples 8, 9 and 10 all performed similarly with regard to co-efficient of friction at only a moderate value, and only that of Example 10 exhibited the required low wear characteristics, but this grease was not considered to provide a sufficiently low co-efficient of friction. However, the grease of Example 7, in accordance with the invention, showed not only a suitably low co-efficient of friction, but also the required low wear characteristic.

[0038] In Examples 11 and 12 which follow, the base grease comprises a mixture of polybutene and mineral oil containing the lithium-based complex soap thickener, also with the addition of conventional additives as previously mentioned.

EXAMPLE 11

[0039] A grease in accordance with the invention was made using the last-mentioned base grease and adding there-

to:

- 4% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiophosphate
2% of an organo-metallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate,
2% of an organo-sulphur compound comprising a sulphurised fatty acid ester,
2% of an organo-phosphorus compound comprising tri-xylenyl phosphate.

EXAMPLE 12

[0040] A further grease, also in accordance with the invention was made in accordance with Example 11 but with the amounts of the specified additives reduced by 50% whilst retaining the same ratio to one another.

[0041] These two greases were tested in the same manner as the greases of Examples 1 to 3 and 7 to 10 and the friction results are included in Figures 1 and 4 for ease of comparison with the earlier examples.

[0042] As can be seen, results for Example 11 showed slightly higher friction than for Examples 1 and 12 but less than those for Example 2, whereas the results for Example 12 are virtually indistinguishable from those for Examples 1 and 7.

[0043] In the case of both these greases, no wear was detected at the end of the SRV test.

[0044] Practical testing of these greases has confirmed the superiority of formulations in accordance with the invention relative to both prior art formulations and also various comparative formulations as described above which do not fall within the invention as claimed. Thus in a series of road tests a subjective assessment of noise, vibration and harshness (NVH rating) was carried out using vehicles fitted with constant velocity joints packed with such greases. Additionally laboratory tests were carried out on joints packed with greases in order to determine the life-time of the joint under typical conditions.

[0045] The results of such tests are illustrated in Figure 7 which plots the subjective NVH rating against joint life-time. As can be seen prior art grease A had a high (poor) NVH rating but a life-time of greater than 150,000 kilometres (duration of test) whereas prior art grease B achieved an improved NVH rating but failed to survive a 100,000 kilometre test. The grease according to Example 2 (not in accordance with the invention) achieved an NVH rating similar to grease B but only just survived a 100,000 kilometre test, showing signs of serious wear and accordingly not meeting the life-time achieved by grease A.

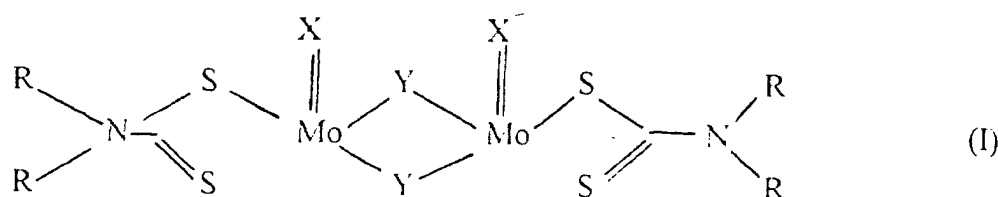
[0046] By contrast greases according to Examples 1 and 7 in accordance with the invention, not only achieved NVH ratings somewhat better than grease B, but also survived 160,000 kilometre life-time tests.

Claims

1. A grease consisting essentially of a base oil and a lithium-based soap thickener in combination with:-

- (1) 2 - 5% by weight of an organo-molybdenum complex capable of functioning as a friction reducing additive and selected from the group comprising alkyl molybdenum di-thiophosphates and alkyl molybdenum di-thiocarbamates and mixtures thereof;
- (2) 1 - 2% by weight of an anti-wear/anti-oxidant compound comprising a zinc di-thiophosphate;
- (3) 1 - 2% by weight of an organo-sulphur compound extreme pressure additive selected from the group comprising sulphurised synthetic sperm oils, sulphurised fatty acid esters and mixtures thereof; and
- (4) 1 - 2% by weight of an organo-phosphorus compound extreme pressure additive comprising a tri-aryl phosphate.

