

Feb. 14, 1950

A. J. MORWAY ET AL

2,497,133

LUBRICATING GREASE COMPOSITIONS

Filed June 6, 1947

3 Sheets-Sheet 1

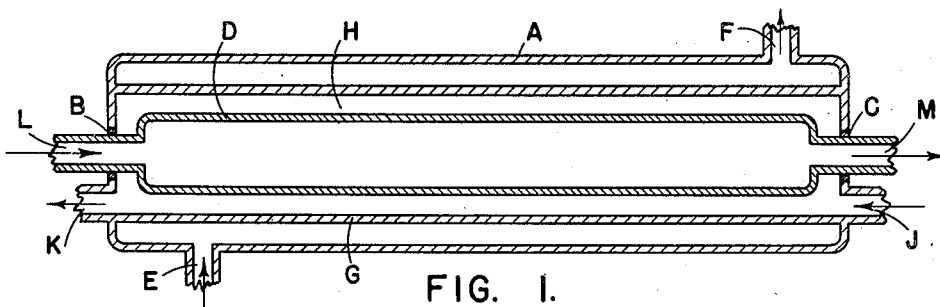


FIG. 1.

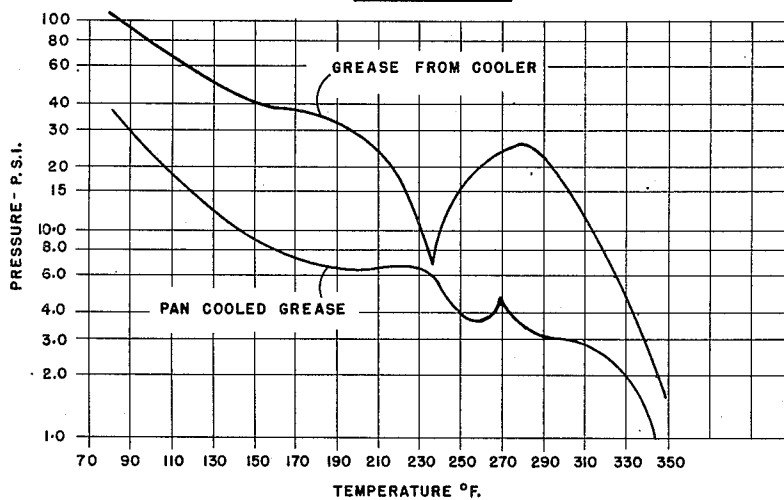


FIG. 2.

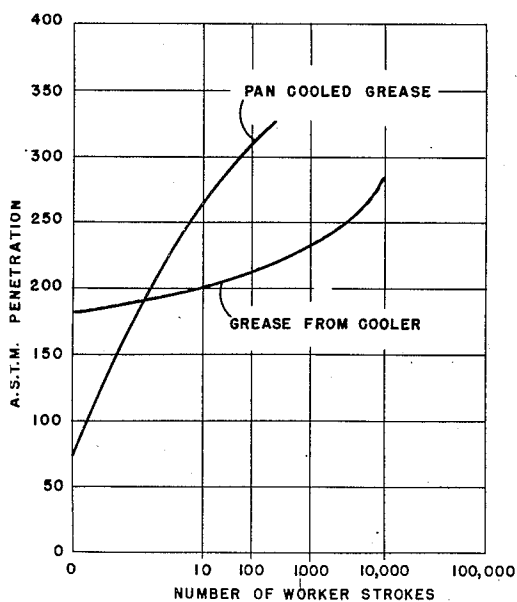


FIG. 3.

Arnold J. Morway,
Alan Bierbower, INVENTORS.
John C. Zimmer.
BY
P. R. Young ATTORNEY.

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FIG. 4.

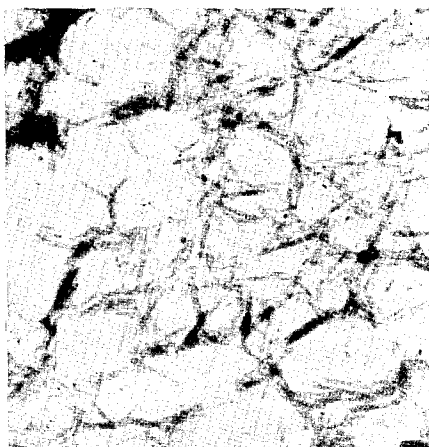


FIG. 5.



