July 25, 1950 A. J. MORWAY ET AL 2,516,137

HIGH-TEMPERATURE LUBRICATING GREASES

Filed Nov. 17, 1948 2 Sheets-Sheet 1

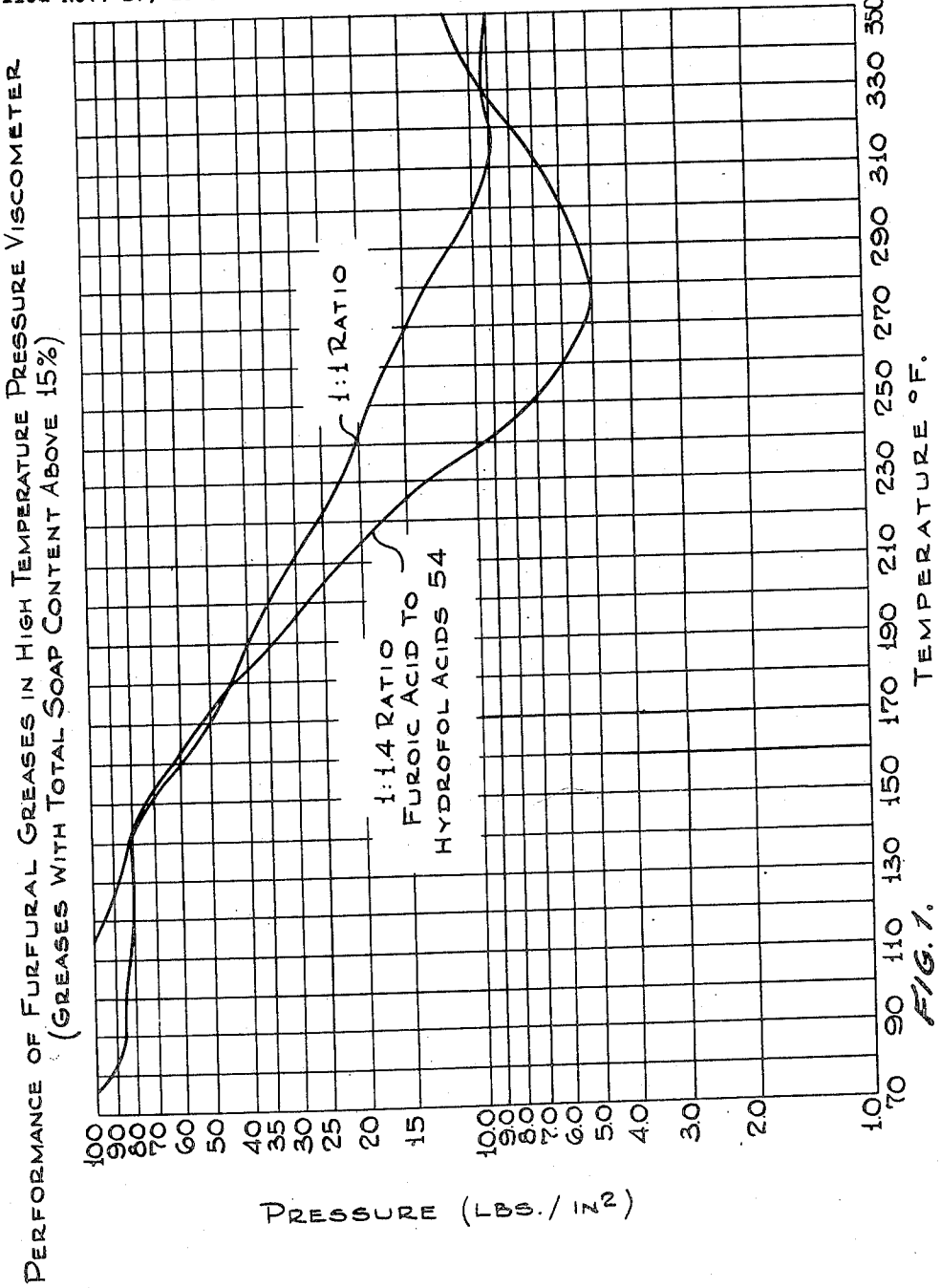


FIG. 1.

