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(54) A MIXED COMPLEX-BASED GREASE COMPOSITION AND METHOD FOR PREPARATION THEREOF

(57) The present invention relates to a mixed complex soap based grease composition comprising a lubricating base oil; a saponifiable material; a metal oxide; an alkali/alkaline metal hydroxide; and a complexing acid. The present invention also discloses a single-step, open kettle, energy-efficient process which gives smooth textured zinc-alkali/alkaline earth metal mixed complex grease composition with relatively low thickener content while still maintaining desired consistency. The zinc-alkali/alkaline earth metal mixed complex grease composition is tailor made to have dropping point in a range of 180 °C to 300 °C comparable to lithium and lithium complex grease composition, have inherent oxidation stability, extreme pressure, anti-wear properties, and water resistance properties. The zinc-alkali/alkaline earth metal mixed complex grease composition shows excellent additive response good mechanical stability, low temperature properties, pumpability, and corrosion resistance.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a mixed complex soap based grease composition. Specifically, the present invention relates to a zinc-alkali/alkaline earth metal mixed complex grease composition. More specifically, the present invention relates to a Zinc-Na/Li/Ca mixed complex soap based grease composition having inherent oxidation stability, extreme pressure, and anti-wear and water resistance properties. The present invention also discloses a single-step, open kettle, energy-efficient process for preparation of a zinc-alkali/alkaline earth metal mixed complex soap based grease composition which gives smooth textured grease composition with relatively low thickener content while maintaining desired consistency.

BACKGROUND OF THE INVENTION

[0002] Zinc (Zn) complex greases having dropping points comparable to lithium greases and tailor-made dropping points of 180 to 300 °C have been disclosed in US patent 11236285, European patent EP3845622A1, Indian Application no. 202021000297 and Indonesia Patent Application no. P00 2020 10687. These prior-art documents also disclose a process of manufacturing zinc complex greases through reaction of fatty acids and complexing agent with zinc oxide in lubricating oils. US patent 11236285 discloses pure zinc complex greases which require around 34 wt% thickener content to make NLGI 2 grade greases and need a high amount of metal oxide during processing. High thickener content makes zinc complex greases relatively dense and costlier, and this may cause hindrances in applications and production. In view of this, greases with lower thickener content and improved characteristics are desired to make these compositions more viable.

[0003] US patent 2457582 discloses the compositions with sodium tallow soap having zinc stearate as a minor component. Dropping points are in the range of 130 to 176 °C and no complexing agents are used. The ratio of sodium and zinc varies from 5:1 to 1:1 in compositions disclosed under this invention. US patent 2445936 discloses use of 1-3% Zn 12-Hydroxystearate to improve the water resistance of sodium and lithium greases. British patent 1039753 describes a method of preparation of lubricating gel where zinc oxide fine particles having improved surface area coated with organic carboxylic acids resulted in improved grease with excellent water resistance and excellent stability at high temperatures.

[0004] However, prior arts disclose several mixed soap based grease compositions, but zinc based mixed complex soap based grease composition is not available. In the reported prior-art documents as discussed above, zinc complex grease composition made with 100% zinc complex soap that can be used at high temperatures are disclosed and these grease compositions have relatively high thickener content which makes them relatively dense and costly.

[0005] Therefore, there is a need for economical grease composition with tailor made dropping point and high performance characteristics that can work in high temperature ranges and a method of preparation of such grease composition.

OBJECTIVES OF THE PRESENT INVENTION

[0006] It is a primary objective of the present invention to provide a mixed complex soap based grease composition.

[0007] It is another objective of the present invention to provide a mixed complex soap based grease composition with dropping points 180 to 300 °C comparable to lithium base and lithium complex grease composition having inherent oxidation stability, extreme pressure, anti-wear properties, and water resistance properties.

[0008] It is another objective of the present invention to provide a mixed complex soap based grease composition with excellent additive response, good mechanical stability, low temperature properties, pump ability, and corrosion resistance.

[0009] It is further objective of the present invention to provide a single-step, open kettle, energy-efficient process which gives smooth textured mixed complex soap based grease composition with relatively low thickener content while still maintaining desired consistency.

SUMMARY OF THE INVENTION

[0010] This summary is provided to introduce a selection of concepts, in a simplified format, that are further described in the detailed description of the invention.

[0011] The present invention provides a lubricating zinc-alkali/alkaline earth metal mixed complex grease composition, comprising:

i) a base oil;

ii) a saponifiable material;
iii) zinc oxide or zinc hydroxide;
iv) an oxide or hydroxide of an alkali or alkaline earth metal;
v) a complexing acid; and
vi) optionally, a performance additive.

[0012] The present invention also provides an open kettle single step process for preparing zinc-alkali/alkaline earth metal mixed complex grease composition, the process comprising:

a) mixing a saponifiable material to a base oil to form a mixture;
b) adding a complexing acid, a zinc oxide and an aqueous solution of oxide or hydroxide of an alkali or alkaline earth metal to the mixture obtained in step a);
c) heating and dehydrating the mixture obtained in step b) with continuous stirring to obtain a solid mass;
d) adding base oil to the solid mass obtained in step c) to form a mixture;
e) cooling the mixture obtained in step d) and optionally adding a performance additive; and
f) homogenizing the mixture obtained in step e) to obtain the mixed complex grease composition.

ABBREVIATIONS

[0013]

ZDDP: Zinc dialkyldithiophosphates
12-HSA: 12-hydroxy stearic acid
PAO: polyalphaolefins
PAG: polyalkyl glycol

DETAILED DESCRIPTION OF THE INVENTION

[0014] The NLGI grade expresses a measure of the relative hardness of a grease used for lubrication, as specified by the standard classification of lubricating grease. The present invention includes all the NLGI consistency grades harder and softer than NLGI 2 and 3 grades which can be made by varying the thickener content.
[0015] The wt% used in the description is based on total weight of the grease composition.
[0016] The present invention discloses a zinc-alkali/alkaline earth metal mixed complex grease composition preferably Zn-Na mixed complex grease composition and a single-step, open kettle energy efficient process with relatively low thickener content which gives smooth textured grease composition while maintaining desired consistency. Also, in the present invention, the poor thickening ability of zinc soap is compensated by the good thickening ability of sodium soap while the hydrophilic nature of sodium soap is compensated by hydrophobic zinc soap to result in water resistance complex grease.
[0017] The present invention provides a zinc-alkali/alkaline earth metal mixed complex grease composition, comprising:

i) a base oil;
ii) a saponifiable material;
iii) zinc oxide or zinc hydroxide;
iv) an oxide or hydroxide of an alkali or alkaline earth metal;
v) a complexing acid; and
vi) optionally, a performance additive.