2. A grease according to Claim 1 wherein the organo-molybdenum complex comprises a molybdenum di-thiocarbamate in accordance with the formula:

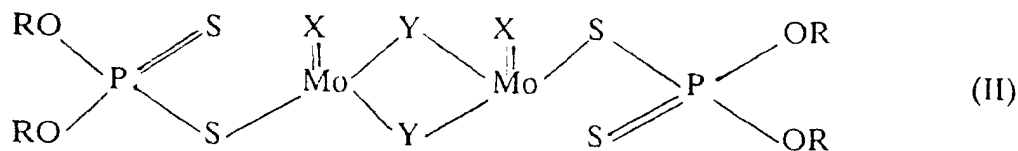


wherein:

X or Y = S or O

R = a primary or secondary alkyl group.

3. A grease according to Claim 1 wherein the organo-molybdenum complex comprises a molybdenum di-thiophosphate according to the formula:

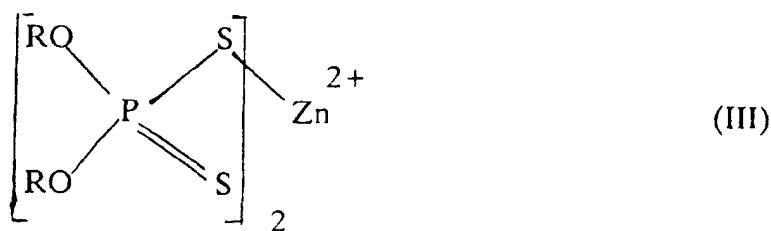


wherein

X or Y = S or O

R = a primary or secondary alkyl group.

4. A grease according to Claim 1 wherein the anti-wear/anti-oxidant compound comprises a zinc di-thiophosphate according to the formula:



wherein:

R = secondary alkyl

5. A grease according to Claim 1 wherein the thickener is selected from the group comprising simple and complex lithium soaps.
6. A grease according to Claim 1 wherein the base oil is selected from the group comprising mineral oils, synthetic oils and mixtures thereof.
7. A method of lubricating a constant velocity joint **characterised by** the use of a grease in accordance with any one of the preceding claims.
8. A constant velocity joint packed with a grease in accordance with any one of Claims 1 to 6.

Patentansprüche

1. Ein Schmierfett, welches im wesentlichen aus einem Basisöl und einem Seifenverdicker auf Lithium-Basis besteht, in Kombination mit:

(1) 2-5 Gew.-% eines Organomolybdänkomplexes, der als ein reibungsvermindernder Zusatz wirken kann

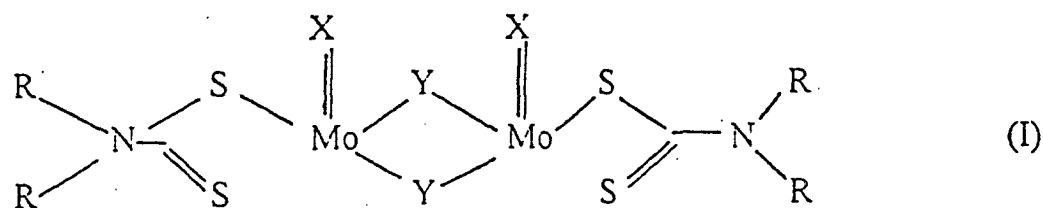
und ausgewählt ist aus der Gruppe, die Alkylmolybdändithiophosphate und Alkylmolybdändithiocarbamate und Mischungen derselben umfaßt;

(2) 1-2 Gew.-% einer Antiverschleiß/Antioxidationsverbindung, die ein Zinkdithiophosphat umfaßt;

(3) 1-2 Gew.-% eines Extremdruckzusatzes aus einer schwefelorganischen Verbindung, ausgewählt aus der Gruppe, die geschwefelte synthetische Spermele, geschwefelte Fettsäureester und Mischungen derselben umfaßt; und

(4) 1-2 Gew.-% eines Extremdruckzusatzes aus einer phosphororganischen Verbindung, der ein Triarylphosphat umfaßt.

2. Ein Schmierfett nach Anspruch 1, wobei der Organomolybdänkomplex ein Molybdändithiocarbamat entsprechend der Formel umfaßt:

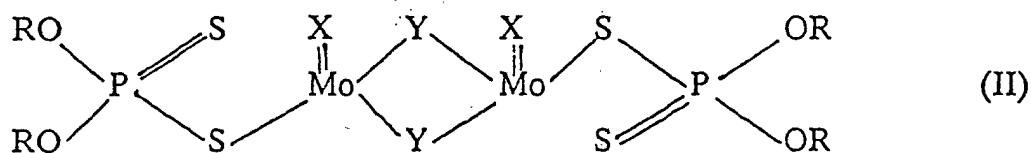


worin:

X oder Y = S oder O

R = eine primäre oder sekundäre Alkylgruppe.