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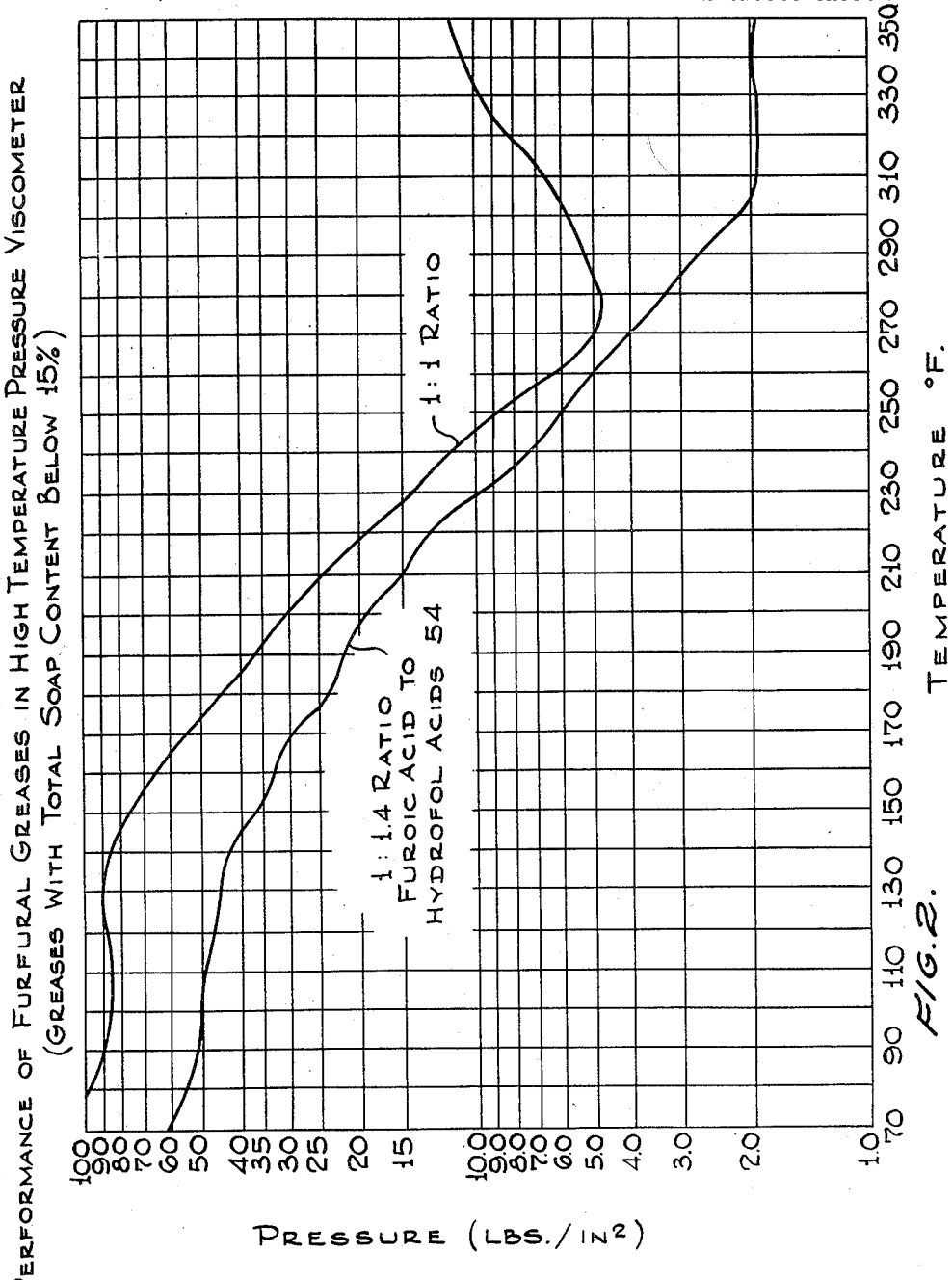


FIG. 2.

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UNITED STATES PATENT OFFICE

2,516,137

HIGH-TEMPERATURE LUBRICATING GREASES

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Application November 17, 1948, Serial No. 60,615

22 Claims. (Cl. 252—42)

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The present invention relates to the production of high temperature lubricating grease compositions, and the like, and particularly to the production of a new type of lubricating grease which retains high temperature structure stability over extended periods of time. The invention relates further to a process for preparing such greases from a combination of high molecular weight metal soaps and low molecular weight salts of certain organic acids, especially certain heterocyclic compounds. It relates particularly to a process for incorporating the metal salts of such compounds, especially of carboxylic acids, in situ in grease compositions.

The invention further comprises a process for preparing the desired salts of such carboxylic acids, and the like, in lubricating greases by subjecting certain types of aldehydes to treatment with alkaline materials, thereby causing them to undergo the well-known Cannizzaro reaction to make the carboxylic acids available.

It has previously been suggested in the prior art, that for some purposes it is advantageous to combine certain metal salts of relatively low molecular weight with the metal soaps ordinarily employed as thickeners for lubricating grease compositions. There appear to be a number of opinions as to the effect of such combination on ingredients, but various investigators have found that the addition of metal salts of relatively low molecular weight organic acids has some utility in grease compositions. Some have suggested that the addition of the low molecular weight acid compounds to the relatively high molecular weight soaps results in the formation of a complex of salt and soap, with superior grease thickening effect and of improved stability, for example, at elevated temperatures. On the other hand, it may be that the provision of a lower organic salt to be used with the soap tends to offset a normal tendency of some of the soaps of certain of the higher fatty acids, especially the more unsaturated acids, to break down into lower molecular weight substances. It is probable that the equilibrium existing in the soaps is shifted somewhat by the addition of these lower molecular weight materials.

Whatever may be the phenomena involved, the addition of salts, and the like, of relatively low molecular weight compounds appears to be advantageous especially in alkali and alkaline earth metal base greases. These materials, in many cases at least, improve physical structure of greases and are particularly useful in stabilizing them structurally at elevated temperatures be-

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cause the ingredients themselves are more stable. Greases which include them appear to be quite susceptible, also, to further stabilization by conventional oxidation inhibitors.

