GREASE PROCESS UTILIZING THE ALKALI 
FUSION OF ALDEHYDES

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The present invention relates to an improved method 
of preparing lubricating greases and to grease composi-
tion-type products, produced thereby. More specifi-
cally, the invention pertains to improvements in the manu-
facture of grease thickeners and to greases containing such thick-
eners. The invention provides for making grease thick-
eners by fusing aldehydes, particularly branched-chain aldehydes with caustic alkali, producing a metal soap 
from the acid so formed and incorporating this metal 
soap into a lubricating oil in grease making proportions. 

In a preferred embodiment of the invention, the fusion 
is carried out in the presence of lubricating oil.

Lubricating greases normally consist of lubricating oils 
thickened by alkali and alkaline earth metal soaps or 
other thickeners to a solid or semi-solid consistency.

The soaps may be prepared by the neutralization of high 
molecular weight fatty acids or by the saponification 
of fats which is usually carried out in a portion of the oil 
to be thickened.

The present invention pertains to highly valuable, stable 
lubricating greases in which the high molecular weight 
fatty acids are replaced or at least supplemented by a 
new grease making material. It has now been found that 
such greases may be prepared by incorporating into 
lubricating oils a grease thickener obtained by fusing suit-
able aldehydes, particularly branched-chain aliphatic alde-
hydes with alkali, particularly caustic alkali, whereby oils 
at temperatures of about 350°—420° F., preferably about 
300°—360° F., for a time sufficient to form the alkali 
metal salt of the acid corresponding to the aldehyde 
used. The chemical reaction taking place during the 
fusion process may be illustrated by the following equa-
tion:

\[ \text{RCHO} + \text{MOH} \rightarrow \text{R} + \text{RCOOM} \]

wherein \( R \) may be a branched-chain aliphatic radical and 
M is an alkali metal such as sodium or potassium.

The discovery of the utility of alkali fusion of alde-
hydes for grease making increases the wealth of raw 
materials available for grease production. Heretofore, 
ester-type fats, oils or high molecular weight fatty acids 
have been used almost exclusively in the manufacture of 
soap-thickened greases and these starting materials have 
been believed indispensable for the purpose. All these 
materials have numerous other industrial uses, a situ-
ation conducive to the development of shortages forcing 
frequent variations in grease making procedures and 
grease characteristics. The discovery of an entirely new 
and large class of suitable raw materials eases this situ-
ation considerably.

The use of aldehydes introduces no complication into 
the grease making procedure. While alkali fusion of 
the aldehyde may be carried out in a separate preliminary 
acid-forming stage, the greases are preferably produced 
 eigentlich in a single process step in which the aldehyde 
is fused with alkali in the lubricating oil base in grease 
making proportions and at grease making conditions, al-
though at somewhat higher temperatures. At the con-
clusion of the fusion process a finished grease is obtained.

Aldehydes useful for the purposes of the present in-
vention have become available in large quantities as inter-
mediate or final products of various synthesis processes 
and more particularly as products and by-products of 
the well-known "Oxo" synthesis. The last-named process 
involves the catalytic reaction of olefins with carbon mon-
oxide and hydrogen at elevated temperatures, say about 
300°—400° F., and pressures of about 2500 to 4000 
psi. In the presence of group VIII metal catalysts, 
particularly cobalt catalysts, to form saturated aldehydes 
having one carbon atom more than the olefin originally 
used.

Quite generally, aldehydes may be used which, upon 
alkali fusion, yield acids or salts having about 10—30 
carbon atoms per molecule. As to the type of aldehydes 
suitable for the invention, straight or branched-chain al-
dehydes may be used. C2—aldehydes having 10 or more 
carbon atoms are preferred. However, lower molecular 
weight aldehydes, such as Ca and C4 aldehydes may be 
used by promoting an aldol condensation in the course 
of the soap-making process. Also, in a closed system, 
aldehydes of even lower molecular weight, such as Ca 
or C4 aldehydes, may be used in this case in combination 
with aldehydes of higher molecular weight to form aldos 
containing 10 or more carbon atoms. Examples of such 
aldehydes are acetdehyde, propionaldehyde, butyralde-
hyde, etc.