FIG. 6

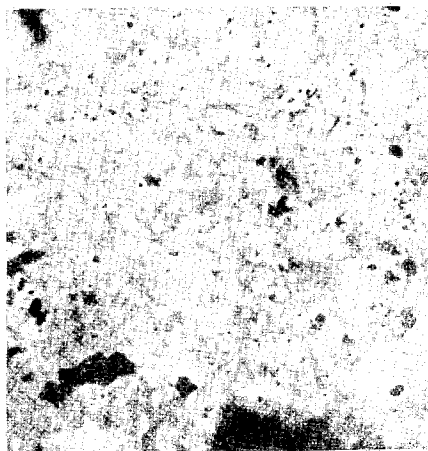


FIG. 7.

Arnold J. Morway,
Alan Beerbower, INVENTORS.
John G. Zimmer.
BY *P. H. Young* ATTORNEY.

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A. J. MORWAY ET AL
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FIG. 8.



FIG. 9.

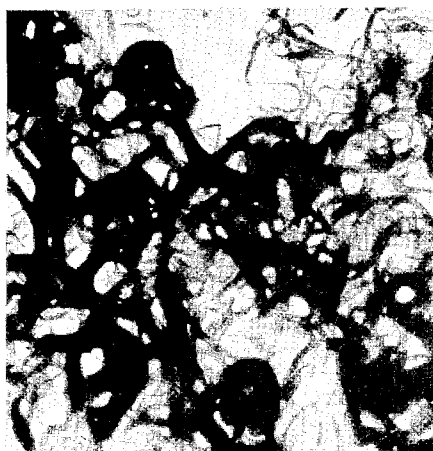


FIG. 10.

Arnold J. Morway.
Alan Bierbower. INVENTORS.
John C. Zimmer.
BY.

P. L. Young ATTORNEY.

UNITED STATES PATENT OFFICE

2,497,133

LUBRICATING GREASE COMPOSITIONS

Arnold J. Morway, Clark, N. J., Alan Beerbower,
Baltimore, Md., and John C. Zimmer, Union,
N. J., assignors to Standard Oil Development
Company, a corporation of Delaware

Application June 6, 1947, Serial No. 753,112

1 Claim. (Cl. 252-36)

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This invention pertains to lubricating grease compositions and particularly to grease compositions having a controlled crystalline or micelle structure of a desirable and uniform character.

In the past numerous types of greases have been prepared for special purposes by dispersing in lubricating oils various metal soaps of fatty materials such as the animal, marine and vegetable fats and acid derivatives thereof. Mixing to effect such dispersion has normally been done at elevated temperatures, that is temperatures above the melting point of the soaps, to accomplish complete dispersion or solution of the soap in the oil. Thereafter the mixture is commonly permitted to cool and set in suitable vessels to form a grease structure having desired characteristics of consistency, that is plasticity, hardness, resistance to penetration, resistance to flow, and the like.

The stability of grease structures against syneresis or separation of the oil from the soap, commonly termed "bleeding," depends among other things on the crystalline structure or what is sometimes known as the micelle structure of the grease as it sets on cooling. This structure which results from crystallization of the soap, varies with the materials employed. Generally speaking, preparation of the more satisfactory greases involves the dispersion of soap in oil or at least the formation of a very stable colloidal suspension and such formation appears to be very materially dependent upon the rate of cooling and also upon active working while cooling. Soaps which are freely miscible in oils at elevated temperatures, for example about 400° F. or more, commonly separate out at lower temperatures and in such cases must be modified, sometimes by wetting agents and the like, to form a stable and satisfactory grease composition. In other cases cooling results in the formation of a grease structure, apparently crystalline in character, which, although not actually unstable, varies considerably depending on the rate and conditions of cooling. The present invention has particular application to grease compositions prepared from such soaps. A particular application has to do with the preparation of high temperature greases from lithium soap and certain esters such as di-(2 ethyl) hexyl sebacate, and related materials.

It is an object of the present invention to control closely the formation of the grease structure by controlling the formation of the crystalline or micelle structure in a definite manner. Another object is to secure such control by a careful and accurate control of the conditions under which greases are cooled. A further and specific object is to prepare a grease which is stable at high temperatures and against working, wherein the lubricant or dispersant is a polar solvent, such

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as a suitable ester, rather than a conventional mineral oil.