[0018] The present invention also provides an open kettle single step process for preparing zinc-alkali/alkaline earth metal mixed complex grease composition, the process comprising:

a) mixing a saponifiable material to a base oil to form a mixture;
b) adding a complexing acid, a zinc oxide and an aqueous solution of oxide or hydroxide of an alkali or alkaline earth metal to the mixture obtained in step a);
c) heating and dehydrating the mixture obtained in step b) with continuous stirring to obtain a solid mass;
d) adding base oil to the solid mass obtained in step c) to form a mixture;
e) cooling the mixture obtained in step d) and optionally adding a performance additive; and
f) homogenizing the mixture obtained in step e) to obtain the mixed complex grease composition.

[0019] According to an embodiment of the present invention, the base oil has viscosity in a range of ISO VG 2 to 3200 or a mixture thereof.

[0020] According to an embodiment of the present invention, the base oil is selected from mineral base oils of API groups I-III, synthetic base oils of API group IV, ester base oil, paraffinic base oil, naphthenic base oil, and re-refined base oil; the synthetic base oil is selected from polyalphaolefins (PAO), polyalkyl glycol (PAG), polyol esters, diesters and alkylated aromatics.

[0021] According to another embodiment of the present invention, the base oil is present in a range of 65.0-90.0 wt%.

[0022] According to another embodiment of the present invention, the saponifiable material is present in a range of 8.0-18.0 wt%.

[0023] According to another embodiment of the present invention, the oxide and hydroxide of an alkali and alkaline earth metal is present in a range of 0.20-3.0 wt%.

[0024] According to an embodiment of the present invention, the complexing acid is present in a range of 1.0-5.0 wt%.

[0025] According to an embodiment of the present invention, the performance additive is present in a range of 0.01-3 wt%.

[0026] According to an embodiment of the present invention, the saponifiable material is a fatty acid selected from 12-hydroxy stearic acid, stearic acid, oleic acid or a mixture thereof.

[0027] According to an embodiment of the present invention, the oxide or hydroxide of an alkali or alkaline earth metal is selected from sodium hydroxide, calcium oxide, calcium hydroxide, hydrated lime, lithium hydroxide, or lithium hydroxide monohydrate.

[0028] According to an embodiment of the present invention, the complexing acid is a dicarboxylic acid having C3 to C10 selected from malonic acid(C3), succinic acid(C4), glutaric acid(C5), adipic acid(C6), pimelic acid(C7), suberic acid(C8), azelaic acid(C9) or sebacic acid(C10).

[0029] According to an embodiment of the present invention, the mixing of step a) is performed at temperature in a range of 25 to 80 °C.

[0030] According to another embodiment of the present invention, the heating is performed in three consecutive steps in a sequence of specified steps, the steps comprising:

i) heating at temperature in a range of 90-100 °C for 1 hour;
ii) heating at temperature in a range of 130-140 °C for next 1 hour; and
iii) heating at temperature in a range of 165-175 °C for another next 0.5 to 1.0 hours

[0031] According to another embodiment of the present invention, the performance additive is selected from rust and corrosion inhibitor, metal deactivator, metal passivator, antioxidant, pressure additive, polymer, tackifier, dye, chemical marker, fragrance imparter, anti-wear additive or a combination thereof.

[0032] According to an embodiment of the present invention, the performance additive is a multifunctional performance additive selected from zinc dialkyldithiophosphates (ZDDP).

[0033] Disclosed grease composition is found to have inherent oxidation stability, extreme pressure & anti wear properties and water resistance properties along with excellent additive response, good mechanical stability, low temperature properties, pumpability, and corrosion resistance. The grease composition having tailor made dropping points from 180 °C to 300 °C, made through in-situ formation of mixed complex soap by reacting with a hydroxy fatty acid and a dicarboxylic acid with zinc oxide and sodium hydroxide in single-step.

[0034] In-situ incorporation of sodium in zinc complex soap complex resulted in grease composition with superior properties such high dropping point, excellent water resistance, excellent shear stability, inherent extreme pressure characteristics, and inherent anti-wear performance. The hydrophobic nature of zinc complex soap helped in compensating hydrophilic nature of sodium soap and this resulted in water resistant grease composition.

[0035] According to another embodiment of the present invention, Zn-Li and Zn-Ca mixed soap complex grease composition prepared with reduced thickener content, are found to have comparatively low dropping points.

[0036] According to the present invention, Zn-Na mixed complex grease composition were made with one or a mixture of mono carboxylic fatty acids having C12 to C20 carbon, preferably C16-C18 along with a complexing acid which is a dicarboxylic acid having C2-C12 carbon, preferably C6 to C10 chain length. The mono carboxylic fatty acid may preferably have hydroxyl functionality such as 12-hydroxy stearic acid (12-HSA). The resultant Zn-Na mixed complex grease was found to show a high dropping point and good water resistance.

[0037] According to a preferred embodiment of the present invention, Zn-Na mixed complex grease comprises: 70.0-90.0 wt% of a base oil; 5.0-20.0 wt% of a saponifiable material; 0.20-5.0 wt% of zinc oxide, 0.20-3.0 wt% sodium hydroxide and 1.0-5.0 wt% one or more of a complexing acid.

[0038] According to the embodiment of the invention, Zn-Na mixed complex grease having dropping points similar to simple lithium base /lithium complex grease composition was made with a process involving maximum temperatures of 165-175 °C in an open kettle thus saving time and expense associated with higher temperature reported in prior art processing methods of simple lithium / lithium complex grease composition.

