Feb. 24, 1953 J. B. MATTHEWS ET AL **2,629,695**

MANUFACTURE OF LITHIUM LUBRICATING GREASES

Filed May 1, 1951 2 SHEETS--SHEET 1

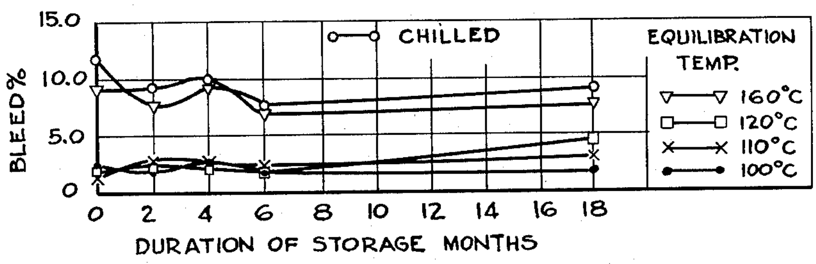

FIG. 1

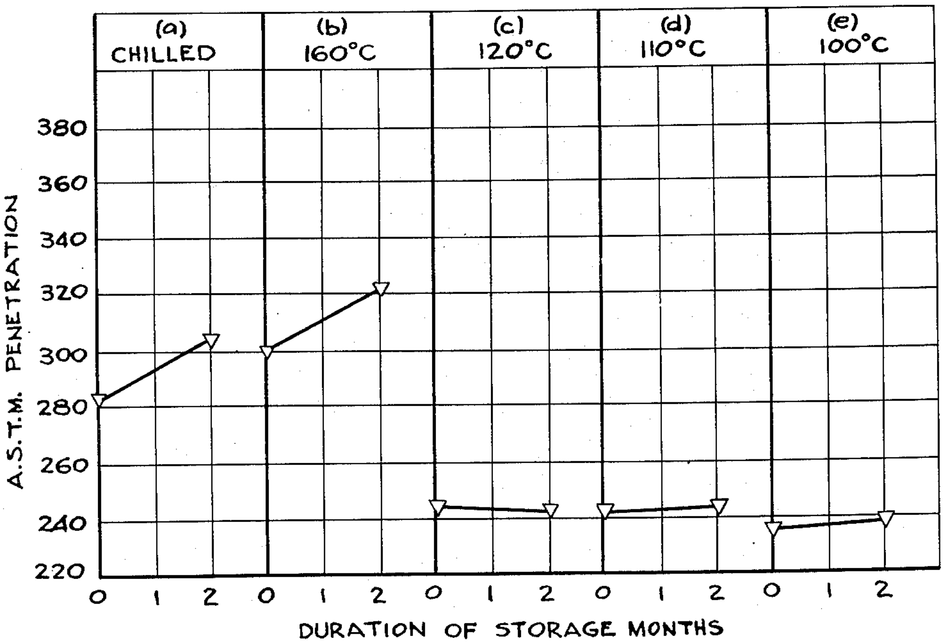

FIG. 3

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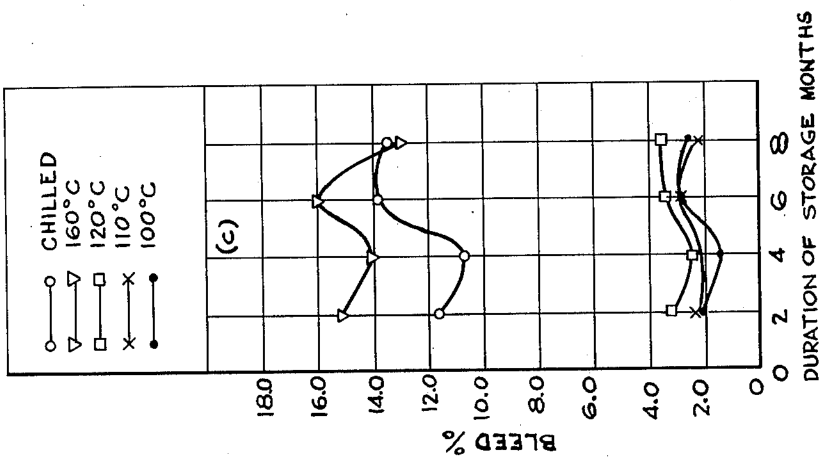