Although various low molecular weight compounds have been proposed recently, such as the salts of acetic and propionic acids and certain of the lower unsaturated acids, such as acrylic and crotonic acid, and the like, as being particularly useful as grease modifiers, these acids are not always suitable and the more desirable of them are rather expensive. Hence, one object of the present invention is to replace such low molecular weight acids with a material which is abundantly available and relatively inexpensive, as well as being particularly effective as a modifying agent.

A further and important object of the present invention is to take advantage of the well-known principles of the Cannizzaro reaction to convert inexpensive aldehydes directly into low molecular weight compounds which are highly useful for modifying soap-thickened lubricating greases, thus making unnecessary the use of costly acids or their salts.

Another object of this invention is to produce lubricating greases having the usual desired grease structure forming ingredients, i. e., metal soaps of higher fatty acids, along with metal salts of low molecular weight unsaturated compounds, in a simple, direct and inexpensive manner.

An additional object is to improve the Cannizzaro reaction process, as applied to furfural and like aldehydes, by controlling the reaction, causing it to take place under controlled conditions in the presence of a liquid hydrocarbon such as mineral oil.

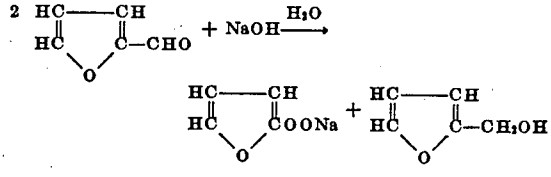
Still another object is to utilize inexpensive raw materials, such as effluents from hydrocarbon treating processes as well as the by-products which may be formed in the Cannizzaro reaction either by incorporating them with suitable modification, into the finished grease composition as useful ingredients thereof. Other and further objects will become more fully apparent as this description proceeds.

According to the present invention, the salts of certain low molecular weight acids, which may be derived from corresponding aldehydes, preferably the aldehydes of cyclic compounds, and particularly heterocyclic carboxylic acids such as furoic acid, are highly useful as ingredients of lubricating greases and are very easily and inexpensively prepared in such greases. While the salts of furoic acid are referred to in detail here-

inafter, it will be understood that the related cyclic and heterocyclic compounds, including the thio compounds, are contemplated as being useful in this invention.

According to the Cannizzaro reaction principle, an aldehyde which has no hydrogen directly attached to the alpha carbon atom may be treated with an alkaline material such as sodium hydroxide, for example, to oxidize one molecule of aldehyde to an acid radical at the expense of an adjacent molecule which is converted to the alcohol. Thus, an aldehyde of the general formula $R_nC—CHO$, where R may be any organic substituent, is treated with strongly alkaline material, resulting in converting half of the aldehyde into the corresponding alcohol and the other half into the metal salt of the corresponding carboxylic acid. This Cannizzaro reaction is obviously applicable to formaldehyde, as may be seen in any standard work on organic chemistry, as well as to the higher aldehydes having no hydrogen on the alpha carbon atom, where an alpha carbon atom is present. Hence, by using a suitable aldehyde, the general reaction proceeds to form the salt of the corresponding carboxylic acid along with the corresponding alcohol. The latter, being volatile or relatively more volatile than the other ingredients, may be removed by evaporation, although in some instances the alcohol, or part thereof, may be allowed to remain in the finished grease, to be esterified or to be unchanged as a useful ingredient of the final composition. The latter feature is a further aspect of the present invention.

Furfuraldehyde, commonly referred to as furfural, is abundantly available and quite inexpensive, being a by-product of certain of the cereal grain industries such as as the oatmeal industry. It is recoverable in large quantities by the sulfuric acid treatment of materials containing pentosans, such as corn cobs, oat hulls, bran, and the like. The Cannizzaro reaction, as applied to furfural, proceeds as follows:



The resulting products are respectively the sodium salt of furoic acid (pyromucic acid) and furfuryl alcohol.

One aspect of the present invention is the superior results obtained by conducting the Cannizzaro reaction in the presence of a control diluent such as a hydrocarbon oil. Where a lubricating grease is to be produced, the diluent may be the same oil as is to serve as the liquid phase of the lubricant. This is not always necessary however. The Cannizzaro reaction taking place under the control afforded by an oil solution appears to have particular merit per se, aside from the final use to which the reaction products are put. A light oil or a volatile hydrocarbon may be used, to be evaporated later if the reaction products, especially the salt, is the desired product. If a grease is to be prepared, as hereinafter described, a heavier oil, or an oil of any desired grade, may be compounded with the salt or other products of reaction.

The Cannizzaro reaction releases alcohol, as previously noted. Where the temperature is permitted to rise appreciably, the alcohol derived from furfural under the Cannizzaro reaction may be polymerized. The resulting polymers, whose molecular weight, viscosity, and other properties vary with the temperature and with other reaction conditions (pressures, presence of catalytic materials, and the like) may be of value for several purposes. The inclusion of at least a small amount of such polymers in the grease appears to be advantageous in at least some instances and is a further feature of the present invention. The combination of the metal furoate and the polymerized alcohol, along with the lubricating oil and soap, forms a grease of superior properties.