In aldehyde, two molecules of aldehyde condense 
with the elimination of water to yield an unsaturated 
aldehyde of higher molecular weight. In carrying out 
the invention, aldolization generally occurs to some ex-
tent with all aldehydes that have an alpha hydrogen 
atom. Thus, the alkali-fused product consists of a mix-
ture of soaps of the acid corresponding to the original 
aldehyde and of the acid corresponding to the aldol 
product.

Particularly desirable starting materials are the Oxo 
aldehydes obtained by oxonation of polymerized olefins 
or olefins from cracked waxes, cracked petroleum and 
other high molecular weight hydrocarbon products, for 
example Fischer-Tropsch olefins. Especially useful are 
the branched-chain aldehydes produced by oxonation of 
olefin polymers, such as polymers of propylene, butylene, 
isobutylene, amylene, etc., for example tetrapropylene, 
trisobutylene, pentapropylene, tetraisobutylene, hexa-
propylene, penta isobutylene, etc., as well as copolymers 
such as those produced from propylene and butylene, 
etc. Among the suitable aldehydes are dodecanal, dode-
canal, isododecanal, isotridecanal, tetradecanal, isopenta-
decanal, isohexadecanal, octadecanal, iso-octadecanal, iso-
oxadecanal, iso-nonadecanal, iso-pentacosanal, iso-hexa-
cosanal, etc.

While the composition and structure of many Oxo alde-
hydes are not fully known, those of the C8 aldehyde ob-
tained from a mixture of C6 olefins of the type described 
above and more specifically of C6 olefins derived from a 
refinery gas stream containing propylene and mixed 
normal and iso-butylene are now well understood. This
Oxo-aldehyde is a mixture of aldehydes having the following composition:

Structure of C₈ Oxo-aldehyde prepared from C₂₋₄ copolymer heptenes

<table>
<thead>
<tr>
<th>Percent</th>
<th>C₂₋₄ Oxo-aldehyde prepared from C₂₋₄ copolymer heptenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>C₁₀H₁₈O₄</td>
</tr>
<tr>
<td>25</td>
<td>C₁₀H₂₁O₄</td>
</tr>
<tr>
<td>17</td>
<td>C₁₀H₂₄O₄</td>
</tr>
<tr>
<td>16</td>
<td>C₁₀H₂₅O₄</td>
</tr>
<tr>
<td>2.3</td>
<td>C₁₀H₂₆O₄</td>
</tr>
<tr>
<td>1.4</td>
<td>C₁₀H₂₇O₄</td>
</tr>
</tbody>
</table>

Salicylaldehydes

Others

103.0

Other Oxo-aldehydes are believed to have compositions generally analogous to that specified above, chain lengths and degree of branching depending on the type of olefins used. It is noted in this respect that even when pure straight-chain olefins are used as the starting materials, the aldehydes have some branching.

When carrying out the aldehyde fusion in the lubricating oil itself so as to form the grease thickening soap in situ in accordance with the preferred embodiment of the invention, it has been observed that the alkali has a strong tendency to settle out of the reaction mixture to the bottom of the reactor in the form of a cake which does not fully participate in the reaction. Highly efficient stirring or agitation will counteract this tendency. However, in many cases more efficient stirring is required than may be obtained in conventional grease kettles and special equipment would have to be used. This settling tendency of the alkali in the lubricating oil-aldehyde mixture is negligible when a sufficient amount of a solid suspending agent is present in the reaction mixture. Most desirable suspending agents are those which serve simultaneously as grease thickeners, such as soaps of high molecular weight fatty acids, silica gel, carbon black, bentonites, Attapulgus clay modifications, etc. Soaps, particularly sodium soaps of high molecular weight fatty acids are preferred for this purpose. However, the melting points of most of these soaps in lubricating oil is rather low, usually below 400° F. Thus, at the high reaction or fusion temperature of about 500° F. or thereabove, these soaps are liquid when used as such and do not entirely counteract the settling tendency of the alkali. This difficulty may be overcome in accordance with a specific embodiment of the invention by using the salt, preferably the alkali metal salt, of a low molecular weight acid in addition to the high molecular weight fatty acid soap. In this manner, soap-salt complexes are formed which melt well above 500° F. and thus form an excellent suspending agent.