FIG. 2

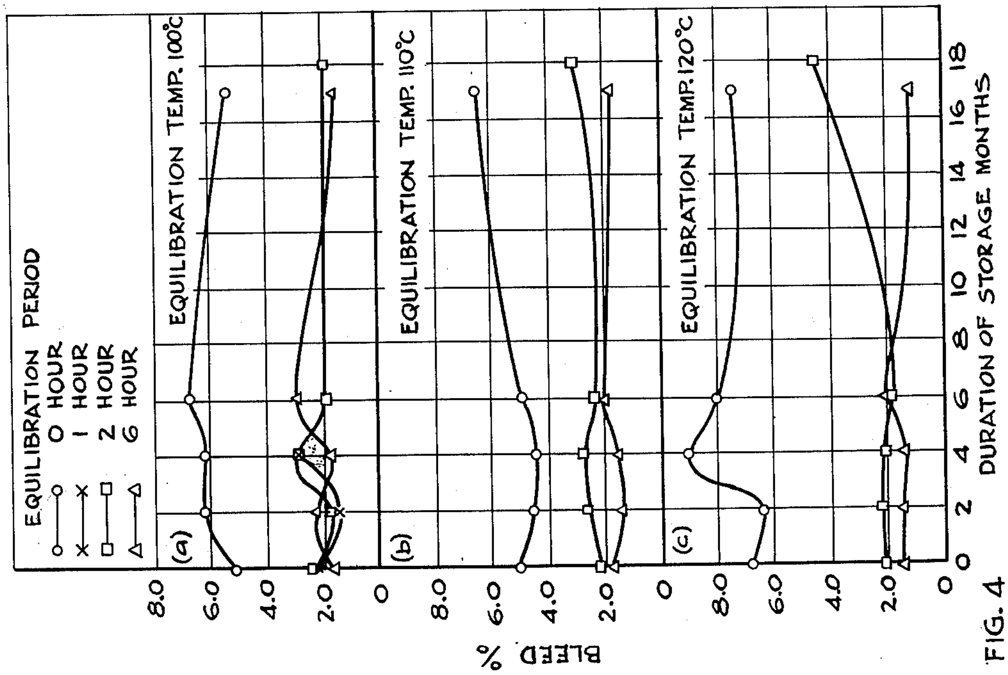

FIG. 4

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2,629,695

MANUFACTURE OF LITHIUM LUBRICATING GREASES

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Application May 1, 1951, Serial No. 223,894
In Great Britain January 13, 1948

16 Claims. (Cl. 252—41)

This invention relates to the art of manufacturing lubricating greases comprising mineral oil or other suitable oleaginous vehicles and a metal salt of a fatty acid, and more particularly, to the production of lithium soap greases of improved yield possessing excellent thixotropic and lubricating properties, and having reduced bleeding characteristics

The term "yield" as used herein is intended to denote the relation between the A. S. T. M. penetration and the soap content of the grease.

In the manufacture of lithium soap greases such as lithium stearate greases, it has generally been proposed to proceed in three stages. First, the mineral oil or other suitable oleaginous vehicle and a soap such as lithium stearate are heated together at a high temperature sufficient to effect dissolution of the soap; the resulting solution is cooled to cause gelation; and the gelled product homogenized or mechanically worked to impart a suitable grease texture. All three stages are essential but the second has a special significance in providing a means of influencing the nature and properties of the finished grease. However, the conditions adopted in this second stage of cooling to cause gelation have been largely empirical, and the rate of chilling as well as the extent of chilling have been the subject of arbitrary choice with the frequent consequence that the resulting greases show a poor yield and moreover in use or even in storage tend to "bleed," i. e., to separate into soap and oil phases.

More recently the need for a more scientific foundation in grease manufacture generally has received some recognition and arising out of this, suggestions have been put forward, for example, to cool a hot aluminum soap grease while agitating to a point near to the temperature designated, the transition temperature at which the soap or soaps present are no longer soluble in the oil and the composition changes from a stringy nature to a gel. It appears to have been considered that agitation should cease shortly before the transition temperature is reached in order to avoid impairing the gel structure, causing, for example, bleeding of the oil out of the gel lattice. It has further been proposed to chill a hot grease rapidly with agitation in suitable apparatus to a so-called "critical" temperature, defined as the lowest temperature below the transition temperature at which a stable grease of maximum hardness can be obtained with a given amount of soap.