Recently there has been developed a satisfactory process for the continuous manufacture of grease whereby the constituents of the composition such as lubricating oil and soap, and other materials such as extreme pressure additives, structure modifiers, stringiness additives, and other agents and modifiers of various types, are combined in a more or less continuously flowing system, the ingredients being suitably heated, mixed together, worked and chilled while in continuous motion. We have discovered that by working the grease and cooling it in thin layers as it passes from the heated and melted or liquid condition to a set or congealed state the foregoing objects can be successfully accomplished. Although this may be accomplished in various ways the accompanying drawings indicate one means by which the foregoing object has been accomplished, as will be described more fully in the following specification. Other and equivalent means will suggest themselves to those skilled in the art.

Figure 1 is a longitudinal sectional view of a cooling unit which we have found satisfactory for controlling the cooling of various types of greases, as more fully specified hereinafter.

Figure 2 is a chart showing the temperature-pressure viscosity characteristics of two greases of identical ingredients prepared by two different methods.

Figure 3 is another chart showing the penetration characteristics of worked greases prepared from identical ingredients but produced by two different processes.

Figures 4 to 10, inclusive, are electron micrographs showing the soap structure of certain lithium soap greases which have been variously cooled and worked, these photographs representing a magnification of about 2000X in the drawings as filed herewith.

Referring first to Figure 1 there is disclosed a grease working and cooling or chilling unit. This, as shown, is preferably a close clearance cooler comprising an external housing or jacket A which is provided with bearing elements B and C at its opposite ends for the reception of a revolving internal member D. This member may be driven in rotation about its axis by any conventional means, not shown. The jacket A is provided with an inlet port E and an outlet port F though which cooling water may be admitted and discharged. The inner wall G separates the jacket or casing from the revolving internal member D leaving a thin annular space H between the member D and the inside of the jacket or casing G. Grease to be cooled is admitted to this thin annular space at one end as indicated at J and is discharged at the other end as indicated at K.

The member D is mounted to rotate in the

bearing elements B and C previously mentioned and consists of a hollow rotor having an inlet for cooling fluid such as water at one end, as indicated at L, and a discharge port M at its other end. Water connections may be maintained through suitable annular or end fittings, as will be obvious to those skilled in the art.

It will be understood that grease from a mixing unit is admitted at J under suitable pressure and is forced continuously through the thin annular channel H between the revolving member D and the jacket inner wall G to be discharged through the opening K. Cold water or other suitable cooling medium thus surrounds the annular cooling channel H in the outer jacket member and also in the internal rotatable member. The temperature of the cooling medium and its rate of flow may, of course, be regulated as desired to obtain the desired rate of cooling. The rate of flow of grease or the like through the cooling apparatus may also be controlled.

The internally cooled rotor D may be turned at from 50 to 1,000 R. P. M. and may be separated from the externally cooled shell by a space of, for example, 0.005 to 0.250 inch. These dimensions, of course, may be varied within other limits as desired.

As an example of our invention, a batch of grease of the following composition was prepared:

EXAMPLE I

	Per cent
Hydrogenated fish oil	15.0
Hydrogenated fish oil acids	5.0
Sodium hydroxide	2.4
Barium hydroxide octahydrate	3.2
Mid-Continent distillate of 45 S. S. U. viscosity at 210° F.	74.4

The fat was saponified in the presence of the acids and an equal amount of mineral oil. The fat and acid mixture was partially saponified with the barium hydroxide and the sodium hydroxide was added later to complete the saponification. After saponification was completed, the resulting soap and oil dispersion was dried out by heating to remove most of the moisture therefrom. The temperature for drying was preferably below the melting point of the soap. The remainder of the oil then was added and the entire grease composition was heated to a temperature of about 400° F. As a result of this heating, all of the residual moisture was removed and the soap appeared to be completely dissolved in the mineral oil. Half of this composition was then pumped at a rate of 0.72 lb./min. through a grease cooler of the close clearance type exemplified in Figure 1. In this example the internal rotor was driven at a speed of 175 R. P. M., the radial clearance, that is the width or thickness of the annular channel H, being 0.125 inch in this instance.

In the foregoing example, the first half of the batch was cooled in the manner described above to a resulting temperature of 64° F., although it has been found subsequently that such extreme cooling is not necessary. The remainder of the hot molten batch was drawn into pans and cooled in the conventional manner without further agitation. It was worked down the next day to a smooth grease. Both products were smooth, homogenous and buttery in appearance but they differed widely in their high temperature performance and their ability to withstand mechanical working.

