OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,226,734**
(86) 1996/07/10
(87) 1997/01/30

(72) FLETCHER, Robert Anthony, GB
(71) Shell Canada Limited, CA

(51) Int.Cl.[6] C10M 125/22, C10M 117/00, C10M 137/10, C10M 129/58
(30) 1995/07/11 (95304827.9) EP

(54) **GRAISSES LUBRIFIANTES**
(54) **LUBRICATING GREASES**

(57) Composition lubrifiante comprenant une huile de base d'origine minérale et/ou synthétique associée à une combinaison additive à réduction de frottement contenant du bisulfure de molybdène, du naphténate de zinc et un ou plusieurs dithiophosphates métalliques, et éventuellement un ou plusieurs dithiocarbamates métalliques. Une graisse lubrifiante de cette composition associée à un épaississeur, qui peut être un composé uréique, un simple savon de lithium ou un complexe de lithium, s'avère particulièrement utile pour la lubrification des joints homocinétiques, tels que les joints à rotule homocinétiques.

(57) A lubricating composition comprising a base oil of mineral and/or synthetic origin in combination with a friction-reducing additive combination comprising molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates. A lubricating grease comprising such a composition in combination with a thickener, which may be a urea compound, a simple lithium soap or a lithium complex, is particularly suitable for lubricating constant velocity joints such as constant velocity ball joints.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C10M 141/10, 169/06 // (C10M 141/10, 125:22, 129:58, 135:18, 137:10) (C10M 169/06, 117:00, 119:24, 125:22, 129:58, 135:18, 137:10), C10N 10:00, 10:02, 10:06, 30:06

A1

(11) International Publication Number: **WO 97/03152**

(43) International Publication Date: 30 January 1997 (30.01.97)

(21) International Application Number: PCT/EP96/03058

(22) International Filing Date: 10 July 1996 (10.07.96)

(30) Priority Data:
95304827.9 11 July 1995 (11.07.95) EP
(34) Countries for which the regional or international application was filed: GB et al.

(71) Applicant *(for all designated States except CA)*: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) Applicant *(for CA only)*: SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA).

(72) Inventor: FLETCHER, Robert, Anthony; 40 Oaklands, Guilden Sutton, Chester CH3 7HE (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: LUBRICATING GREASES

(57) Abstract

A lubricating composition comprising a base oil of mineral and/or synthetic origin in combination with a friction-reducing additive combination comprising molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates. A lubricating grease comprising such a composition in combination with a thickener, which may be a urea compound, a simple lithium soap or a lithium complex, is particularly suitable for lubricating constant velocity joints such as constant velocity ball joints.

LUBRICATING GREASES

The present invention relates to lubricating compositions, particularly to lubricating greases containing such compositions, and more particularly to lubricating greases for use in constant velocity joints such as constant velocity ball joints.

The primary purpose of lubrication is separation of solid surfaces moving relative to one another, to minimise friction and wear. The materials most frequently used for this purpose are oils and greases. The choice of lubricant is mostly determined by the particular application.

Lubricating greases are employed where heavy pressures exist, where oil drip from the bearings is undesirable or where the motion of the contacting surfaces is discontinuous so that it is difficult to maintain a separating film in the bearing. Because of design simplicity, decreased sealing requirements and less need for maintenance, greases are almost universally given first consideration for lubricating ball and roller bearings in electric motors, household appliances, automotive wheel bearings, machine tools or aircraft accessories. Greases are also used for the lubrication of small gear drives and for many slow-speed sliding applications.

Lubricating greases consist primarily of a fluid lubricant, such as an oil, and a thickener. Essentially, the same type of oil is employed in compounding a grease as would normally be selected for oil lubrication. Fatty acid soaps of lithium, calcium, sodium, aluminium and barium are most commonly used as thickeners. However, thickeners may be one of a variety of solid materials, including clays, complexes such as those of lithium, and urea compounds.