3. Ein Schmierfett nach Anspruch 1, wobei der Organomolybdänkomplex ein Molybdändithiophosphat entsprechend der Formel umfaßt:

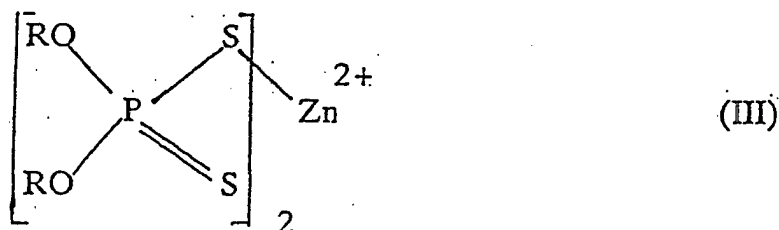


worin

X oder Y = S oder O

R = eine primäre oder sekundäre Alkylgruppe.

4. Ein Schmierfett nach Anspruch 1, wobei die Antiverschleiß/Antioxidationsverbindung ein Zinkdithiophosphat entsprechend der Formel umfaßt:



worin:

R = sekundäres Alkyl.

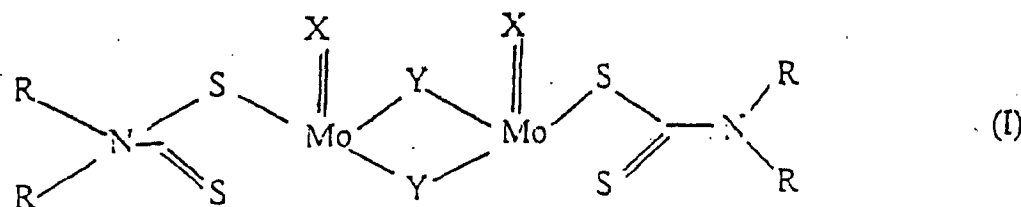
5. Ein Schmierfett nach Anspruch 1, wobei der Verdicker ausgewählt ist aus der Gruppe, die einfache und komplexe Lithiumseifen umfaßt.
6. Ein Schmierfett nach Anspruch 1, wobei das Basisöl ausgewählt ist aus der Gruppe, die Mineralöle, synthetische Öle und Mischungen derselben umfaßt.
7. Ein Verfahren zum Schmieren eines Doppelgelenks, **gekennzeichnet durch** die Verwendung eines Schmierfettes nach einem der vorangehenden Ansprüche.
8. Ein Doppelgelenk, das eingepackt ist mit einem Schmierfett gemäß einem der Ansprüche 1 bis 6.

Revendications

1. Graisse consistant essentiellement en une huile de base et un épaississant de savon à base de lithium, combinée :

(1) à une quantité comprise entre 2% et 5% en poids d'un complexe organique avec du molybdène pouvant fonctionner comme un additif réduisant le frottement et sélectionné dans le groupe comprenant les dithiophosphates alkylés de molybdène, les dithiocarbamates alkylés de molybdène et un mélange de ces substances ;
 (2) à une quantité comprise entre 1% et 2% en poids d'un composé anti-usure/antioxydant comprenant un dithiophosphate de zinc ;
 (3) à une quantité comprise entre 1% et 2% en poids d'un additif pour pression extrême à base d'un composé organo-sulfuré sélectionné dans le groupe comprenant les huiles synthétiques sulfurées de spermaceti, les esters d'acides gras sulfurés, et un mélange de ces substances ; et
 (4) à une quantité comprise entre 1% et 2% en poids d'un additif pour pression extrême à base d'un composé organo-phosphoré comprenant un phosphate de triaryle.

2. Graisse selon la revendication 1, dont le complexe organique avec du molybdène comprend un dithiocarbamate de molybdène selon la formule :

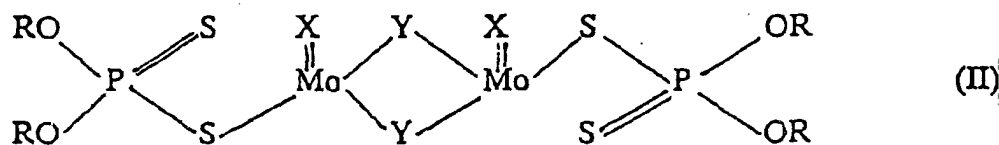


où

X ou Y = S ou O

R = un groupe d'alkyle primaire ou secondaire.