The sodium salt and the alcohol may be produced during the ordinary grease-forming reaction by adding the alkaline material in suitable quantities to cause the Cannizzaro reaction to proceed. At the same time or preferably subsequently, there may be formed the soap by saponifying conventional higher fatty acids with a suitable base. Preferably, the aldehyde and the alkali are reacted first in the presence of some part of the lubricating oil. The use of some of the oil, which is chemically inert, helps to reduce the violence of the reaction, which is exothermic, and thereby control the temperature. The fatty acids to be saponified are added later, together with additional alkali, if required. The remainder of the lubricating oil, which forms the liquid element of the grease, preferably is added last.

The use of salts of relatively low molecular weight organic acids, such as furoic acid, is not to be confused with the use of related esters having entirely different purposes. Thus, in the Zimmer and Morway U. S. Patent No. 2,113,754, granted April 12, 1938, there is disclosed the use of certain esters, including some furoic acid esters, as oiliness agents in various materials including both lubricating oil and lubricating greases. The esters used, however, are entirely different from the salts employed in the present instance, and their function is not related in any way to the function of the furoic acid salts and their equivalents.

In the present case, these salts are added to improve the temperature stability of the grease and to amplify the thickening effect of the soaps. The present process is particularly meritorious because the ingredients may all be combined in a single kettle and the same alkaline material which is used to promote the Cannizzaro reaction may be and preferably is used to saponify the higher fatty acids. Thus, both the soap and the salt are formed in situ in the grease. The undesired reaction products such as water and alcohol, or at least part thereof, and other volatile constituents which may be present, are readily removed by evaporation.

The relative proportions of the high molecular weight soaps and the low molecular weight salts, prepared from aldehydes as indicated above, may be varied rather widely. Broadly, molecular proportions of about 1 to 4 parts of soap may be used with about 1 to 4 parts of the salt. In general, however, it is preferable that the molecular proportions be more nearly equal and molar proportions of about 1 to 1 or 1 to 2 are usually preferred. The total quantity of these ingredients to be used in a given grease composition will vary depending upon the type of grease desired. For a very stiff grease, the proportions of total thickener may approach 50% total whereas for a soft grease the total of soaps and salts may be as low as about 5%, based on the weight of the total composition. In general, the grease will consist

of a lubricating oil containing 3 to 30% by weight of the metal soap of C_{12} to C_{22} fatty acids along with 2 to 20% of the metal salt of the low molecular weight heterocyclic carboxylic acid. Narrower limits of 5 to 25% soap and 3 to 15% of salt are usually adequate.

With regard to the relative proportions of high molecular weight soaps and low molecular weight salts, it appears that a fairly high molar ratio of salt to soap is desirable where the soap content of the finished grease is 15% or more by weight. When the soap content is less, the salt content should be reduced more than proportionally. Thus, when these greases were prepared with relatively large concentrations of soap (15% or more) the optimum ratio to give the best grease structure and performance was a ratio of 10 parts furfural to 15 parts hydrogenated fish oil acids or 2:3 by weight. These data are shown below:

EXAMPLE I

Furfural (forms sodium furoate by Cannizzaro reaction) (58% conversion)
Hydrogenated fish oil acids[1]
Sodium hydroxide
Diol 55

Structure of greases prepared with varying ratios of furfural to Hydrofol Acids 54 [1] charged

Percent Weight Charged		Ratio (Wgts.), Furfural: Hyd. Acids 54	Mol Ratio, Furoic Acid: Hydrofol Acids 54	Grease Structure
Furfural	Hydrofol Acids 54			
10	5	2:1	3:1	None.
10	10	1:1	3:2	Poor—grainy.
10	15	2:3	1:1	Excellent.
7.5	15	1:2	1:1.4	Good—rubbery at elevated temperatures.

[1] Saturated high molecular weight aliphatic acids of C_{18} average chain length.

The above data show that a 1:1 mol ratio of furoic acid to Hydrofol Acids 54 gives the best grease structure. Data below will show performance characteristics of these greases.

Lowering of the soap content of the greases to below 15.0% (total soap) indicates that a more desirable structure with better performance can be obtained by increasing the concentration of the high molecular weight soap to give ratios of 1:1.4 or even 1:1.6 or even 1:2 mol ratios of furoic acid to Hydrofol Acids 54 or a charging ratio of 2 parts fatty acids to 1 part furfural.

Furfural greases containing less than 15% total soap

Percent Weight Charged		Ratio (Wgts.), Furfural: Hyd. Acids 54	Mol Ratio, Furoic Acid:[1] Hydrofol Acids 54	Grease Structure
Furfural	Hydrofol Acids 54			
4	8	1:2	1:1	Excellent, smooth.
5	7.5	2:3	1:1.4	Excellent, smooth, somewhat heavier consistency at elevated temperatures.

[1] 58% conversion of furfural charged to furoic acid by Cannizzaro reaction.

The above data has shown that when quantities of soap are employed to thicken the greases (total soap above 15%), the greases containing a ratio of furfural to Hydrofol Acids 54 of 1:2 give greases of somewhat rubbery structure. This structure is undesirable in anti-friction bearing lubrication due to the tendency of the grease to pull out of the bearing. This rubbery structure is also more pronounced in those greases having high soap content. This thickening at elevated temperatures is shown by pressure viscosity determination shown graphically in the attached Figure I.