The base oil may be of mineral or synthetic origin. Base oils of mineral origin may be mineral oils, for example produced by solvent refining or hydroprocessing. Base oils of synthetic origin may typically be mixtures of C_{10-50} hydrocarbon polymers, for example liquid polymers of alpha-olefins. They may also be conventional esters, for example polyol esters. The base oil may also be a mixture of these oils. Preferably the base oil is that of mineral origin sold by the Royal Dutch/Shell Group of Companies under the designations "HVI" or "MVIN", is a polyalphaolefin, or a mixture of the two. Synthetic hydrocarbon base oils, for example those sold by the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark) may also be used.

A lubricating grease preferably contains 5 to 20% by weight of thickener.

Lithium soap thickened greases have been known for many years. Typically, the lithium soaps are derived from C_{10-24}, preferably C_{15-18}, saturated or unsaturated fatty acids or derivatives thereof. One particular derivative is hydrogenated castor oil, which is the glyceride of 12-hydroxystearic acid. 12-hydroxystearic acid is a particularly preferred fatty acid.

Greases thickened with complex thickeners are well known. In addition to a fatty acid salt, they incorporate into the thickener a complexing agent which is commonly a low to medium molecular weight acid or dibasic acid or one of its salts, such as benzoic acid or boric acid or a lithium borate.

Urea compounds used as thickeners in greases include the urea group (-NHCONH-) in their molecular structure. These compounds include mono-, di- or polyurea compounds, depending upon the number of urea linkages.

Various conventional grease additives may be incorporated into the lubricating greases, in amounts normally used in this field of application, to impart certain desirable characteristics to the grease, such as oxidation stability, tackiness, extreme pressure properties and corrosion inhibition. Suitable additives include one or more extreme pressure/antiwear agents, for example zinc salts such as zinc dialkyl or diaryl dithiophosphates, borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds made, for example, by reacting a dialkoxy amine with a substituted organic phosphate, amine phosphates, sulphurised sperm oils of natural or synthetic origin, sulphurised lard, sulphurised esters, sulphurised fatty acid esters, and similar sulphurised materials, organo-phosphates for example according to the formula $(OR)_3P=O$ where R is an alkyl, aryl or aralkyl group, and triphenyl phosphorothionate; one or more overbased metal-containing detergents, such as calcium or magnesium alkyl salicylates or alkylarylsulphonates; one or more ashless dispersant additives, such as reaction products of polyisobutenyl succinic anhydride and an amine or ester; one or more antioxidants, such as hindered phenols or amines, for example phenyl alpha naphthylamine; one or more antirust additives; one or more friction-modifying additives; one or more viscosity-index improving agents; one or more pour point depressing additives; and one or more tackiness agents. Solid materials such as graphite, finely divided molybdenum disulphide, talc, metal powders, and various polymers such as polyethylene wax may also be added to impart special properties.

To reduce friction levels, those skilled in the art have largely looked to using organic molybdenum-based formulations, and there are numerous proposals in patent literature of such lubricating compositions.

The use of molybdenum disulphide is known from, for example, *"Solid Lubricant Additives - Effect of Concentration and other Additives on Anti-Wear Performance", Bartz, Wear, 17 (1971) pages 421-432,* to have the effect of reducing wear when incorporated in lubricating oils. In *"Interrelations between Molybdenum Disulfide and Oil Soluble Additives", Bartz, NLGI Spokesman, December 1989*, there is discussion of the use of molybdenum disulphide in combination with certain zinc dialkyldithiophosphates. However, it is shown there that such a combination caused higher wear than when using either of those additives alone. Clearly such an antagonistic effect would make such a combination of additives quite unattractive for the reduction of friction levels.

Zinc naphthenate is the zinc salt form derived (usually by reaction with zinc oxide) from naphthenic acids, predominantly monocarboxylic acids obtained from petroleum during the refining of various distilled fractions, and can be defined by the general formula

$$R(CH_2)_n\ COOH$$

in which R represents a cycloalkyl group which may be substituted or unsubstituted by one or more lower (e.g. from C_{1-10}) aliphatic groups, especially alkyl groups, e.g. methyl. The cyclic nucleus is usually a cyclopentane ring, but may be a cyclohexane ring.