[0039] According to one preferred embodiment of this invention, at least one saponifiable material, one complexing acid, zinc oxide, and sodium hydroxide have been employed. Softer or harder grades of grease are made by varying the metal zinc oxide/sodium hydroxide ratios and saponifiable material and complexing acids ratios. Tailor made dropping points is achieved by varying complexing acids and their ratios and metal zinc oxide/sodium hydroxide ratios.

[0040] According to the present invention, poor thickening ability of zinc complex soap is compensated by the good thickening ability of sodium soap while the poor water resistance behavior of sodium soap is compensated by water repellent nature of zinc complex soap leading to water resistance. Zn-Na mixed complex grease composition requires low thickener content in comparison to pure zinc complex grease for desired consistency. As per the invention, complexing acid not only boost the dropping points but also enhance the thickening ability of complex thickeners and resulting in a better structure of grease.

[0041] According to the present invention, the saponifiable material refers to fatty acids, hydroxysubstituted fatty acids, their esters, and their mixtures. Among saponifiable materials, 12-hydroxystearic acid and stearic acid are preferred and 12-hydroxystearic acid is most preferred. The amount of saponifiable material in the embodiment of this invention vary between 8 wt% and 18 wt%. Preferably, the amount of saponifiable material in NLGI grade 2 grease is between 10%wt to 16%wt and most preferably between 12 wt% to 14 wt%.

[0042] According to an embodiment of the present invention, the saponifiable material is reacted with 1.0-5.0 wt% zinc oxide and 0.20-3.0 wt% an oxide or hydroxide of an alkali or alkaline earth metal or their mixtures to make grease composition. Among the oxide and hydroxide of an alkali and alkaline earth metal, sodium hydroxide is more preferred. All the metal oxides/hydroxides fatty acids, and complexing acids are commercially available and of LR grade.

[0043] According to one embodiment of the invention, Zn-Na mixed complex grease composition having dropping points similar to lithium complex grease composition are produced by incorporating one or more complexing acid and these are added either prior or along with the addition of alkali/alkaline hydroxide. The total amount of complexing acid is between 1.0 wt% to 5.0 wt%, preferably 2.0 wt% to 4.0 wt% and most preferably 2.5 wt% to 3.5 wt%. The suitable dicarboxylic acid is C3 to C10 dicarboxylic acid selected from malonic acid(C3), succinic acid(C4), glutaric acid(C5), adipic acid(C6), pimelic acid(C7), suberic acid(C8), azelaic acid(C9) and sebacic acid(C10).

[0044] According to an embodiment of the present invention, water is used to dissolve sodium hydroxide pellets, which also helps in increasing the reaction rate, but the use of excess water more than three times of sodium hydroxide produced excessive frothing.

[0045] Any commonly used oil, such as petroleum based naphthenic and paraffinic (API Group I-III) are well known in prior arts and can be used according to the present invention. Synthetic base oils such as polyalphaolefins (PAO), polyalkylene gycol (PAG), and alkylated aromatics are also used for making grease composition. In some cases, base oils having less solvency adversely affect the thickening efficiency leading to softer grease composition and this is easily understood by those having ordinary skills in grease making. In some cases, oils such as diesters and polyol esters are added after saponification to avoid interaction with alkaline/alkali hydroxides.

[0046] According to an embodiment of the present invention, the total amount of base oil added will be typically between 65.0 to 90.0 wt% and most probably 80.0 to 85.0 wt% for NLGI grade 2 grease.

[0047] The compositions according to the invention are preferably made according to the method described herein. This method comprises the following steps: (1) adding and mixing in a suitable open grease kettle- the first portion of base oil, hydroxy fatty acids, and complexing acids at a temperature that ranges between ambient temperature and about 80 °C (2) addition of zinc oxide and sodium hydroxide (preferably dissolved in water) with continuous mixing (3) continue to mixing while gradually heating the mass to 90-100 °C in one hour (4) gradually raise the mass temperature to 130-140 °C and maintained at this temperature for around one hour (5) gradually raise temperature to 165-175 °C in one hour and dehydrate for 0.5-1.0 hour (6) addition of the second portion of base oil with continuous stirring and cooling to below 90 °C (7) adding the performance additives below 90 °C, if desired; (8) milling/homogenisation the final grease to obtain the Zn-Na grease.

[0048] According to the present invention, certain steps of the process are not critical for obtaining the grease. The temperature at which base oil, hydroxy fatty acid, and complexing acid are added is not critical, but it is preferred that they may be added below 80 °C. The addition sequence of base oil, hydroxy fatty acid, dicarboxylic acid, zinc oxide, and sodium hydroxide is also not critical with respect to each other. In grease composition processing, the single-step open kettle process is preferred over 2 steps process where complexing acid or zinc oxide or sodium hydroxide can be added in the second stage.

[0049] After saponification, water is removed from the grease by heating gradually and maintaining at a certain temperature. Generally, the heating temperature should be between 150 to 180 °C, most preferably between 165 to 175 °C. Further heating to above 180 °C does not provide any additional advantage and developed more brown color to the product. A vacuum is applied along with heating for quick removal of water. Water facilitates the dissolution of sodium hydroxide and helps in reaction initiation. However, grease processing is possible without water, therefore water is not critical for processing.

EXAMPLES:

[0050] The examples are provided for the purpose of illustrating the invention only and are not intended to limit the scope of the invention in any way.