In the lower soap content greases, the rubbery structure at elevated temperatures of the greases having an acid ratio of 1:2 is less pronounced. The tendency of the greases to become heavier (increase in apparent viscosity) at elevated temperatures is desirable since the greases containing a 2:3 ratio thin out too much and may not remain in the bearings. See Figure II.

Wheel bearing lubrication tests employing the CRC laboratory Wheel Bearing tester also show the greases prepared from 5.0% furfural and 7.5% fatty acids, such as the hydrogenated fish oil acids mentioned above, become soft and tend to flow out of the wheel hub, while greases prepared from 4.0% furfural and 8.0% of the same fatty acids remain in the hub and show only minor separations of oil. These data are shown below:

Wheel bearing tests at 220° F.

Percent Weight Charged		Ratio Weight, Furfural: Hydrofol Acids 54	Results of Wheel Bearing Tests
Furfural	Hydrofol Acids 54		
5	7.5	2:3	Flows from wheel hub.
4	8.0	1:2	Remains in wheel hub trace of oil separation.

Greases with higher soap content than those shown above give excellent results with no flow from the hub whether prepared with 2:3 or 1:2 molar ratio of furfural to fatty acid.

Although the sodium soaps and salts are specifically preferred for many purposes, there are many instances where other metals are more desirable. Lithium base greases may be prepared by the same method as may also greases of calcium, strontium or barium base. Mixed base greases may also be prepared.

For most purposes, the mineral base lubricating oils are preferred, ranging from viscosities from as low as about 100 S. S. U. at 100° F., or about 35 S. U. S. at 210° F., up to as high as about 1,000 S. U. S. at 210° F. The invention is not limited, however, to the use of mineral base oils since various synthetic oils may also be used as part or all of the liquid phase of the grease, as is well-known in the art of grease making. Certain synthetic esters, especially the dibasic acid esters like di-2-ethylhexyl sebacate and related materials are preferred for certain purposes where unusual temperature conditions are encountered, particularly in unusually low temperatures. The grease-thickening ingredients of the present invention are just as useful in synthetic or mixed oil greases as in those based entirely on mineral lubricating oils.

The invention will be more fully understood by reference to the following further specific examples:

EXAMPLE II

A series of soda base greases were prepared using respectively 10%, 7.5%, and 5%, by weight, based on the total ingredients, of furfural, the other ingredients being adjusted proportionately. These greases were graded as heavy, medium, and light, respectively. The compositions thus prepared and some of the inspection data are indicated in Table I.

TABLE I

Furfuraldehyde greases

Ingredients	Per Cent Weight		
Grade	Heavy	Medium	Light
Furfural (Cannizzaro)	10.0	7.5	5.0
Sodium Hydroxide (Cannizzaro)	3.2	2.4	1.6
Mineral Oil [1] (Cannizzaro)	10.0	10.0	10.0
Hydrogenated fish oil acids ("Hydrofol 54")	15.0	11.3	7.5
Sodium Hydroxide	2.3	1.6	1.2
Phenyl alpha naphthylamine	1.0	1.0	1.0
Mineral Oil [1]	58.5	66.2	73.7
Free Alkalinity, per cent NaOH	0.4	0.2	0.2
Worked Penetration, mm./10	200	250	332
Penetration after 75,000 Strokes, fine hole plate, mm./10	230	265	290
Dropping Point, °F.	500+	500+	500+
Water Washing, per cent Loss 125° F. Water	5.0	0.0	0.0
Oil Separation (50 Hours at 210° F.), per cent	0.0	1.5	3.5
10,000 R. P. M. Spindle, 300° F., Hours	1,178	500	500
Norma Hoffman Glass, Hours for 5 p. s. i. drop in oxygen pressure	500+	500+	500+

[1] Light color low pour naphthenic oil of 55 S. S. U. vis. at 210° F.= 40 V. I.

When the grease is heated to high temperatures of the order of about 500° F., the alcohol which is released in the Cannizzaro reaction is evaporated to the atmosphere along with water and the more volatile constituents of the mineral oil unless steps are taken to salvage these materials. It is usually desirable to save the alcohol, and this may be done by condensing the water and alcohol mixture. The alcohol solution or part thereof may be added back to the grease after cooling, if desired, to serve as an oiliness agent. It may be used also in other types of grease, being a good mutual solvent or solubilizer for low molecular weight materials, as where other low molecular weight salts are used such as sodium acetate, and the like. The alcohol which is water soluble, forms therewith an azeotropic mixture and must be specially treated to separate the water. Ordinarily, it is not desirable to utilize all the alcohol in the grease and in many cases it is preferable to remove it entirely. Furfuryl alcohol is highly combustible and care should be taken in its withdrawal. The polymerized furfuryl alcohol, as previously noted, is a good additive for greases. The alcohol and its polymers serve as plasticizers which are usually desirable. These may be replaced wholly or in part, however, with other plasticizers which are known in the art.