These soaps or soap-salt complexes are preferably formed in situ by neutralization of the corresponding acids in the aldehyde-oil mixture with alkali added in amounts sufficient for this neutralization and for the subsequent fusion which takes place at considerably higher temperatures. High molecular weight acids useful for this purpose include hydrogenated fish oil acids, C₁₂₋₁₈ naturally occurring acids of animal or vegetable origin, etc. These acids may be used in amounts ranging from about 2–30 wt. percent based on the finished product. Suitable low molecular weight acids include acetic, furfuroic, acrylic and similar acids to be used in proportions of about 1–10 wt. percent based on the finished product. Esters of the high and/or low molecular weight acids, particularly those containing mono basic acid esters may be used in place of the free acids in corresponding proportions. In this case, the alcohol portions of the esters are converted into acids and the corresponding soaps by alkali fusion. If esters of low molecular weight alcohols are used, elevated pressures may be employed to prevent volatilization of the alcohols. Of course, esters of non-volatile low molecular weight alcohols, such as polyhydroxy alcohol esters, e.g. sorbitol acetate, glycol acetate, etc. may be used. Particularly the high molecular weight type of acids or their esters used for this purpose may also be prepared by alkali fusion of Oxo aldehydes. In this case, a portion of the product of the alkali fusion process in which the principal grease thickener is prepared in accordance with the invention may be returned to the fusion stage to serve as an agent preventing settling of the alkali.

Soaps of high molecular weight fatty acids and/or soap-salt complexes of the type specified may be incorporated in the greases of the present invention to improve high temperature or other characteristics even if no suspending agents are required. This is useful when branched-chain aldehydes are employed, since it has been found that the use of soaps of branched chain acids as the sole grease thickeners often tend to form rubbery or cohesive structures which may be undesirable. However, when these branched chain soaps are mixed with straight chain soaps derived from fatty acids, this cohesive structure is largely eliminated or modified to an extent that is desirable for certain purposes.

The soaps formed by alkali fusion of aldehydes in the presence of other fatty acid soaps consistently yield excellent smooth greases. Other conventional thickeners, anti-oxidants, corrosion inhibitors, tackiness agents, load-carrying compounds, viscosity index improvers, oiliness agents, and the like may be added prior, during and/or after the fusion process as will be apparent to those skilled in the art.

The base oil used as menstruum during the fusion process should be a mineral lubricating oil. After the fusion is completed, synthetic lubricating oils, such as a dibasic acid ester (e.g. di-2-ethyl hexyl sebacate, adipate, etc.), polyglycol type synthetic oils, esters of dibasic acids and polyhydric alcohols, etc., as well as alkyl silicates, carbonates, formals, acetics, etc., may be used alone or in addition to mineral lubricating oil to bring the grease to the desired consistency. The oil base preferably comprises about 50 to about 95% of the total weight of the finished grease.

As indicated above, the alkali fusion of the invention may be carried out in two stages. When so operating, the aldehyde to be fused may be added to a molten mixture of alkali and mineral oil, preferably a heavy paraffinic oil maintained at fusion temperature of, say, about 400°–620° F. The aldehyde and alkali may be used in substantially stoichiometric proportions. When all the aldehyde has been added, heating may be continued at these temperatures until gas evolution substantially ceases.

The acid formed may be recovered from the reaction
5 mixture after cooling, by dilution with water followed by extraction of the oil and any unreacted aldehyde with a light hydrocarbon solvent, such as heptane or the like, and acidicfaction of the aqueous raffinate. If desired, the aldehyde may be purified by vacuum distillation. The acid so prepared may then be introduced into a lubricating oil base stock, other high and/or low molecular weight fatty acids as well as other grease additives may be added and the mixture may be converted into a grease by the addition of at least sufficient caustic alkali, preferably in aqueous solution, to neutralize the acids present. Conventional grease making conditions including temperatures of about 550°- 500° F. may be used in this stage. The soap derived from the aldehyde by alkali fusion should form at least 20 wt. percent and preferably about 30-50 wt. percent of the grease thickener or about 2.0-20 wt. percent of the finished grease. The remainder of the grease thickener is preferably made up by a suitable soap- salt complex of the type described above. The proportion of soap derived from aldehyde to soaps and salts derived from other acids may be about 1:4 to 4:1 and preferably is about 1:1.