[0051] The development of zinc-mixed soap complex thickened grease composition is based on our earlier work on high temperature zinc complex grease composition. To compensate poor thickening ability of zinc soaps, soaps of alkali and alkaline earth metals such as lithium, sodium, potassium, calcium, and magnesium are made in-situ by reacting fatty acids and dicarboxylic acid with their respective oxides/hydroxides. The general manufacturing procedure for mixed zinc soap based complex grease composition is as follows: in a suitable open grease kettle- adding and mixing the first potion of paraffinic base oil (Group I, ISO VG 150), fatty acids, and complexing acids at a temperature that ranges between ambient temperature and about 80 °C. Addition of zinc oxide and alkali/alkaline oxide/hydroxide and water with continuous mixing and heating the mass to 90-100 °C in one hour. Further raising the mass temperature to 130-140°C and maintaining for one hour. After that, the mass temperature was gradually raised to 165-175 °C in one hour time for dehydration under vacuum followed by addition of second portion of base oil with continuous mixing. The mass was cooled to 90 °C with continuous stirring, followed by milling to obtain the final product. If required, additives can be added prior to milling.

[0052] Prior art example grease was made by reaction of 25 wt% of 12-HSA and 4 wt% of sebacic acid with 5 wt% of zinc oxide. As shown in Table 1, Example 1-5 grease composition s were made using the same equipment, and manufacturing process as the prior art example, except following changes. In Example, 1-5 grease composition, saponifiable material reduced from 25 to 15 wt%, 0.5 wt% of different alkali/alkaline oxide/hydroxide were used and a stoichiometric amount of zinc oxide was reduced. Example 1 grease was processed in a suitable open grease kettle, adding and mixing 50% of total paraffinic base oil (Group I, ISO VG 150), fatty acids, and complexing acids at a temperature that ranges between ambient temperature and about 80 °C. Addition of zinc oxide and sodium hydroxide (aqueous solution in the equal proportion of water) with continuous mixing, continue gradual heating the mass to 90-100 °C in one hour. The mass temperature was further raised to 130-140 °C and maintained for one hour. After that, the mass temperature gradually raised to 165-175 °C in one hour time. The resultant mass was completely dehydrated under vacuum for 0.5 to 1.0 hours and the second portion of base oil was added with continuous mixing. The mass was cooled to 90 °C with continuous stirring, followed by milling to obtain the final product. Compositions and Test results of Example 1-5 grease composition along with prior art example are given in Table-1.

Table-1

Characteristics	Test Method	Prior art example	Example 1	Example 2	Example 3	Example 4	Example 5
12-HSA, wt%	-	25.00	15.00	15.00	15.00	15.00	15.00
Sebasic acid, wt%	-	4.00	3.00	3.00	3.00	3.00	3.00
Zinc oxide, wt%		5.00	2.73	2.75	2.76	2.89	2.88
Sodium hydroxide, wt%	-	0.00	0.50	0.00	0.00	0.00	0.00
Lithium hydroxide monohydrate, wt%	-	0.00	0.00	0.50	0.00	0.00	0.00
Hydrated lime, wt%	-	0.00	0.00	0.00	0.50	0.00	0.00
Magnesium hydroxide, wt%	-	0.00	0.00	0.00	0.00	0.50	0.00
Potassium hydroxide, wt%	-	0.00	0.00	0.00	0.00	0.00	0.50
Group I paraffinic base oil (95 cSt at 40 °C), wt%	-	39.60	47.26	47.25	47.24	47.17	47.17
Group I paraffinic base oil (425 cSt at 40 °C), wt%		26.40	31.51	31.50	31.49	31.44	31.45
Zn: alkali/alkaline metal		--	7.63: 1	26.75: 1	6.20: 1	11.14: 1	6.62: 1

(continued)

Characteristics	-	Prior art example	Example 1	Example 2	Example 3	Example 4	Example 5
Thickener, wt %	-	34.00	21.23	21.25	21.26	21.39	21.38
Unworked penetration	ASTM D217	273	291	333	279	333	373
Worked penetration	ASTM D217	272	295	335	288	395	377
Dropping point, °C	ASTM D2265	262	263	225	182	125	204
Water washout at 80 °C, percent loss by mass	ASTM D 1264	0.9	1.1	4.9	2.3	-	-
Roll stability, 16 hrs, 25 °C, percentage of change in penetration	ASTM D1831 (modified)	13.6	17.2	26.6	18.7	-	-
Wet Roll stability, 2 hrs, 25 °C, percentage of change in penetration	ASTM D8022	11.7	14.6	24.1	11.1	-	-

[0053] Example 1 having mixed zinc complex grease with a minor quantity of sodium soap resulted in NLGI grade 2 grease with the highest dropping point among all used alkali/alkaline oxides/hydroxides. Hence, the poor thickening ability of zinc soaps has been compensated by sodium soaps and it also leads to more effective complexing as evidenced by a higher dropping point. Similarly, As Example 2 mixed zinc complex grease with lithium soap in a minor portion having processed with 0.50 wt% of lithium hydroxide monohydrate resulted in grease in NLGI grade 1 with dropping point of 225 °C indicating lithium soap also gives a certain improvement in thickening ability or improved yield. Example 3 mixed zinc complex grease made with calcium soap as a minor portion was also found to be in NLGI grade 1-2 consistency, but the dropping point was found to be around 190 °C only. Example 4 made with magnesium soap as a minor portion was found to be softer with poor structure and a lower dropping point around 125 °C. Example 5 with potassium soap as a minor portion was found to be softer with poor grease structure and a lower dropping point below 180 °C.

[0054] Further, Examples 7 to 10 were processed using the same equipment and manufacturing process as mentioned in Example 1 except lithium hydroxide monohydrate and hydrated lime were used at different treat levels to get Zn-Li and Zn-Ca mixed complex grease composition having minor lithium soap and calcium soap respectively. As shown in Table 2, Example 6 having composition similar to our prior art with pure zinc complex grease with lower thickener content resulted in softer grease of NLGI 0 with a dropping point above 260 °C and Example 7 was processed with 0.25 wt% of lithium hydroxide monohydrate, resulted in grease composition with worked penetration of 331 and dropping point of 228 °C indicating Zn-Li complex grease having better consistency than pure zinc complex grease but dropping point is slightly lower. Example 8 where 1.00 wt% of lithium hydroxide monohydrate, resulted in softer grease indicating with incorporation of lithium soap in zinc complex grease resulting in softer consistency and with dropping point around 180 °C.