Zinc naphthenate is known for use in lubricating compositions to improve corrosion-resistance as an anti-rust additive, for example as documented in US Patent Specification No. 3,158,574. It has also been documented as a suitable organo-zinc source for use to avoid flaking, a fatigue phenomenon also termed pitting or spalling, in European Patent Specification No. 508115 A1 in grease compositions for constant velocity joints.

However it is not a common additive in lubricating compositions as other anti-rust additives and organo-zinc sources are generally more favoured.

Zinc naphthenate is a viscous substance and to improve handling it is usually used in diluted form. Conventionally zinc naphthanate is used in mineral oil to give a dispersion having an elemental zinc content of 8% by weight. However other concentrations are known such as 6% wt zinc, 10% wt zinc and 12% wt zinc. The viscosity and physical nature of a zinc napthenate dispersion depends not just upon the concentration of zinc naphthenate in the dispersion but also on the nature and viscosity of the diluent mineral oil.

European Patent Specification No. 191608 A3 concerns lubricating grease for rock drill bits. The examples disclose the preparation and properties of three lubricating greases containing base oil, lithium complex soap, molybdenum disulphide and other additives, being zinc dialkyldithiophosphate and zinc naphthenate (8% zinc); two of the greases contain 7% wt. molybdenum disulphide, 3% wt dithiophosphate and 1% zinc naphthenate (8% zinc) and the third contains 15% wt. molybdenum disulphide, 3% wt. dithiophosphate and 1% zinc naphthenate (8% zinc). The quantity of neat zinc naphthenate present can be calculated to be 0.6% wt in each case. The three greases were tested for load carrying, wear and flow properties, the latter a property particularly desired as the greases would need to be pumpable to the drill bit head in use.

It has now been found that an unexpected and enhanced low friction performance can in fact be attained using the combination of molybdenum disulphide and metal dithiophosphates by adding zinc naphthenate to such a combination. When incorporated into greases and used in constant velocity joints this combination allows for the joints to operate at lower temperatures, which may in turn allow drive shafts to be designed into vehicles with permanently installed angles and/or it may allow for the joints to be reduced in size.

In accordance with the present invention there is provided the use of molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates, as a friction reducing additive combination in a lubricating composition comprising a base oil of mineral and/or synthetic origin.

Also provided by the invention is use of the friction reducing additive combination in a lubricating grease which comprises a base oil of mineral and/or synthetic origin and a thickener.

Such a lubricating grease preferably contains molybdenum disulphide in the amount of from 0.5 to 10% by weight, more preferably 1 to 4% by weight. It also preferably contains (neat) zinc naphthenate in the amount of from 0.05 to 12% by weight, more preferably 0.3 to 2.4% by weight. It further preferably contains said one or more metal dithiophosphates in the total amount of from 0.15 to 10% by weight, more preferably 1 to 3% by weight. All amounts are based on total weight of the grease composition.

In accordance with the present invention there is further provided a lubricating composition comprising a base oil of mineral and/or synthetic origin in combination with molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates, in which the ratio of the amount of molybdenum disulphide to the amount of metal dithiophosphate is in the range of from 1:0.15 to 1:1 and the ratio of the amount of metal dithiophosphate to the amount of zinc naphthenate is in the range of from 1:0.2 to 1:3.0 and the ratio of the amount of molybdenum disulphide to the amount of zinc naphthenate is in the range of from 1:0.1 to 1:1.2, the amount of zinc naphthenate being calculated as neat zinc naphthenate.

The present invention also extends to a lubricating grease comprising a thickener in combination with a lubricating composition according to the present invention.

The metal in the metal dithiophosphates and/or metal dithiocarbamates is preferably selected from zinc, molybdenum, tin, manganese, tungsten and bismuth.

Preferably, the one or more metal dithiophosphates is/are selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates, and the one or more metal dithiocarbamates is/are selected from zinc dialkyl-, diaryl- or alkylaryl-dithiocarbamates, in which dithiophosphates and/or dithiocarbamates any alkyl moiety is straight chain or branched and preferably contains 1 to 12 carbon atoms.