In order to prepare a grease by alkali fusion of the aldehyde in situ in accordance with a more desirable embodiment of the invention, the grease making procedure may be quite generally as follows. A mineral lubricating oil base is mixed with the aldehyde and the mixture is heated to about 130°-180° F. The alkali is added preferably in the form of an aqueous solution of about 30-50% concentration. The mass is then dehydrated at temperatures of about 300°-400° F. for about 2-4 hours. Thereafter, the temperature is increased to a fusion temperature of about 400°-620° F. and maintained within this range until gas evolution has reached a peak value, which takes place usually after about 1-3 hours. The grease may then be allowed to cool under stirring to about 200°-250° F. at which level further additives may be introduced. Finally, the grease may be poured into pans to be cooled to room temperature.

A similar procedure is employed when the aldehyde is subjected to alkali fusion in situ in the presence of suspending agents, such as soaps of high molecular weight fatty acids or complexes of such soaps with low molecular weight fatty acids in accordance with the preferred embodiment of the invention. In this case, the high molecular weight acids are added to the mineral oil together with the aldehyde while the low molecular weight acid may be added after the initial heating stage immediately prior to the alkali addition. After sufficient alkali to neutralize the acids and convert the aldehyde to soap is added, preferably in the form of an aqueous solution of about 40-50% and the mixture is heated at a saponification temperature of about 300°-400° F. until the acids are converted to soaps and salts and all the water is volatilized. Alfalfa fusion is then carried out substantially as described above, except that less violent stirring is required.

The invention will be best understood by reference to the following specific examples which represent preferred modifications of the invention.

### Example I
Octadecylnaldehyde prepared by oxonitration of dioctylbutylene followed by aldozation of the Oxo-nonylaldehye was used in preparing a grease as follows:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecylnaldehyde</td>
<td>10.00</td>
</tr>
<tr>
<td>Hydroxylic Acid 54</td>
<td>10.00</td>
</tr>
<tr>
<td>Glacial acid</td>
<td>4.00</td>
</tr>
<tr>
<td>Phenyl alpha-naphthylamine</td>
<td>1.00</td>
</tr>
<tr>
<td>NaOH</td>
<td>6.50</td>
</tr>
</tbody>
</table>

Naphthenic-type lubricating oil distillate having a viscosity of 50 S. S. U. at 210° F. was 68.50

### Example II
Preparation — The aldehyde, the hydroxylic Acid 54 and 1/2 of the mineral oil was charged to a grease kettle and warmed to 150° F. The glacial acetic acid was added followed immediately by a 40% aqueous solution of the NaOH. The mixture was dehydrated and heated to 400° F. for 3 hours when the balance of the mineral oil was added. Heating was continued to 560° F. and the mixture was held at this temperature for 100 minutes. The grease then was cooled while stirring to 200° F. At 225° F. the phenyl alpha-naphthylamine oxidation inhibitor was added. A portion of this batch was homogenized in a Gaulin homogenizer at 3000 p. s. i., very high rates of shear and without concurrent mixing.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unhomogenized</th>
<th>Homogenized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Penetration, 77° F., mm./10:</td>
<td>Excellent smooth somewhat fluid in the case</td>
</tr>
<tr>
<td>Unworked</td>
<td>154</td>
<td>198</td>
</tr>
<tr>
<td>Worked 60 Strokes</td>
<td>179</td>
<td>196</td>
</tr>
<tr>
<td>Worked 100,000 Strokes</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Water Washing Test, Percent Loss</td>
<td>None</td>
<td>800+</td>
</tr>
<tr>
<td>Norma-Hoffman Oxidation Test, Hours to 6 p. s. i. Drop in Oxygen Pressure</td>
<td>None</td>
<td>114</td>
</tr>
</tbody>
</table>

1) 210-144° hole worker plate.