Table-2

Characteristics	Test Method	Example 6	Example 7	Example 8	Example 9	Example 10
12-HSA, wt%	-	15.00	15.00	15.00	15.00	15.00
Sebasic acid, wt%	-	3.00	3.00	3.00	3.00	3.00
Zinc oxide, wt%		3.24	3.00	2.27	3.00	2.29
Lithium hydroxide. monohydrate, wt%	-	0.00	0.25	1.00	0.00	0.00
Hydrated lime, wt%		0.00	0.00	0.00	0.25	1.00

(continued)

Characteristics	Test Method	Example 6	Example 7	Example 8	Example 9	Example 10
Group I paraffinic base oil (95 cSt at 40 °C), wt%	-	47.26	47.25	47.24	47.25	47.23
Group I paraffinic base oil (425 cSt at 40 °C), wt%		31.50	31.50	31.49	31.50	31.48
Characteristics	**-**	**Example 6**	**Example 7**	**Example 8**	**Example 9**	**Example 10**
Thickener, % wt	-	21.24	21.25	21.27	21.25	21.29
Zn: alkali/alkaline		--	58.55: 1	11.09: 1	13.47: 1	2.57: 1
Unworked penetration	ASTM D217	351	329	361	342	213
Worked penetration	ASTM D217	363	331	373	350	231
Dropping point, °C	ASTM D2265	261	228	181	181	180

[0055] As Example 3 mixed zinc complex grease with calcium soap in minor portion having processed with 0.50 wt% of hydrated lime resulted in grease NLGI grade 2 with dropping point around 180 °C. As shown in Table 2 Example 9 gave softer grease and dropping point 181 °C, further Example 10 resulted in grease composition of NLGI grade 3 with dropping points around 180 °C Hence, increase of calcium soap content in Zn-Ca mixed complex grease only enhances thickening but dropping points are found to be around 180 °C.

[0056] As mentioned in Table 1, the Zn-Na mixed combination gave the best outcome compared to other mixed zinc-alkali/alkaline metals soap combinations. Further optimization of the zinc to sodium ratio was done to optimize the thickener content for obtaining grease with desired consistency and properties. As shown in Table 3, Examples 11 to 15 were processed using same ingredients, equipments and manufacturing process similar to Example 1 grease except, sodium hydroxide content was increased, and zinc oxide content was reduced stoichiometrically. Compositions and test data of Examples 11 to 15 grease composition are given in Table 3.

Table-3

Characteristics	Test Method	Example 11	Example 12	Example 13	Example 14	Example 15
12-HSA, wt%	-	15.00	15.00	15.00	15.00	15.00
Sebacic acid, wt%	-	3.00	3.00	3.00	3.00	3.00
Zinc oxide, wt%		2.98	2.48	2.22	1.17	0.21
Sodium hydroxide, wt%	-	0.25	0.75	1.00	2.00	3.00
Group I paraffinic base oil (95 cSt at 40 °C), wt%	-	47.26	47.26	47.27	47.30	47.25
Group I paraffinic base oil (425 cSt at 40 °C), wt%		31.51	31.51	31.51	31.53	31.54
Characteristics	**-**	**Example 11**	**Example 12**	**Example 13**	**Example 14**	**Example 15**
Thickener, % wt	-	21.24	21.23	21.22	21.17	21.23
Zn: Na		16.67: 1	4.61: 1	3.11: 1	0.82: 1	0.10:1.00
Unworked penetration	ASTM D217	297	271	261	191	211
Worked penetration	ASTM D217	291	279	266	193	207
Change in penetration after 10^5X double strokes	ASTM D217	+30	+24	+29	+37	+71

(continued)

Characteristics	-	Example 11	Example 12	Example 13	Example 14	Example 15
Dropping point, °C	ASTM D2265	265	271	267	259	251
Water washout at 80 °C, percent loss by mass	ASTM D1264	2.07	1.53	1.81	3.51	38.70
Roll stability, 16 hours, 25 °C, Change in penetration	ASTM D1831 (modifie d)	11.3	15.5	16.2	15.5	43.55
Wet Roll stability, 2 hours, 25 °C, Change in penetration	ASTM D8022	8.1	10.8	9.9	15.3	22.81

[0057] As shown in Table 3, the increase in sodium soap content resulted in better consistency of grease composition from Examples 11 to 15. No adverse effects on dropping points were observed with increase in sodium soap content as shown in Table-3. The introduction of sodium soap resulted in changes in water resistance behavior. However, water resistance behavior was found to be within limits as hydrophilic characteristics of soda soap have been compensated by water repellent characteristics of zinc soap. In Examples 14 grease where sodium content is more than zinc content that is 0.82: 1.00, water washout characteristics still maintained but increased comparatively. As shown in Table-3, the water resistance behavior of Zn-Na mixed complex grease composition is well maintained if zinc is major compared to sodium. In Example 15, further increase in sodium soap content resulted in better consistency of grease. Going towards more sodium soap compared to zinc soap affected the water washout behavior adversely. The water resistance behavior of Zn-Na mixed complex grease composition is well maintained if zinc is major compared to sodium. Further increase in sodium more than zinc effected water resistance properties where the dominant role of sodium soap in water solubility is evident.

[0058] To study the effects of complexing acid content on grease performance, Examples 16 to 21, were processed using the same equipment and manufacturing process as mentioned in Example 1, except sebacic acid content, was varied from 0.00 to 5.00 wt% carried out along with required amount of zinc oxide while using 13 wt% of 12-HSA and 1.00 wt% of sodium hydroxide. As shown in Table 4, Example 16 made with 0.00 wt% of sebacic acid, resulted softer grades with dropping point below 180 °C indicating complexing acid is required for thickening as well as increasing dropping point. Gradual increase in consistency and dropping points was observed with increase in complexing acid content as shown in Table-4. Hence complexing acids are not only increasing the dropping points but also help to boost the thickening efficiency of the Zn-Na mixed complex thickener system. Example 19, grease made with 3.00 wt% of complexing acid and having total thickener content of around 19 wt% and dropping point above 270 °C is more preferred composition.