3. Graisse selon la revendication 1, dont le complexe organique avec du molybdène comprend un dithiophosphate de molybdène selon la formule :

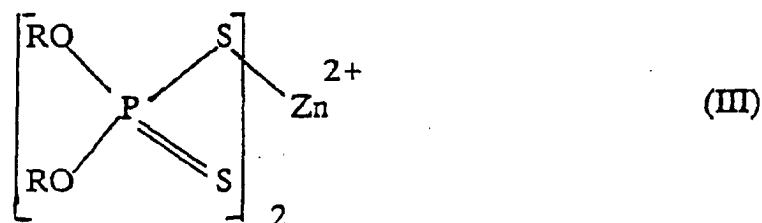


où

X ou Y = S ou O

R = un groupe d'alkyle primaire ou secondaire.

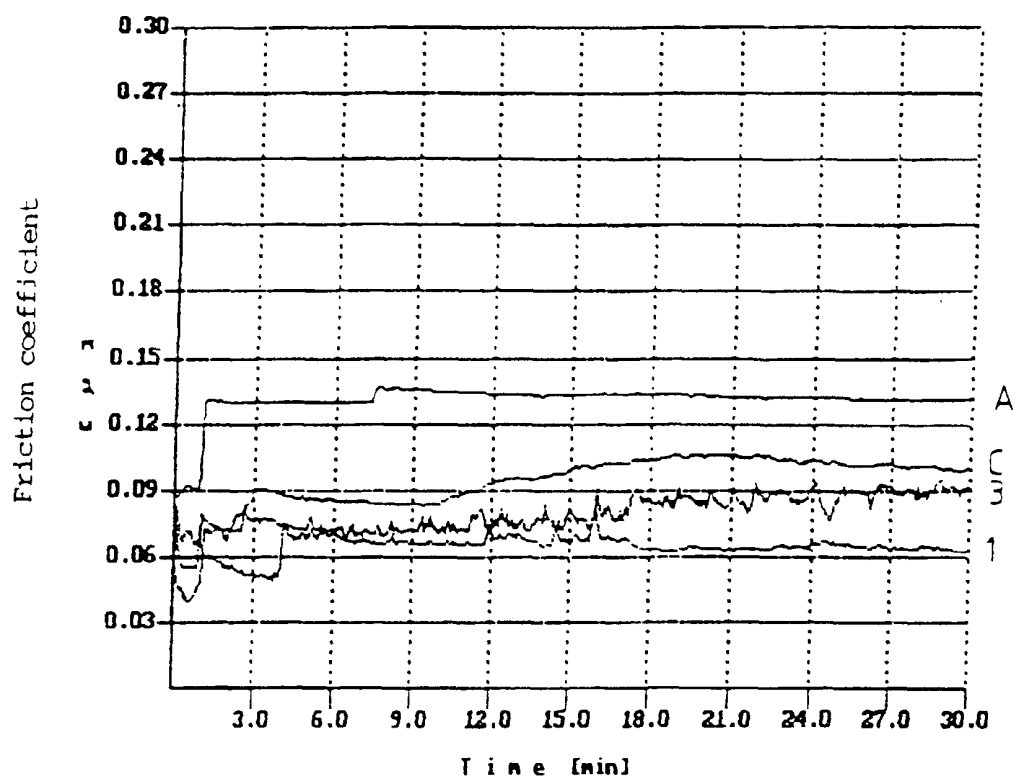
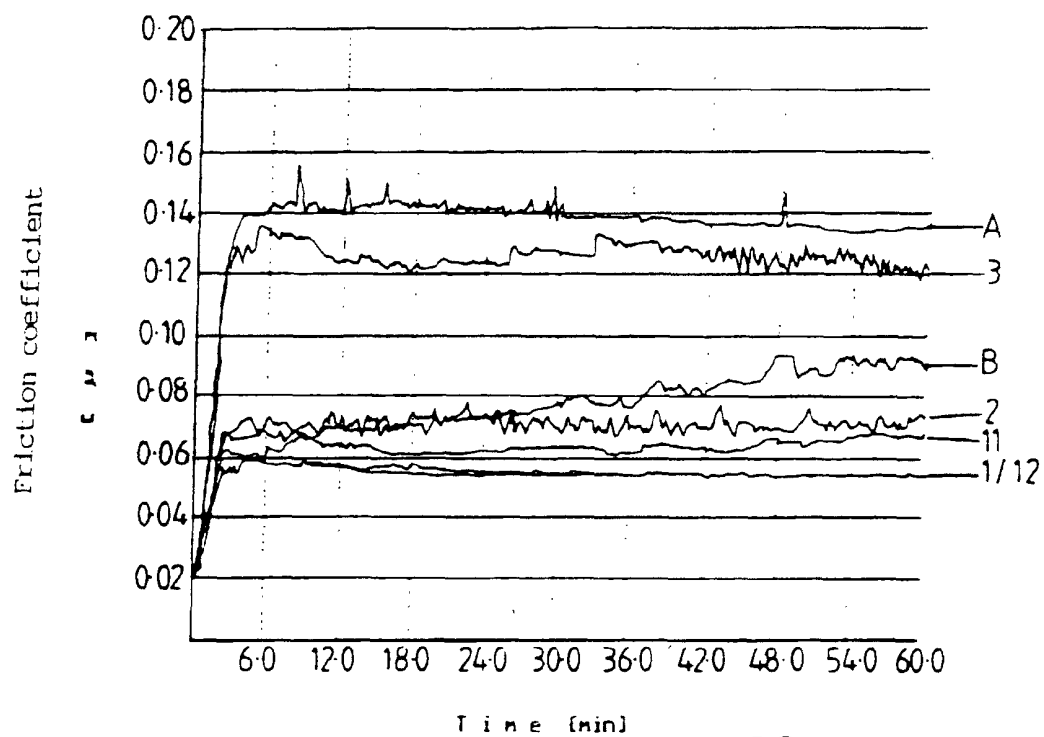
4. Graisse selon la revendication 1, dont le composé anti-usure/anti-oxydant comprend un dithiophosphate de zinc selon la formule :