These and other proposals reveal an appreciation of the importance of the cooling process and of the circumstance that the thermal history of a grease can influence its final properties. The extent to which this influence is attributable to the existence of phase transformations in the oil-soap system when the grease composition is subjected to temperature variations has not yet been systematically elucidated and in relation to lithium soap greases specifically a more scientific approach to manufacture, taking account of the foregoing circumstances has not yet been published.

Investigations into the thermal properties of lithium fatty acid soap greases have now brought to light that in the case of greases containing lithium soaps of the higher fatty acids a series of phase transformations in the oil-soap system can occur, each approximately definable by reference to a different temperature and each doubtless associated with a change in the condition of the soap phase rather than that of the oil phase. For instance, work was undertaken with a grease containing 8.5 per cent by weight of lithium stearate in a mineral lubricating oil of specific gravity 0.861 at 60° F., flash point 275° F., viscosity 61 secs. Red. 1 at 70° F., pour point —70° F., and F. B. P. of 370° C. It was found that on cooling such a grease from about 210° C. to room temperature, gel formation sets in at about 195° C. but a series of phase transformations can be detected at 196° C., 167° C., 120° C. and 94° C. These phase transformations can, for example, be detected by a thermal analysis of the grease wherein the occurrence of a transformation from one phase to another is evidenced by a latent heat effect. Arising out of these discoveries and forming the basis of the present invention is the further discovery that by taking suitable steps to secure that the soap phase assumes the structure which is stable between the two lowest phase transformation points occurring above 50° C. it is possible to secure greases which are markedly superior in stability and which have a consistency much superior to that obtainable by the normal technique already outlined.

According to this invention a lubricating grease comprising an oleaginous vehicle and a lithium soap of a higher fatty acid is made by heating the ingredients until a homogeneous composition is formed, cooling this homogeneous composition to a temperature which lies between the temperatures of its two lowest phase transformation points which occur above 50° C., isothermally gelling the composition while it is at such temperature and subsequently cooling and homogenizing the gel.

The precise temperature at which the composition is isothermally gelled (hereinafter called the "equilibration temperature") is not critical provided that the whole of the composition is in the particular condition which is stable between its two lowest phase transformation points which occur above 50° C. To ensure that the whole of the composition is in the desired condition when isothermally gelled, it is highly desirable that the rate of cooling to the equilibration temperature be sufficiently slow to enable the grease to complete the phase transformations occurring at higher temperatures. Since, however, the compositions are liable to suffer some oxidation if held at high temperatures for long periods, and since the oxidation products have a deleterious effect on the yield and on the bleed values, it is preferable to adopt a rate of cooling which while sufficiently slow to ensure completion of the phase transformations occurring above the equilibration temperature, is not such as will result in considerable oxidation of the grease. The optimum rate of cooling to the equilibration temperature will thus vary with the particular composition employed and with the tendency of the composition to oxidize and also with other factors such as whether stirring is employed, and if it is, the rate of such stirring. In actual practice under normal conditions it has been found that the optimum rates of cooling to the equilibration temperature lie between 1° and 3° C. per minute.

During the period of cooling to the equilibration temperature, the composition may be left static, or it may be stirred either continuously or intermittently. If left static gel formation takes place before the equilibration temperature is reached and it is generally necessary to break the gel by agitation of the composition. However, if the grease is cooled in thin layers, for example, on a belt, such agitation may not be necessary.

Data are presented in the examples which follow indicating that it is preferable to permit the grease to remain in a static condition during both this cooling period and the equilibration period which follows rather than employing stirring or other means of agitation. Examination of the data will show that the bleeding values obtained either originally or after storage are of a relatively lower order when the grease is cooled and equilibrated in a quiescent state than if stirring had been employed. Hence, it is a preferred version of the present invention to conduct either the cooling step or the equilibration period or both with substantially no agitation of the grease.