Table-4

Characteristics	Test Method	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21
12-HSA, wt%	-	13.00	13.00	13.00	13.00	13.00	13.00
Sebasic acid, wt%	-	0.00	1.00	2.00	3.00	4.00	5.00
Zinc oxide, wt%		0.75	1.15	1.55	1.95	2.35	2.76
Sodium hydroxide, wt%	-	1.00	1.00	1.00	1.00	1.00	1.00
Group I paraffinic base oil (95 cSt at 40 °C), wt%	-	49.75	50.31	49.47	48.63	47.79	46.95
Group I paraffinic base oil (425 cSt at 40 °C), wt%		35.50	33.54	32.98	32.42	31.86	31.30

(continued)

Characteristics	-	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21
Thickener, wt%	-	14.75	16.15	17.55	18.95	20.35	21.76
Zn: Na		1.05: 1	1.60: 1	2.17: 1	2.73: 1	3.29: 1	3.85: 1
Worked penetration	ASTM D217	465	345	288	265	258	242
Dropping point, °C	ASTM D2265	155	211	261	277	288	301

[0059] To demonstrate the effect of different complexing acids other than sebacic acid(C10), Example 22 to 28 grease composition were processed using same equipment and manufacturing process as mentioned in Example 1. Different complexing acids ranging from C3 to C10 dicarboxylic acids such as malonic acid(C3), succinic acid(C4), glutaric acid(C5), adipic acid(C6), pimelic acid(C7), suberic acid(C8), azelaic acid(C9) and sebacic acid(C10) were used at 3.00 wt% to make Zn-Na mixed complex grease. As shown in Table-5, all the dicarboxylic acids resulted in Zn-Na mixed complex grease composition of NLGI grade 2 to 3 with dropping points in the range of 180 to 280 °C. Among different complexing acids, grease composition made with pimelic acid, suberic acid, azelaic acid and sebacic acid were found to have grain free texture along with dropping points of more than 260 °C as shown in Table-5. Use of sebasic acid is shown in example 19 in Table 4. Hence among different dicarboxylic acids, C8 to C10 dicarboxylic acids were found to be best suited for Zn-Na mixed complex grease composition.

Table-5

Characteristics	**Test Metho d**	**Example 22**	**Example 23**	**Example 24**	**Example 25**	**Example 26**	**Example 27**	**Example 28**
12-HSA, wt%	-	14.00	14.00	14.00	14.00	14.00	14.00	14.00
Dicarboxylic acid at 3.00 wt%	-	Malonic acid (C3)	Succinic acid(C4)	Glutaric acid (C5)	Adipic acid(C6)	Pimellic acid(C7)	Suberic acid(C8)	Azelaic acid(C9)
Zinc oxide, wt%		3.23	2.95	2.73	2.55	2.40	2.28	2.18
Sodium hydroxide, wt%	-	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Group I paraffinic base oil (95 cSt at 40 °C), wt%	-	47.26	47.43	47.56	47.67	47.76	47.83	47.89
Group I paraffinic base oil (425 cSt at 40 °C), wt%		31.51	31.62	31.71	31.78	31.84	31.89	31.93
Characteristics	**-**	**Example 22**	**Example 23**	**Example 24**	**Example 25**	**Example 26**	**Example 27**	**Example 28**
Thickener, wt%	-	21.23	20.95	20.73	20.55	20.40	20.28	20.18
Zn: Na		4.51: 1	4.12: 1	3.81: 1	3.56: 1	3.36: 1	3.19: 1	3.04: 1
Grease before milling		Grease with grainy material	Grease with grainy material	Grease with light grainy material	Smooth grease without grains	Smooth grease without grains	Smooth grease without grains	Smooth grease without grains
Worked penetration	ASTM D217	237	259	263	217	301	227	281
Dropping point, °C	ASTM D2265	188	181	232	263	272	279	268

[0060] Different commonly used mono, di, and tri basic organic acids such as acetic acid(mono basic), phthalic acid(di basic), terphthalic acid (di basic), oxalic acid(di basic), salicylic acid(mono basic), benzoic acid(monobasic), boric acid(tri basic), lactic acid(mono basic), citric acid(tri basic) and malic acid(di basic) were used in place of sebacic acid at same treat level of 3.00 wt% and processed as same in Example 1, all the resultant grease composition were found to have dropping points less than 200 °C indicating poor complexing.

[0061] As per one embodiment of inventions, different commonly available saponifiable materials 12-hydroxy stearic acid, stearic acid, hydrogenated castor oil, and mutton tallow were used for making Zn-Na mixed complex grease composition and using same equipment and manufacturing process as mentioned in Example 1. The best results were obtained with 12-HSA and stearic acid. Hydrogenated castor oil and mutton tallow resulted in softer grades with dropping points lower than that of with 12HSA. This may be due to the weak base nature of zinc oxide due to which it is unable to hydrolyze triglyceride esters to obtain free saponifiable acid to form soap. Hydrogenated castor oil or mutton tallow can be used in proportion to sodium hydroxide in the first step for ester hydrolysis followed by saponification. In the second stage, 12-HSA, complexing acids can be reacted with zinc oxide for grease making. 12-HSA and stearic acid are found to be more suitable to make Zn-Na mixed complex grease composition while 12-HSA is preferred.

[0062] Although the examples provided herein fall in NLGI grade 2 or 3, it should be further understood that the scope of this present invention includes all the NLGI consistency grades harder and softer than NLGI 2 and 3 grades. Those of ordinary skill in the art will appreciate upon reading this application, including examples contained herein, that modifications and alterations to composition and methodology for making similar compositions may be within the scope of the present invention.