où

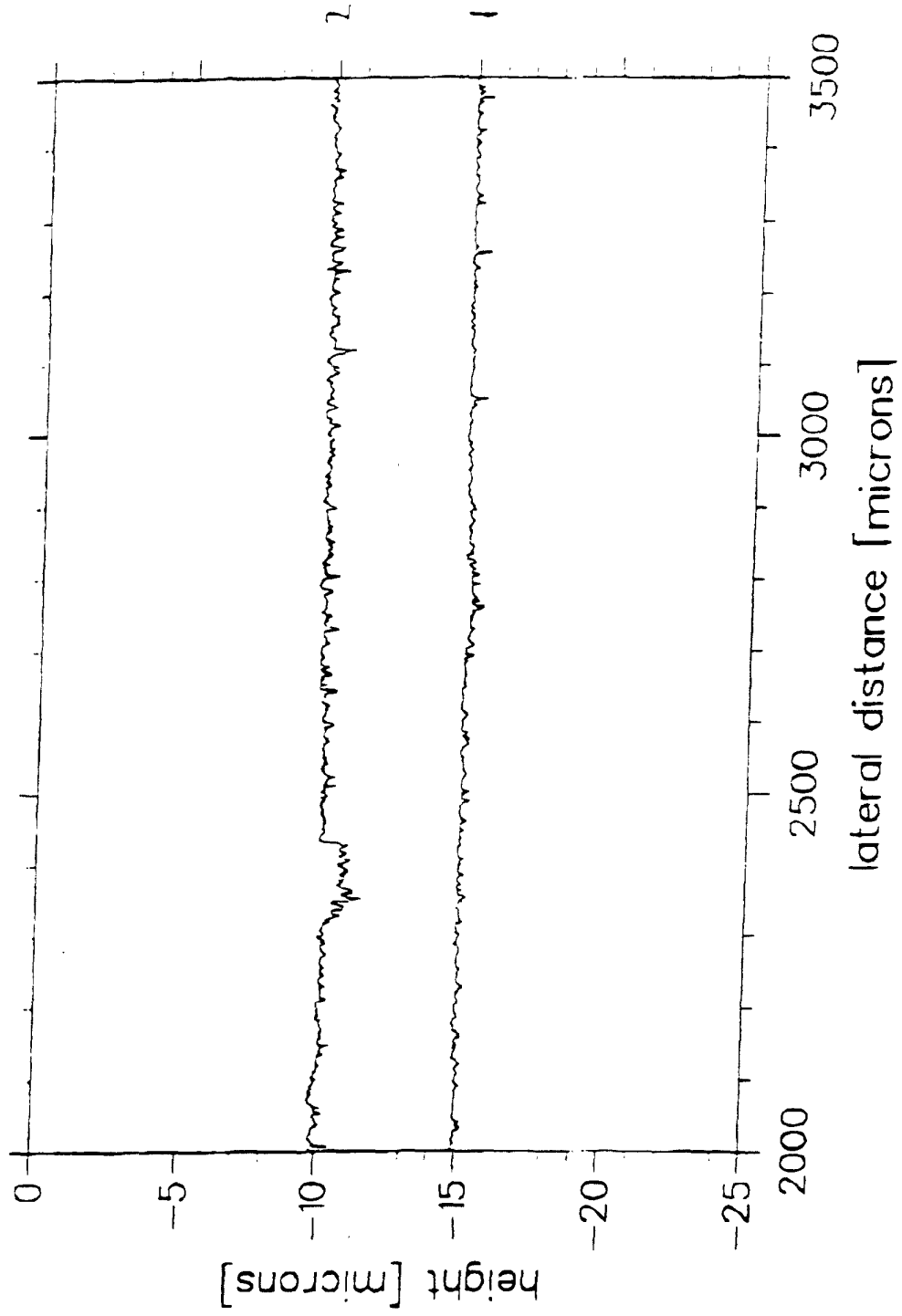
R = un alkyle secondaire.