Figure 2 shows the results of a test whereby the greases described above were run in a pressure viscometer at a slowly increasing temperature. The rate of flow was held constant and therefore the pressure recorded was proportional to the apparent viscosity. It should be noted particularly that the product of the rotor type close clearance cooler is considerably more viscous, generally speaking, than the pan product. Hence it has less tendency to leak from a bearing, for example, from a ball or roller bearing.

Figure 3 shows the relative softening of the same greases, indicating their respective stability to mechanical working. The greases were worked in a modified ASTM grease worker which operates by an electric motor at one stroke per second, causing a plate provided with ¼ inch holes in it to pass through the grease twice per second. This working breaks up the mechanical structure of the grease and normally tends to soften the grease and separate the oil from the soap if there is any tendency towards such separation. The penetration test indicates the degree of softening and it will be noted that the pan cooled grease softened much more readily and to a much greater extent than the grease from the close clearance cooler. After 500 strokes of working the product of the mechanical cooler showed much less of a tendency to soften, the difference being over 100 points of penetration by the standard penetration test.

Tests on a large number of greases have demonstrated that the careful control of the cooling rate, together with rather severe working, which is effected by the rotation of the internal rotor as D, produces a much superior product in comparison with that produced by conventional pan cooling. Greases of the sodium-calcium type, sodium-lithium and other modified sodium greases, as well as those made from single sodium soaps, show marked improvement in stability, resistance to softening, and structure life. Grease of the general character of that shown in Example I may be produced with varying proportions of barium and sodium hydroxides. The proportions of fatty oils and acids may be varied, also. The soap may comprise from 15 to 30% or more of the total composition.

The greases described above are typical of those which are included in our invention, wherein a mineral oil base lubricant is employed. The invention, however, is not limited to lubricants of the mineral oil type and, as suggested above, it has a particularly useful application to greases compounded of certain soaps and certain polar solvents. These solvents are esters which have been found to have useful lubricating properties.

It has recently been found that lithium soap base lubricants employing polar solvents such as di-(2-ethyl) hexyl sebacate, secondary butyl azelate or other esters of dibasic acids as dispersants for the lithium soap provide greases having very good grease structure and possessing excellent high and low temperature properties. These properties cannot both be secured in mineral oil grease lubricants. A typical formula for their composition is as follows:

EXAMPLE II

	Per cent
Lithium stearate	15.00
Zinc naphthenate	1.00
Phenyl alpha naphthylamine	1.00
Di-2-ethyl hexyl sebacate	83.00

When a grease composition having the foregoing formula is prepared in the conventional manner by mixing and heating the ingredients to 400° F. and then pouring the molten grease into cooling pans in normal layers of 6 to 8 inches deep for cooling, the resulting product is not very satisfactory. It readily breaks down with slight working to a semi-fluid condition with almost complete loss of grease structure. Such a lubricant, particularly when used in anti-friction bearings such as ball bearings and roller bearings will leak out of the bearings rapidly, due to its fluid nature causing premature bearing failures. However, when this lubricant is prepared exactly as above but is quickly chilled while being drastically milled or worked, it develops exceptional stability to mechanical working. While the mechanical close clearance chiller or like device produces a superior product, we have found that if the material is poured into cooling pans in thin layers, for example, not over about 1 inch or so in thickness, without mechanical working, a grease is formed which has good stability against mechanical working. Thinner layers are even better, apparently. The thicknesses should be compared with the layer depths of 6 to 8 inches normally used in grease cooling pans.

The foregoing is more surprising when it is realized that the conventional lithium soap greases prepared in relatively non-polar mineral oils normally require very slow pan cooling to obtain maximum stability to mechanical working. The following table shows a comparison of a standard prior art mineral oil base lubricant with the grease described above. The prior art lubricant consisted of 13% lithium stearate, 1% zinc naphthenate, 0.5% phenyl alpha naphthylamine and 85.5% of a gas oil fraction mineral oil.

Mechanical stability of lithium soap greases

[ASTM penetration number]

Product	Slow Pan Cooling				Quick Chilled		
	After Homogenization	160	15,000	1100,000	160	15,000	1100,000
Standard prior art lubricant (mineral oil base).....	285	285	320	Semi-Fluid....	285	Semi-Fluid....	302
Grease of Example II (ester base).....	318	325	370	do.....	275	do.....	302

¹ Number of strokes with 325 1/16" hole worker plate (ASTM Worker).

The composition of lithium soap grease may be varied somewhat, the amount of soap being preferably from 10 to 25% by weight. Small quantities of antioxidants, such as phenyl alpha naphthylamine, and of stability improvers, such as zinc naphthenate, may be used, though commonly they will not be required. When used, these materials will generally be from 0.1 to not more than 2% each. Other conventional additives may be used in minor quantities as will be apparent to those skilled in the art.