[0063] To demonstrate the closed reactor process, a grease batch was made using raw materials and ingredients similar to Example-19 as per following process: In a closed reactor, 50 % of total base oil was charged to reactor followed by 12-hydroxystearic acid, dicarboxylic acid, zinc oxide and sodium hydroxide in equal amounts of water were added. The reactor was sealed, and the mass temperature was gradually raised to 110-115 °C and mass was maintained at this temperature for one hour under continuous stirring. The mass temperature was further raised to 130-140 °C and maintained for one hour. After that, the material was further heated in an hour time to 170-175 °C. Then, the reactor was de-pressurized with caution to avoid any soap leakage. After this, the mixture was maintained at 170-175 °C with continuous stirring for half an hour for complete dehydration under vacuum suction. Cut back was done with remaining base oil. The heating was stopped, and cold oil was circulating to speed up cooling. When mass was cooled to 90-95 °C, grease was milled through homogenizer to get a smooth homogenous product. All test data of close kettle batch grease was found similar to open kettle grease batch (Example-19) indicating that developed composition can be used though both open kettle as well as closed reactor processes. However, open kettle process is preferred as it is not required to have pressurized reactor and dehydration time is low.

[0064] A detailed description of the invention and claims were shown in Table 6. In Example-29 and 30, grease composition was processed using the same equipment and manufacturing process and similar composition as in Example 19 except addition of performance additives and base oil is adjusted to make the difference. Base oil viscosity was adjusted to VG 150 using mixtures of two Group I paraffinic base oils having viscosities of 400 cSt and 95 cSt at 40 °C. As per the invention, NLGI 2 & 3 grade Zn-Na mixed complex grease can be formed with combination of 12-hydroxy stearic acid (13.00 wt%), sebacic acid (3.00 wt%), zinc oxide (2.00 wt%) and sodium hydroxide (1.00 wt%). The resultant grease was found to have dropped point above 260 °C which is in the range of other soap complex grease composition. Mechanical stability was also found to be good, +30 units after 100000 double strokes. Example-19 is a Zn-Na mixed complex base grease without the use of any performance additives. Example-29 and 30, demonstrate that grease composition made as per the present invention are useful for extreme pressure industrial applications. As shown in Table 6, an excellent additive response was observed which gave better extreme pressure and anti-wear properties compared to Example 19. In Example 29 multifunctional grease additive package such as LZ 5235, Hitec 552, etc. gave excellent boosting in weld load from 180 Kg to above 400 Kg by IP239. As shown in Example 30, synergy of zinc-based additives resulted in boost in extreme pressure and anti-wear properties of grease composition. Zinc dialkyldithiophosphates (ZDDP) showed excellent synergy to boost weld load from 180 Kg to above 500 Kg as shown in Table-6. ZDDP additives used are from different sources such as Elco 105, LZ677 and LZ1395 gave similar results. In Examples 29 and 30 apart from excellent results in extreme pressure and anti-wear, other grease properties such as oxidation stability, corrosion resistance also found to be excellent which indicating synergy of the Zn-Na mixed complex grease with zinc containing additives.

Table-6

Components	Example 19	Example 29	Example 30
12-Hydroxysteric acid, wt%	13.00	13.00	13.00
Sebacic acid, wt%	3.00	3.00	3.00

(continued)

Components		Example 19	Example 29	Example 30
Zinc oxide, wt%		2.00	2.00	2.00
Sodium hydroxide, wt%		1.00	1.00	1.00
Group I paraffinic base oil (95 cSt at 40 °C), wt%		48.40	46.00	46.60
Group I paraffinic base oil (425 cSt at 40 °C), wt%		32.60	32.00	32.40
EP additive package		0.00	3.00	0.00
ZDDP		0.00	0.00	2.00
Total		100.00	100.00	100.00
Test	Method	**Example 19**	**Example 29**	**Example 30**
Appearance	Visual	Smooth homogeneous	Smooth homogeneous	Smooth homogeneous
Color	Visual	Brown	Brown	Brown
Unworked penetration	ASTM D217	265	281	288
Penetration worked, 0.1 mm	ASTM D217	269	283	287
Change in penetration after 10^5X double strokes	ASTM D217	+30	+29	+27
Dropping Point	ASTM D2265	272	279	281
Heat Stability at 100 °C for 30 hrs, Oil separation	ASTM D6184	1.85	2.09	2.91
Roll stability, 16 hours, 25 °C, Percentage change in penetration	ASTM D1831 (modified)	+18.9	+17.7	+18.6
Roll stability in presence of 10% water, 2 hours, 25 °C, Change in penetration	ASTM D8022	+11.1	+13.8	+12.7
Cu Corrosion at 100 °C, 24 hours	ASTM D4048	1a	1a	1a
Water washout at 80 °C, percent loss by mass	ASTM D1264	2.1	1.4	1.9
Water Spray off, percent loss by mass	ASTM D4049	42.80	45.2	47.65
Corrosion preventive test rating, max	ASTM D1743	Pass	Pass	Pass
IP dynamic antirust test, distilled water, rating	IP220, EMCOR	0,0	0,0	1,0
Low temperature torque test at -20 °C Starting torque, gm.cm Running torque, gm.cm	IP 186	 2000 750	 1875 750	 1625 500
Elastomer Compatibility, Vol Change, percent Hardness change, durometer-A points	ASTM D4289	1.7 -1.30	1.11 -1.40	1.2 -0.90

(continued)

Test	Method	Example 19	Example 29	Example 30
Leakage and deposit forming tendencies (Wheel bearing test), Leakage by mass, g	ASTM D1263	0.9	1.5	1.6
Oxidation stability (100 h) drop in pressure, kg/cm^2	ASTM D942	0.30	0.20	0.15
Freedom from deleterious particles, permitted number of scratches	ASTM D 1404	5	4	5
Four ball weld load, Kg	IP 239	180	560	620
Four ball wear scar dia, mm	ASTM D2266	0.50	0.45	0.45

[0065] The present invention has the following advantage over the prior arts:

- In the present invention, zinc based mixed soap complex grease composition with alkali/alkaline earth metal salts preferably sodium salts as minor complexing soap are disclosed and these grease compositions have relatively low thickener content in combination of superior properties such as high dropping point, inherent oxidation stability, extreme pressure, anti-wear, and water resistance.
- The Zn-Na complex soap based grease composition of the present invention have tailor made dropping points from 180 to 300 °C.
- The Zn-Na complex soap-based grease composition of the present invention is prepared in an open kettle using time & energy saving processes through in-situ formation of zinc-sodium mixed metal complex soap based by reacting with fatty acids and complexing acid with corresponding metal oxides and hydroxides in a single step.
- In the present invention, the poor thickening ability of zinc soap is compensated by the good thickening ability of sodium soap while the hydrophilic nature of sodium soap is compensated by hydrophobic water repelling zinc soap result in water resistance complex grease.