EXAMPLE III

Employing the Cannizzaro reaction, the following ingredients were used in the weight percentages indicated to prepare a very satisfactory lubricating grease:

10% Furfuraldehyde
5.4% Sodium hydroxide
15.0% Hydrogenated fish oil acids as in Example II
68.6% Mineral oil as in Example II
1.0% Phenyl alpha naphthylamine

The furfural and equal quantity of mineral oil was charged to a cold grease kettle and agitation started. About 60% of the sodium hydroxide was next added in the form of a 33.3% aqueous solution. No attempt was made to control the temperature of reaction, and the temperature rose to about 175° F. Stirring was continued for about 1½ to 2 hours and then the fatty acids and about ⅓ of the mineral oil were charged to the kettle, heat being applied to raise the temperature to about 150–160° F. since the reaction product had cooled somewhat during the stirring interval. The remainder of the sodium hydroxide was then added in a 33% aqueous solution and the temperature thereafter was raised to 350° F. The remainder of the mineral oil was next added in small increments. Thereafter, the temperature was raised to 450° F. to evaporate all the water and other volatile constituents. These constituents were withdrawn. After heating was discontinued, the grease was stirred while cooling down to about 250° F. At this temperature, stirring was discontinued and the grease was allowed to cool in the kettle. When cold, it was paddled in the kettle to a smooth oily appearance and finally filtered into containers. See the "heavy" grease of Table I for the properties of this composition.

In the examples given above, sodium hydroxide was used as the alkaline agent. However, the Cannizzaro reaction will proceed with other alkaline bases such as lithium, potassium, strontium, barium, calcium, aluminum and mixtures thereof. It is not necessary, either, that the furoate and the soap be formed of the same metal base. The strong bases, such as sodium hydroxide, are usually preferred, however.

While the saturated acids of 12 to 22 carbon atoms are particularly suitable because of their stability for forming the soaps, the unsaturated or hydroxy acids of similar molecular weight may also be used, as will be obvious to those skilled in the art.

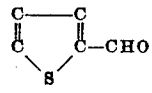
As suggested above, various synthetic oils may be used in lieu of mineral oil. Thus, furfural may be reacted as above, with sodium hydroxide or other metal hydroxides, to form a metal furoate, and the metal furoate, in combination with the soap of a high molecular weight acid, may be dispersed in ester oils such as di-2-ethylhexyl sebacate, or they may be used in glycolate, silicone, fluorinated hydrocarbons, or vegetable oils such as castor oil to form a grease structure. The ester type oils may include those wherein oxo-alcohols are employed to esterify dibasic acids, and the like. The salts and soaps preferably are not prepared in situ in the ester oils because the ester type lubricants tend to hydrolyze during neutralization of the acids. If it is desired to slow down the Cannizzaro reaction, mineral base oil may be used as a diluent, using esters as the remainder of the lubricating oil, so long as such esters or synthetic oils are readily miscible with mineral base oil.

The salts of furoic acid may also be combined with detergent materials such as the sodium or other metal sulfonates. For example, aromatic sulfonates such as toluene-C_{12}-alkylate sulfonates are particularly useful.

Furfural and furoic acid are closely related to the aromatic aldehydes and acids. Hence aromatic aldehydes such as benzaldehyde may be employed in lieu of furfural. In fact, any aldehyde of appropriate molecular weight, i. e., lower than the C_{12} and higher aliphatic carboxylic acids

used in making the soaps, may be employed which undergoes the Cannizzaro reaction such as glyoxal, formaldehyde, substituted aromatic aldehydes, such as tolualdehyde, and the like, though the cyclic materials appear to be preferable in greases. Especially useful are those aldehydes in which the alpha carbon atom does not have any hydrogen atom attached to it. Substituted aromatic aldehydes in which groups other than alkyl are present on the aromatic ring also appear to be suitable. These may include chloro and nitro derivatives which may have some load-carrying properties.

In addition to conventional aldehydes, aldehydes which contain sulfur may be employed as suggested above. These include the various types of aldehydes enumerated above, wherein sulfur is substituted for the oxygen of the conventional aldehyde. Also, aldehydes may be employed which contain sulfur elsewhere in the molecule. An example of the former is the thiophene derivative



By thus incorporating sulfur into the molecule, it is possible to increase the load-carrying properties of the lubricating grease. The hydrogenated derivatives appear also to be applicable, provided the hydrogen atom on the carbon adjacent to the carbonyl group is replaced either with an alkyl group or with some other inert group. Obviously, mixtures of the various aldehydes referred to, may be treated together in the Cannizzaro reaction to produce mixed salts for use as lubricating oil thickeners in grease manufacture.

While the hydroxides, and particularly the hydroxides of alkali and alkaline earth metals, are preferred for neutralizing the acids or for carrying out the Cannizzaro reaction, other strongly alkaline compounds may be used. These include the oxides, carbonates, phenolates, alcoholates and certain sulfides.

In many cases, it is not necessary to catalyze the Cannizzaro reaction, but where the reaction proceeds slowly various peroxides, such as benzoyl peroxide, cumene hydroperoxide, persulfates, and inorganic peroxides may be used to catalyze the reaction.

As previously indicated, some use may be made of the monomeric or the polymeric furfuryl alcohols, or both, (or related alcohols) which are released in the Cannizzaro reaction, and these materials may also be esterified. The excess alcohol may be combined with an excess of fatty acid to form an ester. Thus, a quantity of the high molecular weight fatty acid may be employed which is in excess of that required for saponification. Under the usual grease making conditions, which involve cooking at elevated temperatures, of at least 200° or 250° F. and up to about 500° F., the excess acid esterifies the alcohol which results from the Cannizzaro reaction. The resulting ester may be left in the grease where it is effective to increase the water repellency of the grease and to improve soap dispersion. The following is a specific example.