EXAMPLE III

	Per cent
Lithium stearate.....	20.0
Phenyl naphthylamine.....	1.0
2,6-di-tertiary-butyl-4-methyl phenol.....	0.5
Di(2-ethyl) hexyl sebacate.....	77.5
Zinc naphthenate.....	1.0

A grease having the above formula was prepared by heating and stirring all the ingredients together at 100° F. in a gas fired grease making kettle until the solid ingredients were uniformly

suspended in the ester. As in Example I, the temperature during this period is preferably below the melting point of the soap. The temperature, while stirring, was then increased to 400° F. At this temperature the solid materials went into solution in the ester and thereafter the homogeneous molten mass was treated as follows: One half of the molten grease was rapidly chilled to 80° F., by being passed through the mechanical close clearance cooler described above. The other half was cooled by the conventional pan method, requiring some 10 to 12 hours to reach the same temperature of 80° F. The following table shows the comparative results of the greases of the above formula cooled by the two methods:

Appearance	Chiller Cooled, Smooth, homogeneous non fibrous grease	Pan Cooled, Smooth firm cake
ASTM Unworked Penetration (77° F.) ¹	275	120
ASTM Worked Penetration (77° F.) ¹	276	320
Worked 100,000 Strokes with 325 1/16" hole worker plate.....	275	378 (semi-fluid)
Per cent Oil Separation at 210° F. in 50 hours ²	0.0%	8.5%

¹ Regular ASTM Method and worker.

² Procedure described in Army-Navy Spec. AN-G-3A.

As indicated in the first example the results immediately above show that other things being equal, the chiller cooled grease is much more stable against mechanical breakdown than the normal pan cooled grease and it is also more resistant to oil separation both in accelerated oil separation tests and in actual storage.

Although the mechanical cooler described above appears to be highly desirable, it has been

found that certain of the advantages inherent in the rapid cooling effected by such mechanical means may be gained by the use of thin layer cooling in conventional equipment. Certain greases which are subjected to extreme mechanical working, such as occurs in ball bearings and other moving mechanisms, may be given very good stability by merely cooling them in very thin layers in pans, although cooling combined with working in thin layers is preferable. Where shearing stresses run high and where greases are particularly subject to mechanical breakdown, soaps prepared by conventional pan methods but cooled in layers which are extremely thin as compared with those commonly used, appear to develop similar superior structural characteristics, although to a lesser degree, as compared with those which are prepared by mechanical working in very thin layers in the mechanical cooler.

Figures 4 to 10, inclusive, of the drawings, are electron photomicrographs of the soap structure of the samples of standard prior art lubricant

based on mineral oil and the polar solvent ester lithium grease before and after mechanical working. These show the actual grease structure greatly magnified. They reveal that the rapidly cooled and mechanically worked polar solvent ester grease, of Example II, contains coarse needle-like crystals which do not change materially in character during extended working in the standard ASTM worker described above. In all other cases, the crystals break down and agglomerate during working to balls of soap which do not yield a gel structure. Referring again to the drawings, Figures 4, 5 and 6 show a prior art lubricant of the lithium soap-mineral oil type, pan cooled, wherein the progressive breakdown of crystal structure is quite apparent. In Figure 4 the soap particles are shown dispersed as needle crystals forming a random network throughout the unworked grease. In Figure 5 the same grease is shown after working 5,000 strokes with a fine hole worker plate. The soap crystals in this case have agglomerated along their long axis resulting in a weakened grease structure. In Figure 6 the same grease is shown after 100,000 strokes with the fine hole worker plate. In this figure the soap crystals have completely broken down and have agglomerated into large balls. In such a grease the oil separates from the soap and becomes quite unsatisfactory.

Figure 7 shows grease of the same composition as shown in Figure 4 except that during preparation it was rapidly cooled and drastically worked while cooling. It will be noted upon close examination that needle crystals are present, forming a random network throughout the grease as in Figure 4, but the crystals are much finer and the network is less distinct than is the case in Figure 4. This material is considerably poorer than that shown in Figure 4 showing that slow cooling is desirable in the manufacture of conventional lithium soap-mineral oil greases.

In Figure 8 the polar solvent ester-lithium grease described above in Example II is shown before testing in the ASTM worker. The soap particles are dispersed as rather coarse and curved needle-like crystals, forming a random intermeshing network throughout the grease. This grease was rapidly chilled in the close clearance chiller of Figure 1.