The grease of Example I was mixed with an equal quantity of a high viscosity index, solvent extracted highly paraffinic lubricating grade mineral oil having a viscosity of 383.9 S. S. U. at 100° F. and of 58.2 S. S. U. at 210° F. with a V. I. of 1032. A grease could not be prepared as described in this oil due to the poor solvency and crystalization of the soap in this non-polar medium. However, as large a quantity of this oil is desirable in the grease as is compatible with structural stability due to its low volatility, good oxidation stability and excellent viscosity-temperature relationship. This semi-fluid grease, after mixing, was then homogenized by passage through a Gaulin homogenizer at 3000 p. s. i., very high rates of shear and without concurrent mixing. The resultant product was of excellent, smooth uniform structure.

Properties:

- **Penetrations, 77° F., mm./10:**
  - Unworked: 275
  - Worked, 60 strokes: 310
  - Worked, 100,000 strokes: 345
- **Dropping point, ° F.**
  - 465
- **Water washing test, percent loss:**
  - 10
- **Norma-Hoffman oxidation test, hours to 5 p. s. i. drop in oxygen pressure:**
  - 125
- **Anti-friction Bearing Manufacturers’ Association machine tests, 250° F.**
  - Excellent performance, channeling type grease, no leakage through bearing seal after 1 hour operation.

1) 210-144° hole worker plate.

The invention is not limited to the specific figures of the foregoing examples. The relative proportions of the grease constituents may be varied within the limits indicated above to obtain greases of different consistency and varying characteristics.

What is claimed is:

1. The process of preparing lubricating grease compositions which comprises mixing an aliphatic aldehyde having an alpha hydrogen and from about 10 to 30 car-
bon atoms per molecule and a high molecular weight carboxylic acid having from about 12 to 22 carbon atoms per molecule with a dispersing proportion of mineral lubricating oil, heating the mixture to about 130° to 180° F., adding a low molecular weight carboxylic acid and alkali sufficient for neutralization of said acid and for alkali fusion of said aldehyde to said heated mixture, dehydrating the mixture at a temperature of about 300° to 400° F., heating the dehydrated mixture at a fusion temperature of about 400° to 620° F. sufficient to cause fusion between said alkali and said aldehyde until gas evolution recedes, and then cooling the grease mixture to obtain said lubricating grease composition.

2. The process of claim 1 wherein said aldehyde is an octadeceny aldehyde made by alderization of Oxo ncyt aldehyde prepared by reacting a Ca olefin with carbon monoxide and hydrogen at elevated carbonylation temperatures and pressures in the presence of a group VIII catalyst.

3. The process of claim 1 wherein about 2 to 30 wt. percent of hydrogenated fish oil acids is employed as the high molecular weight carboxylic acid and about 1 to 10 wt. percent of acetic acid is employed as the low molecular weight carboxylic acid.

4. The process of claim 1 wherein the mol ratio of soap derived from the aldehyde to the soap and salt derived from the high and low molecular weight carboxylic acids is within the range of about 1:4 to 4:1.

5. The process of claim 1 wherein said lubricating grease composition is homogenized at a high rate of shear.

6. The process of preparing lubricating greases which comprises admixing an aldehyde, as defined below, with a mineral lubricating oil, heating the mixture to a temperature in the range of 120° to 180° F., adding an aqueous solution of an alkali in an amount sufficient for alkali fusion of said aldehyde, dehydrating the mixture at a temperature in the range of 300° to 400° F., then raising the temperature to a fusion temperature in the range of 400° to 620° F., maintaining said fusion temperature until gas evolution has appreciably receded and fusion between said alkali and said aldehyde has occurred.

7. The process of preparing lubricating greases which comprises admixing an aldehyde, as defined below, with a mineral lubricating oil, heating the mixture to a temperature in the range of 120° to 180° F., adding an aqueous solution of an alkali sufficient for alkali fusion of said aldehyde, dehydrating the mixture at a temperature in the range of 300° to 400° F., then raising the temperature to a fusion temperature in the range of 400° to 620° F., maintaining said fusion temperature until gas evolution has appreciably receded and fusion between said alkali and said aldehyde has occurred.

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