5. Graisse selon la revendication 1, dont l'épaississant est sélectionné dans le groupe comprenant les savons simples et complexes à base de lithium.
6. Graisse selon la revendication 1, dont l'huile de base est sélectionnée dans le groupe comprenant les huiles minérales, les huiles synthétiques et un mélange de ces huiles.
7. Procédé de lubrification d'un joint à vitesse constante, **caractérisé par** l'utilisation d'une graisse selon l'une quelconque des revendications précédentes.
8. Joint à vitesse constante utilisé avec une graisse selon l'une quelconque des revendications 1 à 6.



SRV Wear Scars

FIG 2



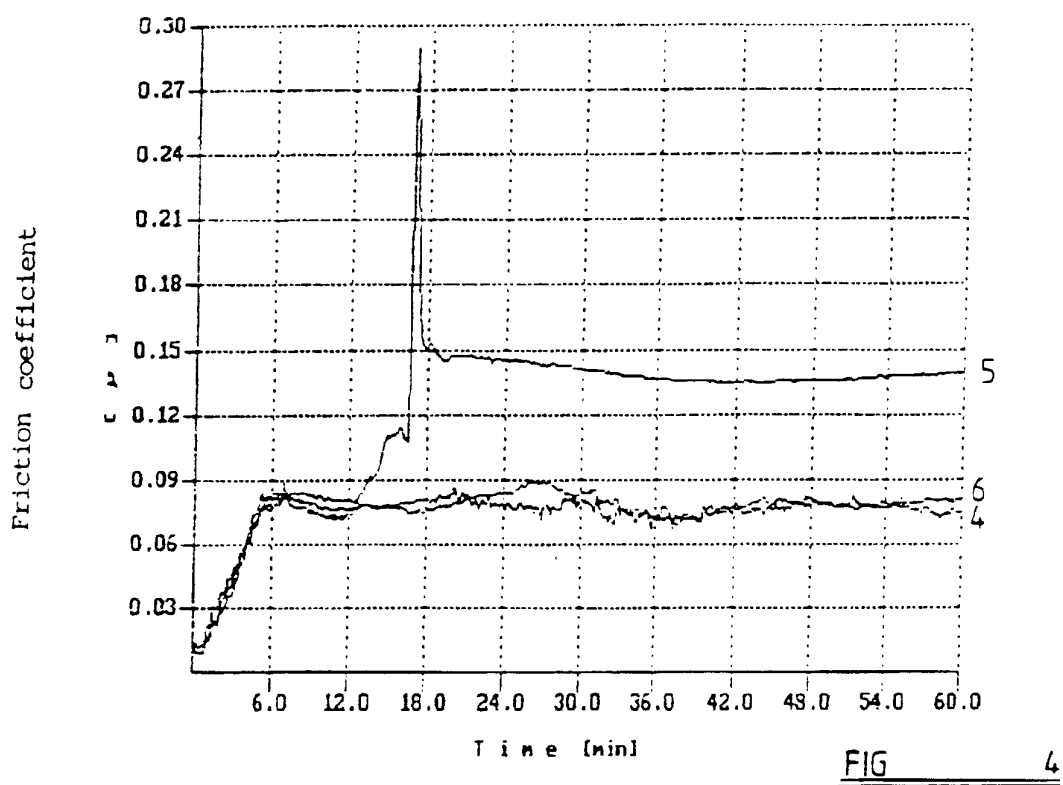


FIG 6

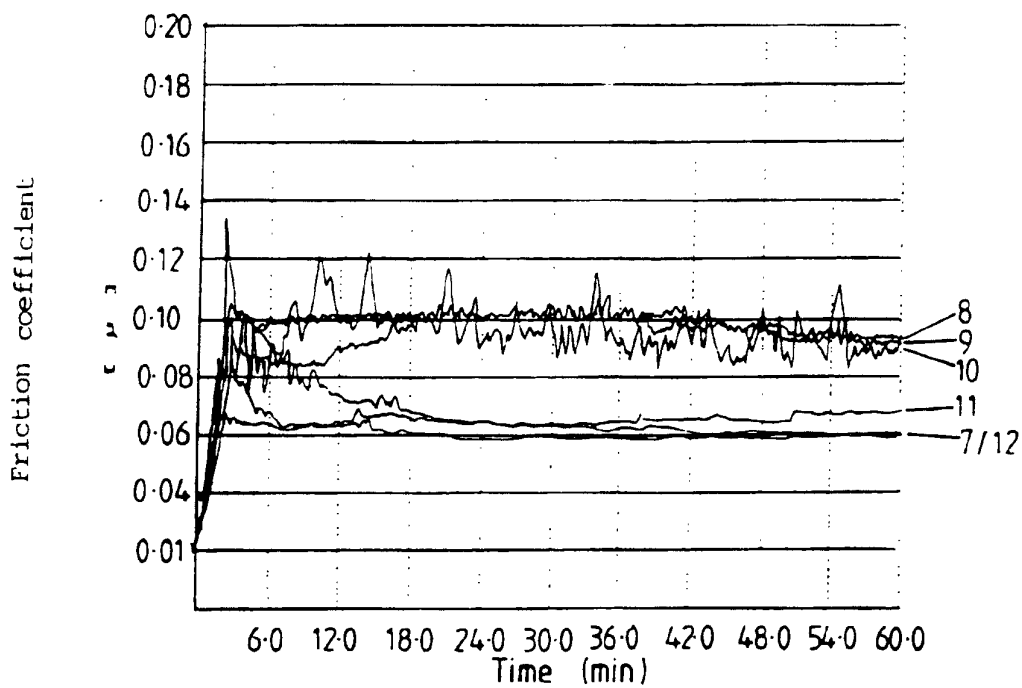
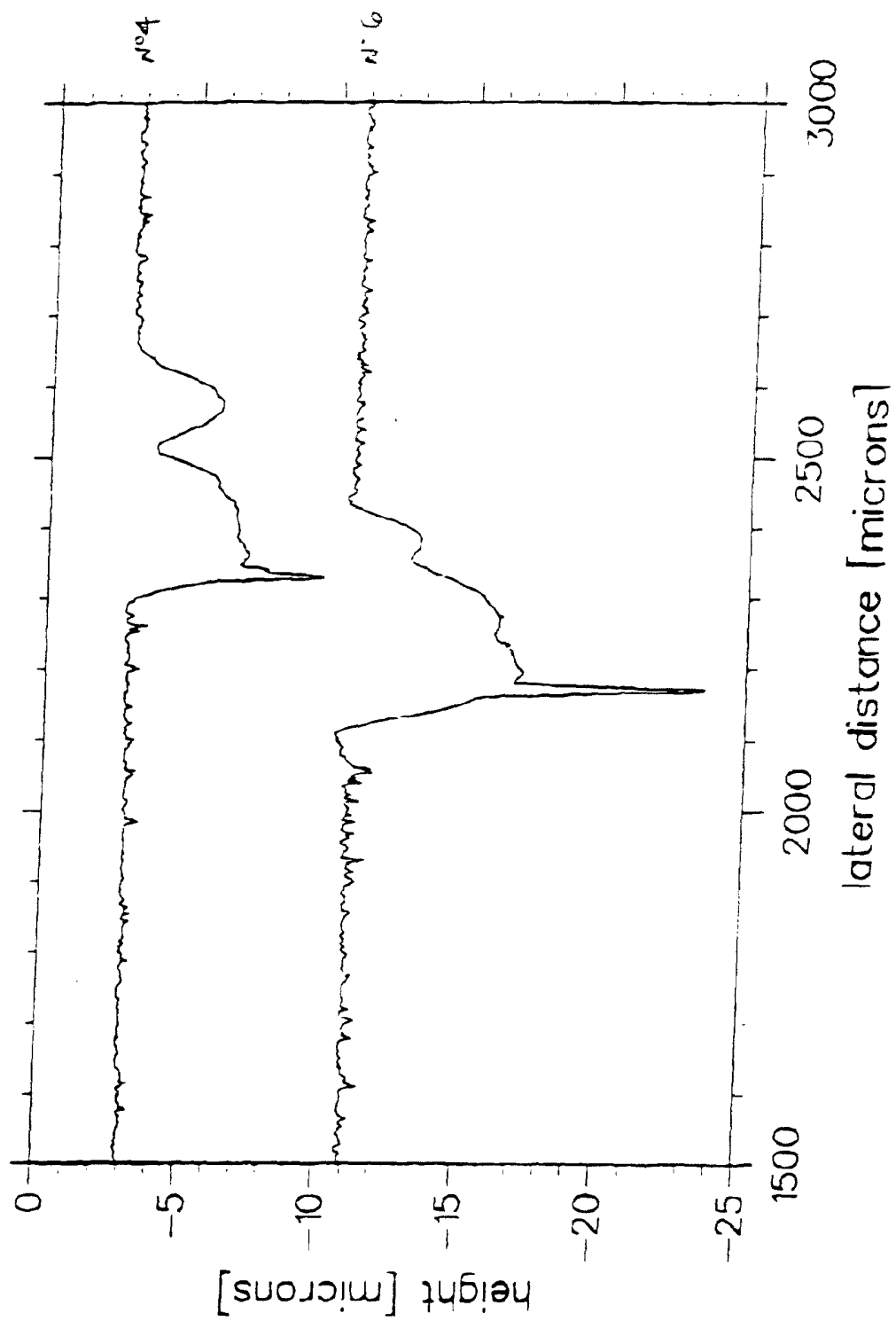