EXAMPLE IV

A quantity of 10 parts by weight of furfural, and 10 parts of mineral lubricating oil, a naphthenic oil of 55 S. U. S. viscosity at 210° F., are charged to a grease kettle of the fire heated type while the kettle is cold. Agitation is started as the kettle begins to heat and 3.18 parts of NaOH, on a dry weight basis, are added as a 33⅓% aqueous solution. This results in the Cannizzaro reaction taking place, as described above.

After the Cannizzaro reaction has been completed, the kettle having been heated above the boiling point of water for a time period sufficient to remove the water, 15 parts by weight of hydrogenated fish oil acids are added, together with about 20 parts additional of the mineral oil. To this are added 1.4 parts, on a dry weight basis, of NaOH, in aqueous solution as before. This is somewhat less than the stoichiometric quantity required to saponify the fatty acids, hence free acids remain, approximately 0.22 part, calculated as NaOH equivalent.

About 40 parts of mineral oil are next added and the mixture is further heated to about 450° F. Thereupon, about 0.5 part of phenyl alpha naphthylamine are added as oxidation inhibitor, and the resulting product is pan cooled and finally homogenized by stirring in the kettle. The product is a smooth, oily, homogeneous grease.

Tests of the product described, by direct titration, ASTM method, show the product to be neutral. When tested by back titration after HCl treatment, according to the S. I. L. method, the product showed 0.24% alkalinity, calculated as NaOH.

These data indicate that when the ester, resulting from the excess high molecular weight acid and furfuryl alcohol, is hydrolyzed, the furfuryl alcohol reacts with the strong acid to form an insoluble resin and there is insufficient alkali to back titrate, thus indicating an alkaline grease.

The grease just described was compounded of the following ingredients:

Cannizzaro reaction { 10% furfural; 3.18% NaOH; 10% mineral oil, 55 S. U. S. viscosity at 210° F
15% hydrogenated fish oil acids, C_{16}–C_{22}
1.4% NaOH
59.92% mineral oil as above
0.5% phenyl alpha naphthylamine

The grease showed the following inspection:

Penetration (worked), 77° F., mm./10	158
100,000 stroke penetration five hole plate	225
Dropping point	486
Water washing test (125° F. water temp.)	No Loss
High speed spindle test 10,000 R. P. M.–300° F. (hours)	648

It has been observed that greases prepared so as to have some free acidity are more water resistant, as a rule, than those which are alkaline, but they are also more corrosive to metal. By using the above method of manufacture, however, a grease having the water resisting properties of acid greases may be prepared that is quite free from corrosive tendencies. The following example shows a comparison between standard hydrogenated fish oil acid soap greases of the prior art and that of Example IV.

Humidity cabinet test

[120° F.–100% humidity]

	Days to Rusting and Etching
Hydrofol Acid—Crotonic Acid Grease, Per Cent Free Alkalinity 0.48 as NaOH	4
Hydrofol Acid—Crotonic Acid Grease, Per Cent Free Acidity 0.45 as oleic acid	1
Grease of Invention	6

In greases where the Cannizzaro reaction does not occur during manufacture, other alcohols preferably high molecular weight alcohols such as oleyl, cetyl, etc., may be added and reacted with the excess acid to form esters in the greases to give greater plasticizations, ease of dispersion of the soap, water repellancy and increased lubrication value. Hence, the invention is not necessarily limited to Cannizzaro reaction products, but these appear preferable at present for reasons of economy.

The quantity of the ester of furfuryl alcohol, or ester of other appropriate alcohol resulting from the Cannizzaro reaction, may vary from as little as about 0.01 to as much as about 5% of the weight of the total composition. The preferred range is from about 0.5 to about 3%. It is understood, of course, that these esters may be omitted altogether for many purposes.

As previously noted, it is desirable, though not always essential, to include a small amount, e. g., 0.1 to about 1.0% of an oxidation inhibitor such as phenyl alpha naphthylamine in the grease. Other conventional inhibitors such as phenyl beta naphthylamine may be used and may be supplemented or replaced by metal deactivators, corrosion inhibitors, and the like. Conventional additives such as extreme pressure agents, tackiness agents, and the like, are contemplated as being within the scope of the invention.

It has been suggested above that although the major part of this specification is directed to a novel improved grease product and a new method for its production, the invention involves other aspects of improved reactions and reaction products. In particular, the Cannizzaro reaction, although long known in its broad aspects, is markedly improved by the selection of the vehicle in which it takes place. The use of an oil as a vehicle has particular merit. This oil may be any of numerous types, ranging from a very light and highly volatile hydrocarbon to a heavy viscous material. The mineral base oils are preferred, but substituted hydrocarbons may be used so long as they are substantially inert to the reactants which enter into the process.

By proper choice of the vehicle and by adjusting the proportions of reactants placed therein, the temperature of the highly exothermic Cannizzaro reaction may be accurately controlled. The formation of polymers, side reaction products, and the like, may be controlled or substantially eliminated. The reaction goes to completion, or substantially so, resulting in improved yields of acid salt and alcohol.