The isothermal gelling of the composition is accomplished by maintaining it statically or with stirring at an equilibration temperature, which, as explained above, lies between the temperatures of the two lowest phase transformations which occur above 50° C.

Although equilibration periods of one hour or more are generally sufficient to obtain the results contemplated by this invention, the practical limits on the time of equilibration are from one to six hours and usually from one to four hours, although equilibration periods longer than about two hours usually show little if any advantage over those obtained by the use of the latter period. If the grease is cooled below the equilibration temperature before gelling is complete, the resulting product has a poor yield and a poor bleed value.

As noted hereinbefore, greases gelled by the presence of lithium fatty acid soaps exhibit more than one critical phase transformation temperature. The greases normally employed in industry show three or more such phase transformation points and with mixtures of soaps the number of phase transformation points are affected by the identity and ratio of the soaps in the mixture. The exact temperatures of the individual transformation points is also affected by the oleaginous base in which the soap is dispersed. The usual greases, namely, those employing mineral lubricating oil bases, generally exhibit two phase transformation points between about 94° C. and 120° C., these two points being the two lowest phase transformation points above 50° C. The preferred version of the present invention, therefore, comprises cooling as described above after homogenization above the temperature at which homogenizing occurs (usually above about 210° C.) and equilibrating the grease isothermally at a temperature between 94° C. and 120° C. However, as the examples will show, the generic conception of the present invention is not restricted to this exact temperature range but on the contrary contemplates isothermal gelling, i. e., equilibrating between the two lowest phase transformation points above 50° C., said points varying with the exact identity of the components as discussed above. Note for example that lithium oleate greases exhibit two phase transformation points of 72° and 142° between which the equilibration should be carried out. The examples also show that the use of lubricants other than mineral oils necessitate investigation of the critical phase transformation points for each particular system. A mixture of bis(2-ethylhexyl)-sebacate and a low viscosity mineral oil in 3/1 weight ratio and containing 8.5% lithium stearate showed phase transformation points of 88°, 127°, 155°, 169°. Hence, the equilibration in this particular system should occur between 98 and 166° C. Attention is also directed to the fact that mixtures of lithium fatty acid soaps with other soaps cause an appreciable alteration in the phase transformation temperatures as shown by the data appearing hereinafter for the phase transformation points of greases containing mixtures of lithium stearate and lithium 12-hydroxy stearate. Ordinarily, the two lowest phase transformation points occurring above 50° C. for the various oleaginous vehicles and soaps contemplated by the present invention are between 90° and 170° C.

Prolonging the isothermal gelling period after gelation is complete appears to have no harmful effects although it is to be avoided, especially if the grease is stirred during the isothermal gelling, in order to reduce oxidation to a minimum.

After gelling the rate of cooling is preferably rapid in order to fix the particular soap structure created at the equilibration temperature. This is not essential, however; simple air cooling may be employed after gelation is complete.

The greases are preferably cooled at a relatively rapid rate to a temperature of at least 60° C. following the isothermal gelling period. By the term "rapid rate" is meant a cooling rate of from about 5° to about 15° C. per minute. This cooling may be conducted by stirring or forcing the grease through apparatus having a high heat transfer capacity such as through tubular assemblies permitting the rapid dispersal of heat. A second method permitting the rapid dispersal of heat from the grease comprises the use of an agitated film cooler. In such an apparatus the grease is introduced into the interior of a drum whose interior walls are continuously scraped by a screw conveyor or paddle arrangement whereby the grease is forced against the walls of the drum-like heat exchanger and continuously moved from the injection point to the outlet of the apparatus. By means of the use of such an apparatus, the film of grease deposited on the interior surface of the drum is continuously sheared by the action of the screw conveyor or paddles and is continuously altered so as to present an ever-changing surface to the heat exchanger for the maximum rate of heat dispersion. This same apparatus may, in fact, be used not only as a cooling apparatus (in which case the exterior surface of the drum is cooled by any well known means) but also may be used during the initial steps of raising the mixture of soap and oil to the homogenizing temperature. In the latter instance the soap may be formed in situ in which case a certain quantity of water is present and must be removed. Under the latter conditions, the heat exchanger as described hereinbefore is operated as a combined heating and dehydrating apparatus. Due to the constant agitation of the film of the mixture, the maximum rate of water removal occurs and subsequently the maximum rate of heating to the homogenizing temperature takes place.