In Figure 9 the same grease is shown after 100,000 strokes with the fine hole worker plate. It should be noted that Figure 9 shows almost exactly the same crystalline structure as is shown in Figure 8. By contrast, a parallel comparison could be made between Figures 4 and 6.

Figure 10 shows the same lubricant cooled by the old pan process and worked 100,000 strokes. Although a few crystals are still evident, it will be noted that the soap crystals have almost completely broken down and have agglomerated much as in the case of Figure 6. The contrast between Figures 9 and 10 is striking and it represents the difference between a rapidly chilled and worked grease of the polar solvent type and one which is allowed to congeal over a long period of time in the conventional manner and without mechanical working during cooling.

It is recognized that the control broadly of crystal growth, for example in the freezing of liquids by control of the rate of cooling, has long been known. It has been employed to some extent in grease manufacture. In the manufacture of the lithium greases, however, as pointed out above, it has been commonly recognized that slow

cooling is necessary to produce desirable structures. Quick chilling with drastic working appears to have unusual merit with lithium soap-ester type greases. With the particular greases enumerated above, it is evident that known methods of grease manufacture may be improved in an unexpected manner with marked results. The control of the crystalline or micelle structure of these greases, in the manner described, results in the production of a product which appears to be superior for some purposes at least, to anything known to the prior art.

It will be evident from the foregoing that we have effected by our invention an important advance in the art of preparing greases and also that in the case of certain particular compositions the products are novel and advantageous as compared with those of the prior art. It will be obvious that the process might be applied to various other types of greases although not necessarily with the same degree of success. The advantages realized can be extended in various ways that will be apparent to those skilled in the art. Hence we do not intend that the scope of our invention be limited to the examples specifically recited hereinabove or otherwise, except as defined by the following claim.

It will also be understood that the invention is particularly applicable to greases which are prepared with soaps which, although freely miscible in oils at elevated temperatures, tend to separate at lower temperatures. By combining the ingredients at moderate temperatures to effect saponification, thereafter heating to a temperature above the melting point of the soap, to obtain a true solution of soap in lubricant, and then chilling with severe mechanical working in close clearance, the advantages of our invention may be fully realized. The invention is particularly applicable to lithium soap-polar solvent (ester) greases; it is applicable to sodium base greases to improve their structural stability against severe mechanical working; it is applicable in general to high temperature anti-friction bearing greases; and it is applicable in lesser degree to various calcium, aluminum, sodium, lithium and other metal soap and mixed metal soap base greases, as will be understood by those skilled in the art.

While the particular apparatus illustrated and the process described appear at this time to be advantageous, it will be understood that other apparatus may be employed and that the process may be varied. Thus the advantages of controlled cooling may be utilized, to a degree at least, without resorting to mechanical working, and vice versa. The ingredients are preferably combined in a manner to effect complete saponification with an aqueous solution of alkali before raising the temperature above the boiling point of water to dissolve the soap in the lubricant, but this may be varied, if desired, as will be understood by those skilled in the art.

The products of our invention may be distinguished by their stable structure after severe use. As shown in Figure 9, for example, the electron micrograph reveals a distinct microscopic needle structure in lithium soap-ester grease even after such severe working as results from 100,000 strokes of the ASTM grease worker. To a lesser degree Figure 10 shows similar properties. Figures 6 and 7 show comparative properties in a standard prior art lithium soap-mineral oil grease.

We have found further that by our method of

manufacture the soap employed, particularly in lithium soap greases in polar solvents, is materially reduced. Thus the same consistency can be obtained with 15% soap by quick chilling the grease as can be obtained with 20% of the same soap in the same solvent when slow pan cooling is practiced.

We claim:

The process of preparing a lubricating grease which is highly stable in severe mechanical working which comprises combining about 15 to 20% by weight of lithium stearate, about 1% of zinc naphthenate, 77.5 to 83% of di-2-ethyl hexyl sebacate, and 1 to 1.5% of antioxidant, stirring the ingredients to prepare a slurry, heating said slurry to a temperature substantially above the melting point of said lithium stearate to obtain a homogeneous solution, and rapidly and continuously chilling said solution to a temperature of about 80° F. simultaneously with severe mechanical working in layers of 0.005 to .25 inch in thickness.

ARNOLD J. MORWAY.
ALAN BEERBOWER.
JOHN C. ZIMMER.

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