Claims

1. A zinc-alkali/alkaline earth metal mixed complex grease composition, comprising:

i) a base oil;
ii) a saponifiable material;
iii) zinc oxide or zinc hydroxide;
iv) an oxide or hydroxide of an alkali or alkaline earth metal;
v) a complexing acid; and
vi) optionally, a performance additive.

2. The grease composition as claimed in claim 1, wherein the base oil is having viscosity in a range of ISO VG 2 to 3200 or a mixture thereof; wherein the base oil is selected from mineral base oils of API groups I-III, synthetic base oils of API group IV, ester base oil, paraffinic base oil, naphthenic base oil, and re-refined base oil; wherein the synthetic base oil is selected from polyalphaolefins (PAO), polyalkyl glycol (PAG), polyol esters, diesters and alkylated aromatics.

3. The grease composition as claimed in claim 1 or 2, wherein the base oil is present in a range of 65.0-90.0 wt%; the saponifiable material is present in a range of 8.0-18.0 wt%; the oxide and hydroxide of an alkali and alkaline earth metal is present in a range of 0.20-3.0 wt%; the complexing acid is present in a range of 1.0-5.0 wt%; and the performance additive is present in a range of 0.01-3 wt%.

4. The grease composition according to any preceeding claim, wherein the saponifiable material is a fatty acid selected from 12-hydroxy stearic acid, stearic acid, oleic acid or a mixture thereof; wherein the oxide or hydroxide of an alkali or alkaline earth metal is selected from sodium hydroxide, calcium oxide, calcium hydroxide, hydrated lime, lithium hydroxide, or lithium hydroxide monohydrate; and wherein the complexing acid is a dicarboxylic acid having C3 to C10 selected from malonic acid(C3), succinic acid(C4), glutaric acid(C5), adipic acid(C6), pimelic acid(C7), suberic acid(C8), azelaic acid(C9) or sebacic acid(C10); and wherein the performance additive is selected from rust and corrosion inhibitor, metal deactivator, metal passivator, antioxidant, pressure additive, polymer, tackifier, dye, chemical marker, fragrance imparter, anti-wear additive or a combination thereof.

5. An open kettle single step process for preparing zinc-alkali/alkaline earth metal mixed complex grease composition, the process comprising:

a) mixing a saponifiable material to a base oil to form a mixture;
b) adding a complexing acid, a zinc oxide and an aqueous solution of oxide or hydroxide of an alkali or alkaline earth metal to the mixture obtained in step a);
c) heating and dehydrating the mixture obtained in step b) with continuous stirring to obtain a solid mass;
d) adding base oil to the solid mass obtained in step c) to form a mixture;
e) cooling the mixture obtained in step d) and optionally adding a performance additive; and
f) homogenizing the mixture obtained in step e) to obtain the mixed complex grease composition.

6. The process as claimed in claim 5, wherein the mixing of step a) is performed at temperature in a range of 25 to 80 °C.

7. The process as claimed in claim 5 or 6, wherein the heating in step c) is performed in three consecutive steps in a sequence of specified steps, the steps comprising:

i) heating at temperature in a range of 90-100 °C for 1 hour;
ii) heating at temperature in a range of 130-140 °C for next 1 hour; and
iii) heating at temperature in a range of 165-175 °C for another next 0.5 to 1.0 hours

8. The process as claimed in any one of claims 5 to 7, wherein the base oil has viscosity in a range of ISO VG 2 to 3200 or a mixture thereof; wherein the base oil is selected from API group I-III mineral base oils, synthetic base oils of API group IV, ester base oil, paraffinic base oil, naphthenic base oil, and re-refined base oil; wherein the synthetic base oil is selected from polyalphaolefins (PAO), polyalkyl glycol (PAG), polyol esters, diesters and alkylated aromatics.

9. The process as claimed in any one of claims 5 to 8, wherein the saponifiable material is a fatty acid selected from 12-hydroxy stearic acid, stearic acid, oleic acid or a mixture thereof; wherein the complexing acid is a dicarboxylic acid having C3 to C10 selected from malonic acid(C3), succinic acid(C4), glutaric acid(C5), adipic acid(C6), pimelic acid(C7), suberic acid(C8), azelaic acid(C9) or sebacic acid(C10); wherein the oxide or hydroxide of an alkali or alkaline earth metal is selected from sodium hydroxide, calcium oxide, calcium hydroxide, hydrated lime, lithium hydroxide, or lithium hydroxide monohydrate; and wherein the performance additive is selected from rust and corrosion inhibitor, metal deactivator, metal passivator, antioxidant, pressure additive, polymer, tackifier, dye, chemical marker, fragrance imparter, anti-wear additive or a combination thereof.

10. The process as claimed in any one of claims 5 to 9, wherein the base oil is present in a range of 65.0-90.0 wt%; the saponifiable material is present in a range of 8.0-18.0 wt%; the oxide and hydroxide of an alkali and alkaline earth metal is present in a range of 0.20-3.0 wt%; the complexing acid is present in a range of 1.0-5.0 wt%; and the performance additive is present in a range of 0.01-3 wt%.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 21 9492

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2 846 392 A (MORWAY ARNOLD J ET AL) 5 August 1958 (1958-08-05) * ex. XII, XIII; claims 1-2 * -----	1,2	INV. C10M117/06 ADD. C10N10/02 C10N10/04 C10N20/02 C10N30/00 C10N50/10 C10N70/00
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TECHNICAL FIELDS SEARCHED (IPC)

C10M
C10N

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	15 April 2024	Greß, Tobias

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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