The process of this invention is applicable to greases wherein the thickening agent is lithium stearate or a lithium soap of a similar higher fatty acid. While unsaturated fatty acids may be employed as the sole, principal or minor acid present in the soap, higher saturated fatty acids are preferred since they appear to have better gelling values than their unsaturated homologs. By the expression "higher saturated fatty acid" as used in this specification and in the claims hereinafter appearing, is meant an acid of the general formula $C_nH_{2n+1}COOH$, wherein n is greater than 12. The invention is thus applicable to greases based on the lithium soaps of myrstic, palmitic, margaric and behenic acids, as well as those based on lithium stearate. Unsaturated fatty acids suitable for use in the formation of the subject soaps include oleic, linoleic and linolenic acids, as well as their homologs having more than 12 carbon atoms in the hydrocarbon radical of the fatty acid.

Mixtures of such soaps may also be employed and in actual practice commercial lithium stearate always contains appreciable percentages of other soaps such as lithium palmitate. The invention is also applicable to greases based on lithium soaps of higher saturated fatty acids mixed with minor percentages of other soaps. These other soaps may be lithium soaps of soap-forming acids other than the higher saturated fatty acids such as lithium hydroxy stearate or lithium naphthenate, or they may be non-lithium soaps such as calcium naphthenate or sodium hydroxy stearate. Some sodium soaps are inevitably present in commercial lithium soaps. Such other soaps must not, however, be present in a quantity sufficient to eliminate the multiple phase transformations which occur with the lithium soaps of the higher saturated fatty acids, and in this specification and in the claims hereinafter appearing the expression "minor percentages" is to be interpreted to this effect. If desired, the lithium soaps and other soaps employed may be prepared in situ in the oleaginous vehicle, although it is preferable to incorporate the finished soap or soaps in such vehicle.

As illustrating the effect of soaps other than lithium fatty acid soaps upon the critical phase transformation temperatures, the following comparative data are presented:

Greases were prepared containing 8% by weight of lithium soaps as given in the table below. The lubricating base was a mineral lubricating oil. As the table shows, the critical phase transformation temperatures were affected by increasing amounts of lithium 12-hydroxy stearate in admixture with lithium stearate. As the proportion of lithium 12-hydroxy stearate was increased the interval between the two lowest phase transformation temperatures above 50° C. became progressively smaller until at a ratio of 70/30 lithium stearate/lithium hydroxy stearate the two phase transformation temperatures were only 3 degrees apart. Similar results are obtained by the presence of other soaps such as sodium hydroxy stearate or calcium naphthenate. In accordance with the data given in the table below, multiple phase transformation temperatures are usually maintained by a soap containing a similar lithium fatty acid soap or mixtures thereof with other soaps, when the minor soap consisting of a soap other than a lithium fatty acid soap is present in an amount up to about 30% by weight of the soap mixture.

TABLE I

EFFECT OF SOAP COMPOSITION (MIXED) ON PHASE TRANSFORMATION TEMPERATURE

	Two Lowest Critical Phase Transformation Temperatures above 50° C.	
100% stearate	96	120
95% stearate, 5% 12-hydroxy stearate	91	113
90% stearate, 10% 12-hydroxy stearate	91	110
80% stearate, 20% 12-hydroxy stearate	100	108
70% stearate, 30% 12-hydroxy stearate	112	115

Greases prepared according to the present invention may contain from about 5 to about 25% based on the weight of the grease of the subject soaps. Preferably, the amount of soap is between about 6.5 and 14% but in the case of high temperature greases or greases prepared from soaps containing a relatively large proportion of unsaturated fatty acid radical greater percentages of soap may be required.