FIG 5

SRV Wear Scars



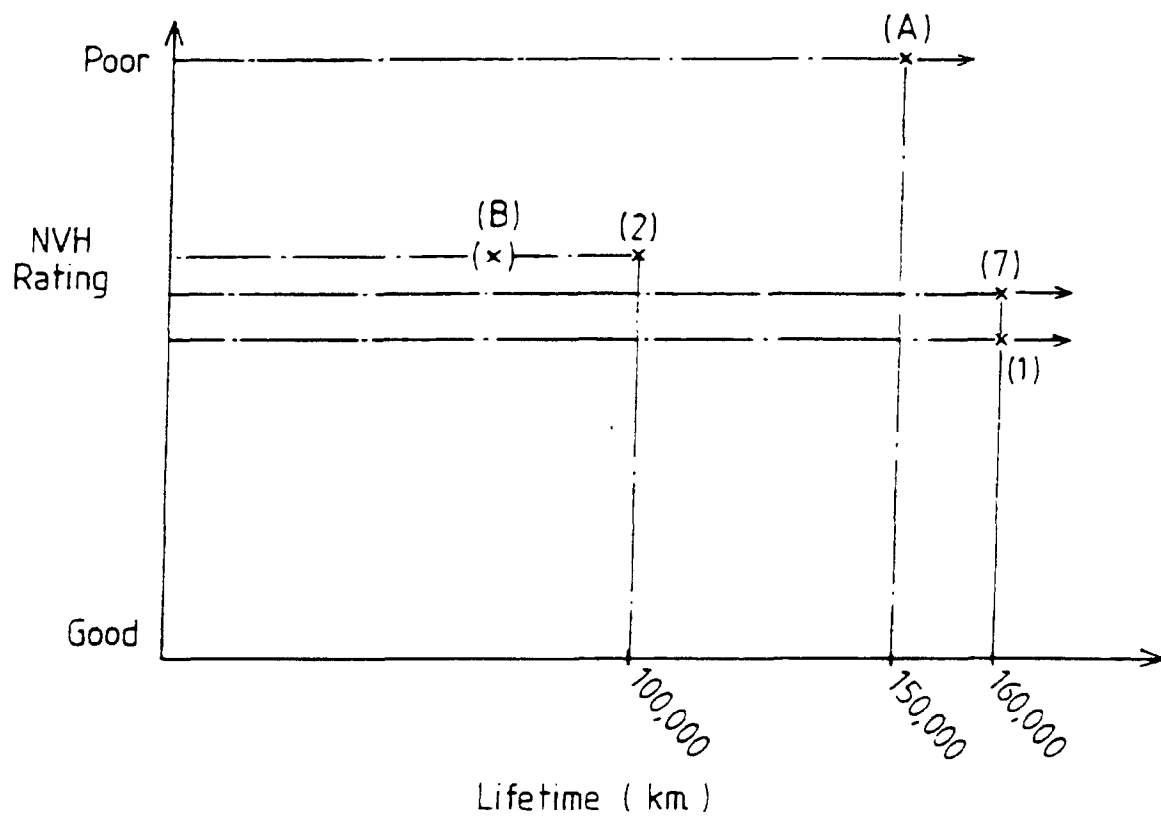


FIG 7