The oil, if volatile, may be evaporated to recover the reaction products, or it may be used as an ingredient or additive in grease making or other processes. For example, a volatile hydrocarbon may be employed to control the Cannizzaro reaction, to be evaporated and replaced by a heavier oil, if a lubricating grease is to be produced.

While sodium hydroxide has been mentioned above as the usual alkaline agent to be used in the Cannizzaro reaction, any strongly alkaline agent may be used. For making grease, the agent should also be capable of saponifying the higher fatty acids, e. g., C_{12} to C_{22} aliphatic acids. The oxides and hydroxides of the alkali metals are generally preferred, but similar compounds of the alkaline earth metals as well as ammonium bases may also be used.

What is claimed is:

1. The process of preparing a lubricating grease composition for high temperature use, which comprises combining a cyclic aldehyde capable of undergoing the Cannizzaro reaction with an alkali to convert part of said aldehyde to a cyclic carboxylic acid salt and part to the corresponding alcohol, adding a saponifiable fatty material and a further quantity of alkali to form a soap and adding lubricating oil, said salt and soap being combined in proportions of 1 to 4 molar parts of said salt with 1 to 4 molar parts of said soap, said combined salt and soap serving to thicken said lubricating oil to a grease consistency.

2. Process according to claim 1 wherein said aldehyde is furfural.

3. Process according to claim 1 wherein said alkali is sodium hydroxide.

4. The process of preparing a lubricating grease composition which comprises combining 2 to 20 parts by weight of furfural with 1 to 10 parts of a metal hydroxide to convert said furfural partly to furfuryl alcohol and to form a metal salt of furoic acid, adding 5 to 30 parts of fatty acid of 12 to 22 carbon atoms, adding 1 to 10 parts further of a metal hydroxide, heating to complete saponification of said fatty acid, adding mineral oil and cooking and stirring to form said grease.

5. Process as in claim 4 wherein at least part of said furfuryl alcohol is esterified by adding excess fatty acid.

6. Process as in claim 4 wherein at least part of said furfural alcohol is removed by evaporation.

7. Process as in claim 1 wherein at least part of said alcohol is removed by evaporation.

8. Process as in claim 1 wherein at least part of said alcohol is esterified with an excess of said saponifiable fatty material.

9. Process according to claim 4 wherein said metal hydroxide is sodium hydroxide.

10. Process as in claim 4 wherein said metal hydroxide is an alkaline earth metal hydroxide.

11. Process as in claim 4 wherein said metal hydroxide is lithium hydroxide.

12. Process as in claim 4 wherein at least a portion of said furfuryl alcohol is incorporated into said grease as a plasticizer.

13. A lubricating grease composition consisting essentially of a lubricating oil thickened to a grease consistency with 5 to 50% by weight, based on the total composition, of a combination of 1 to 4 molar proportions of a soap of aliphatic carboxylic acid of 12 to 22 carbon atoms with 1 to 4 molar proportions of a salt of a cyclic carboxylic acid of lower molecular weight than said aliphatic acid, said composition including also a minor amount of a fatty acid ester of an alcohol corresponding to said cyclic acid.

14. A lubricating grease composition consisting essentially of a lubricating oil thickened to a grease consistency with 5 to 50% by weight, based on the total composition, of a combination of 1 to 4 molar proportions of a soap of aliphatic carboxylic acid of 12 to 22 carbon atoms combined with 1 to 4 molar proportions of a metal salt of furoic acid, said composition containing also a minor amount of a fatty acid ester of furfuryl alcohol.

15. Composition as in claim 13 wherein said oil is mineral base oil.

16. Composition as in claim 13 wherein said oil is predominantly a synthetic oil.

17. Composition as in claim 13 wherein said

alcohol ester comprises 0.01 to 5% of the total weight.

18. Composition as in claim 14 wherein said furfuryl alcohol ester comprises 0.01 to 5% of the total weight.

19. A lubricating grease composition consisting essentially of lubricating oil thickened to a grease consistency with about 5 to 25% by weight, based on the total composition, of metal soap of C_{12} to C_{22} aliphatic carboxylic acid and about 3 to 15% of metal salt of a heterocyclic carboxylic acid of lower molecular weight than said aliphatic acid, and 0.01 to 5% of the ester of said aliphatic acid and the alcohol corresponding to said heterocyclic acid.

20. Composition as in claim 19 wherein said metal is sodium.

21. A lubricating grease composition, consisting essentially of oil of lubricating grade thickened to a grease consistency with 5 to 50% by weight, based on the total composition, of a combination of 1 to 4 molar proportions of a metal soap of fatty acids with 1 to 4 molar proportions of the salt contained in the Cannizzaro reaction products of a cyclic aldehyde of molecular weight below that of C_{12} aliphatic carboxylic acid and a strong base.

22. The process of preparing a lubricating grease composition which comprises combining 1 to 4 molar parts of an aldehyde of relatively low molecular weight and capable of undergoing the Cannizzaro reaction with sufficient proportions of strong base to substantially convert said aldehyde to carboxylic acid salt and the corresponding alcohol, and combining 1 to 4 molar parts of a saponifiable fatty material of relatively high molecular weight having between about 12 and 22 carbon atoms with saponifying agent to form a soap, and incorporating said salt and soap in grease-thickening proportions into lubricating oil.

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