The base lubricant for forming lithium soap greases by the process of this invention may be selected from a wide variety of natural and synthetic oils. Mineral oils of wide viscosity range varying from about 50 to 2000 S. U. S. at 100° F. and having a viscosity index of from below zero to about 80 can be used as well as their mixtures. A preferred mineral oil base may be prepared by redistilling a gas oil over caustic soda, extracting the distillate with sulfur dioxide and refining the raffinate with a suitable adsorbent material to give an oil having the following properties:

Specific gravity at 60° F	0.861
Flash point, ° F	275
Pour point, ° F	—70
Final B. P., °C. (A. S. T. M.)	370

The mineral oils employed may have the following characteristics:

	S. G. Oil (60° F.)	Flash Point Closed (° F.)	Viscosity Red I (secs.)		K. V. I.	Pour Point, ° F.	Leendertse Type analysis		
			140° F.	70° F.			Aromatics	Paraffins	Naphthenes
A	0.861	275		61	64	Minus 70	2	50.5	47.5
B	0.828	275		44		25	6	67	27
C	0.867	300	45		55	Minus 40	1	50	49
D	0.934	370	95		10	Minus 20	18.6	50.5	30.9
E	0.904	410	168		46	Minus 15	10	53	37

Mixtures of mineral oil and fixed oils such as castor oil, lard oil and the like can be used as well as organic synthetic lubricants and mixtures thereof such as:

I. Synthetic lubricants produced by the Fischer-Tropsch, Synthol, Synthine and related processes, e. g.:
  A. Polymerization of olefins such as ethylene, butylene, and the like, and their mixtures in presence of a Friedel-Crafts or other type condensation catalyst under elevated temperatures and pressures.
  B. Polymerization of unsaturated hydrocarbons in presence of a catalyst and then condensing said polymerized product with an aromatic hydrocarbon such as xylol, benzol, naphthalene, etc.
  C. Oxidation of polymerized olefins of lubricating range as noted under A and B.
  D. Process of converting natural gas to carbon monoxide and hydrogen, followed by catalytic reaction under elevated temperature and pressure to produce hydrocarbons of lubricating range (synthol process).

II. Synthetic lubricating products produced by the Bergius process, e. g., by:
  A. Hydrogenation of coal, peat, and related carbonaceous materials under pressure and elevated temperature in presence of a catalyst.
  B. Hydrogenation of asphalts, petroleum residues and the like.

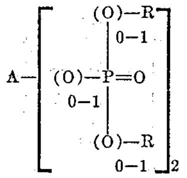
III. Synthetic lubricants produced by the voltolization process, e. g., by:
  A. Voltolization of fatty materials such as fatty oils.
  B. Voltolization of mixtures of fatty oils and petroleum hydrocarbons.
  C. Voltolization of unsaturated hydrocarbons, their mixtures, and the like.

IV. Organic synthetic lubricants:
  A. Alkyl esters of organic acids, e. g.:
    Alkyl lactates
    Alkyl oxalates
    Alkyl sebacates (2-ethylhexyl sebacate)
    Alkyl adipates
    Alkyl phthalates (dioctyl phthalates)
    Alkyl ricinoleates (ethyl ricinoleate)
    Alkyl benzoates
  B. Alkyl, alkylaryl esters of inorganic acids, such as the phosphorus esters.

This particularly desirable class of oleaginous bases for the present compositions comprises organic phosphorus esters including phosphates, phosphonates, phosphinates, as well as the corresponding phosphine oxides. Typical species include:

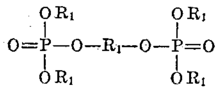
Tricresyl phosphate
Trioctyl phosphate
Tributyl phosphate
Bis(3,5,5 - trimethylhexyl) 2,4,4 - trimethylpentene phosphonate
Tris(3,5,5-trimethylhexyl) phosphate
N-heptenyl bis(3-butylpentane) phosphinate
Bis(3,5,5 - trimethylhexane) octane phosphine oxide