Zinc naphthenate may be used in its conventional diluted forms, and is widely available commercially. Suitable dispersions that may be mentioned are Manchem 8% Zn, Valirex 8% Zn and Adchem 8% Zn (Manchem, Valirex and Adchem are all trade names). The enhanced friction-reduction effect is given by the combination of zinc naphthenate, molybdenum disulphide and metal dithiophosphate, and is not found to vary significantly if different sources of the zinc naphthenate is used.

The thickener of lubricating greases mentioned hereinbefore preferably comprises a urea compound, a simple lithium soap or a complex lithium soap. A preferred urea compound is a polyurea compound. Such thickeners are well known in lubricant grease technology.

In accordance with the present invention there is further provided a method of lubricating a constant velocity joint comprising packing it with a lubricating grease according to the present invention.

In accordance with the present invention there is still further provided a constant velocity joint packed with a lubricating grease according to the present invention.

The present invention will now be described by reference to the following Examples:

Examples 1 to 20

Lubricating greases were prepared by the following procedure.

The lithium soap greases A, B and E were prepared by adding a slurry of $LiOH.H_2O$ and water in the proportions of 1 part $LiOH.H_2O$ to 5 parts water to hydrogenated castor oil or hydrogenated castor oil fatty acid in cold base oil and heating the mix in a sealed autoclave to 150°C. The steam was vented off and heating continued to 220°C before the reaction mass was cooled and the product homogenised.

The lithium complex greases D were prepared by adding a 50% slurry of the $LiOH.H_2O$ and boric acid in water to hydrogenated castor oil fatty acid, calcium alkyl salicylate and calcium octoate in oil and then heating the charge to 210°C with stirring. After slowly cooling to 80°C the other additives to be included in the formulation were added. On further cooling to ambient temperature the resulting grease was homogenised.

The urea greases C were prepared by heating 5% of 4,4'-diphenylmethane diisocyanate in base oil to 70°C and then adding 10.8% stearylamine. The mixture was then further heated to 150°C before being cooled to 80°C. The other additives to be included in the formulation were then added. The formulated grease was then homogenised at ambient temperature.

The components of the prepared greases are set out in Table 1:

TABLE 1

	EXAMPLE											
	1	2	3	4	5	6	7	8	9	10	11	12
Molybdenum disulphide %w	3	3	3	3	3	3	3	3	3	3	3	3
ZNDTP (1) %w	1	1	1	1	2	1	3	-	-	1	1	1
ZNDTP (2) %w	-	-	-	-	-	1	-	1.2	1.2	-	-	-
Zinc naphthenate ** %w ***	K 2.0 1.2	K 0.5 0.3	K 1.0 0.6	K 4.0 2.4	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 4.0 2.4	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2
ZNDTC %w	-	-	-	-	-	-	-	-	-	-	-	-
Antioxidant %w type	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	-	0.5 X	0.5 Y
Thickener	A	A	A	A	A	A	A	A	A	B	B	B
Base Oil	P	P	P	P	P	P	P	P	P	Q	Q	Q

TABLE 1 (continued)

	EXAMPLE										
	13	14	15	16	17	18	* 19	20	21	22	23
Molybdenum disulphide %w	3	3	3	3	1	3	3	4	4	4	4
ZNDTP (1) %w	1	1	1	1	1	1	1	1.3	1.3	1.3	1.3
ZNDTP (2) %w	-	-	-	-	-	-	-	-	-	-	-
Zinc naphthenate %w ** ***	K 0.5 0.3	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 2.0 1.2	K 2.7 1.6	K 2.7 1.6	L 1.6 2.7	M 1.6 2.7
ZNDTC %w	-	-	-	1	-	-	-	-	-	-	-
Antioxidant %w type	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	0.5 X	-	0.5 Y	0.6 Z	0.6 Z	0.6 Z
Thickener	C	C	D	D	E	E	D	C	F	F	F
Base Oil	Q	Q	R	R	S	S	T	U	V	V	V

In the following list all percentages are by weight:

A = 9.15% hydrogenated castor oil, 1.12% $LiOH.H_2O$ cooled at 6-7°C/min

B = 9% hydrogenated castor oil, 1.3% $LiOH.H_2O$ cooled at 1°C/min

C = 5% 4,4'-diphenylmethane diisocyanate, 10.8% stearylamine

D = 7.7% hydrogenated castor oil fatty acid, 2.2% boric acid, 2.6% $LiOH.H_2O$, 1.5% calcium alkyl salicylate, 1.5% calcium octoate

E = 7.8% hydrogenated castor oil, 1.1% $LiOH.H_2O$

F = 4.7% 4,4'-diphenylmethane diisocyanate, 3.6% octylamine, 1.4% dodecylamine

K = Manchem 8% zinc [60% zinc naphthenate; 40% mineral oil]

L = Valirex 8% zinc

M = Adchem 8% zinc

P = MVIN 170 (80%) HVI 170 (5%) HVI 105 (15%)

Q = HVI 160B (75%) HVI 650 (25%)

R = HVI 160B (100%)

S = HVI 160B (78%) MVIN (22%)

T = HVI 160B (67%) HVI 650 (33%)

U = HVI 160B (70%) polyalphaolefin (30%)

V = MVIN 170 (50%) polyalphaolefin (50%)

X = PAN (phenyl alpha naphthylamine)

Y = aromatic amine

Z = 0.4% aromatic amine; 0.2% hindered phenol

ZNDTP (1) = zinc di-4-methyl-2-pentyl dithiophosphate

ZNDTP (2) = zinc di-isobutyl dithiophosphate

ZNDTC = zinc diamyldithiocarbamate

* plus 1.5% triphenyl phosphorothionate

** actual amount of commercial product used

*** calculated amount of active ingredient, zinc naphthenate - i.e. as 13.3% zinc

Example 21

Measurement of friction coefficient

An oscillating SRV friction tester from Optimol Instruments was used for all the friction measurements, with a 10 mm ball on a flat lapped surface as test geometry. The test conditions were varied over a range of loads (200-500 Newtons) and temperatures (40°C to 100°C). An oscillation frequency of 50 Hertz and a stroke of 1.5 mm was used throughout. The friction coefficient was recorded after two hours of operation under fixed test conditions.

The friction coefficients of Examples 1 to 20 as measured on the SRV friction tester at 300 Newtons test load are set out in Table 2:

TABLE 2

Ex.	Friction coefficient 300 N test load at 100°C
1	0.046
2	0.054
3	0.048
4	0.073
5	0.068
6	0.073
7	0.070
8	0.049
9	0.068
10	0.050
11	0.068
12	0.048
13	0.070
14	0.053
15	0.048
16	0.075
17	0.046*
18	0.035*
19	0.068

TABLE 2 (continued)

Ex.	Friction coefficient 300 N test load at 100°C
20	0.055
21	0.058
22	0.053
23	0.065

* at 400N test load at 100°C

Example 22

In order to demonstrate the improved performance of greases containing the three components molybdenum disulphide, zinc dialkyldithiophosphate and zinc naphthenate, friction coefficients and wear scar diameters of greases of Examples 1, 14 and 15 have been compared with respective similar greases containing no zinc naphthenate. The results are shown in Tables 3, 4 and 5.

The friction and wear measurements were made using the oscillating SRV friction tester described in Example 21. Wear was assessed by measuring the diameter of the wear scar on the ball at the end of the two hour test using an optical graticule.

TABLE 3

Grease Composition	Friction coefficient 300 N test load at 100°C	Wear scar diameter (mm) 300N test load at 100°C
Comparative A	0.100	0.85
Example 1	0.046	0.51

Comparative A contains 0.5% PAN, 3% molybdenum disulphide, 1% zinc di-4-methyl-2-pentyl dithiophosphate and thickener A

TABLE 4

Grease Composition	Friction coefficient 300 N test load at 100°C	Wear scar diameter (mm) 300 N test load at 100°C
Comparative B	0.080	0.67
Example 14	0.053	0.59

Comparative B contains 0.5% PAN, 3% molybdenum disulphide, 1% zinc di-4-methyl-2-pentyl dithiophosphate and thickener C

TABLE 5

Grease Composition	Friction coefficient 300 N test load at 100°C	Wear scar diameter (mm) 300 N test load at 100°C
Comparative C	0.070	0.87
Example 15	0.048	0.56

Comparative C contains 0.5% PAN, 3% molybdenum disulphide, 1% zinc di-4-methyl-2-pentyl dithiophosphate and thickener D

It can be seen that in all three cases the addition of the zinc naphthenate to the molybdenum disulphide plus zinc dialkyldithiophosphate results in a substantial reduction in friction coefficient and wear scar diameter.

Example 23

In order to demonstrate the improved performance of greases of the present invention as compared to previously known greases, the friction coefficients of commercially available lithium soap-based, molybdenum disulphide-containing greases were measured by the procedure described in Example 21. The results are set out in Table 6, which for ease of comparison also contains the friction coefficient of Example 1 of the present invention:

TABLE 6

Grease Composition	Friction coefficient 300N test load at 100°C
Example 1	0.046
Comp. D	0.113
Comp. E	0.118
Comp. F	0.105

Comp. D = Molykote VN 2461C
Comp. E = "Retinax" AM (trade mark)
Comp. F = "Glitine 245 MO" (trade mark)

It can be seen quite clearly that the friction coefficient of Example 1 is substantially lower than that of each of the commercially available greases.

As indicated above, the grease formulations of the present invention can include one or more additives which impart certain desirable characteristics to formulations. In particular, further extreme-pressure/antiwear agents can be included, such as borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds, amine phosphates, sulphurised esters and triphenyl phosphorothionate.

CLAIMS

1. The use of molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates, as a friction reducing additive combination in a lubricating composition comprising a base oil of mineral and/or synthetic origin.

2. Use according to claim 1, wherein the metal in the metal dithiophosphates and/or metal dithiocarbamates is selected from zinc, molybdenum, tin, manganese, tungsten and bismuth.

3. Use according to claim 2, wherein the one or more metal dithiophosphates is/are selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates, and the one or more metal dithiocarbamates is/are selected from zinc dialkyl-, diaryl- or alkylaryl-dithiocarbamates, in which dithiophosphates and/or dithiocarbamates any alkyl moiety is straight chain or branched and contains 1 to 12 carbon atoms.

4. Use of the friction reducing additive combination in a lubricating grease which comprises a base oil of mineral and/or synthetic origin and a thickener.

5. Use according to claim 4, wherein the molybdenum disulphide is present in the amount of from 0.5 to 10% by weight, and/or the zinc naphthenate is present in the amount of from 0.05 to 12% by weight, calculated as neat zinc naphthenate, or the one or more metal dithiophosphates is/are present in the total amount of from 0.15 to 10% by weight, all proportions being based on the total weight of the lubricating grease

6. Use according to claim 4 or claim 5, wherein the thickener comprises a urea compound, preferably a polyurea compound, a simple lithium soap or a complex lithium soap.

7. A lubricating composition comprising a base oil of mineral and/or synthetic origin in combination with molybdenum disulphide, zinc naphthenate and one or more metal dithiophosphates, and optionally one or more metal dithiocarbamates, in which the ratio of the amount of molybdenum disulphide to the amount of metal dithiophosphate is in the range of from 1:0.15 to 1:1 and the ratio of the amount of metal dithiophosphate to the amount of zinc naphthenate is in the range of from 1:0.2 to 1:3.0 and the ratio of the amount of molybdenum disulphide to the amount of zinc naphthenate is in the range of from 1:0.1 to 1:1.2, in which the zinc naphthenate is or is calculated as neat zinc naphthenate.

8. A lubricating grease comprising a thickener in combination with a lubricating composition according to claim 7.

9. A method of lubricating a constant velocity joint comprising packing it with a lubricating grease according to claim 8.

10. A constant velocity joint packed with a lubricating grease according to claim 8.