Another highly desirable type of phosphorus lubricants includes the diphosphorus compounds including the four classes referred to above. Preferably, the diphosphorus compounds have a configuration as follows:



$$A-\left[\begin{array}{ccc} & & (O)-R \\ & & |\;0-1 \\ & (O)- & P=O \\ & 0-1 & | \\ & & (O)-R \\ & & 0-1 \end{array}\right]_2$$

wherein A is an organic radical preferably aliphatic or aromatic hydrocarbon radical or alternatively a oxahydrocarbon radical or the corresponding sulfur, selenium or tellurium containing hydrocrabon radicals preferably saturated aliphatic hydrocrabon radicals having from 4 to 12 carbon atoms. The above configuration contemplates diphosphates, diphosphonates, diphosphinates and diphosphine oxides. A particularly desirable configuration comprises those diphosphates having the following configuration:



$$\begin{array}{ccccccc} & OR_1 & & & & OR_1 & \\ & | & & & & | & \\ O= & P & -O- & R_1 & -O- & P & =O \\ & | & & & & | & \\ & OR_1 & & & & OR_1 & \end{array}$$

wherein each R_1 is an aliphatic hydrocarbon radical having from 2 to 6 carbon atoms. It has been found that lubricants of this particular configuration possess unexpectedly extreme low temperature operating characteristics. Species of such lubricants include:

1,4-butanediol bis(dibutylphosphate)
1,3-propanediol bis(diamylphosphate)

V. Synthetic lubricants made by polymerization of alkylene oxides and glycols at elevated temperatures in the presence of catalysts such as iodine, hydriodic acid, etc.
  A. Polymers of alkylene glycol:
    Trimethylene glycol
    Propylene glycol
    Tetramethylene gloycol
    Hexamethylene glycol
    Pentamethylene glycol

B. Copolymers of: :
  Trimethylene glycol and triethylene glycol
  Trimethylene glycol and hexamethylene glycol
  Trimethylene glycol and B-methyltrimethylene glycol
  Trimethylene glycol and diethylene glycol
C. Copolymers prepared from certain epoxides at elevated temperatures and in presence of KOH or BF_3-ether catalyst, e. g.:
  Ethylene oxide and propylene oxide
  Isobutylene oxide and propylene oxide
  Epichlorohydrin and propylene oxide
D. Sulfur containing polymers obtained by treating allyl alcohol, divinyl ether, diallyl ether, diallyl sulfide, dimethallyl ether, glycols, with H_2S in presence of a catalyst such as toluene sulfonic acid, peroxides, ultraviolet light, e. g.:
  Dihydroxy diethyl sulfide
  Dihydroxy dipropyl sulfide
  Trimethylene glycol and dihydroxy dipropyl sulfide
  Trimethylene glycol and dihydroxy diethyl sulfide

VI. Polymers obtained from oxygen-containing heterocyclic compounds, e. g., polymerization of tetrahydrofuran in the presence of a catalyst.

VII. Silicon polymers, e. g.:
  Polyalkyl siloxane and silicate polymers
  Alkylaryl siloxane and silicate polymers
  Dimethyl siloxane and silicate polymers, etc.

Lithium soap greases may be prepared by the process of this invention by dispersing in a suitable kettle or vessel a calculated amount of lithium soap, or the materials used for forming the soap, in a base oil to form a cold slurry and heating said slurry with agitation to a temperature of 230° to about 260° C. until a homogeneous mass is obtained. Additional oil may be added to the mixture as required together with additives such as anti-corrosion, anti-oxidant, anti-bleeding agents, thickeners, etc. The fluid or liquid homogeneous mass is cooled with agitation down to around 210° C. which is above the first transition temperature at which the mixture begins to change phases. From about 210° C. to the predetermined equilibration temperature the grease is cooled slowly with constant stirring. For a lithium stearate grease containing between 5% and 15% soap the time for cooling from about 210° C. to the equilibration temperature of this soap should be between about 30 and 40 minutes. When the grease has been cooled down to its equilibration temperature, it is then gelled isothermally or tempered for a period of from 1 to 4 hours and preferably for about 2 hours and then rapidly chilled to room temperature (20° C. to about 60° C.).

The predetermined equilibration temperature to which a grease is cooled depends upon the consistency of the grease desired, the type of soap used to form the grease, the proportions of soap and base oil, the character of the base oil, the proportions of additive such as anti-bleeding agents, etc., and other variable factors. Thus, it has been observed that on slowly cooling a grease from its solution temperature the grease goes through a series of isothermal phase transformations at which gelation can be observed. By isothermally removing heat at a specific phase transformation, the grease formed at this temperature is allowed to form a particular soap structure of maximum stability at which point it is arrested by rapid chilling.

The data and graphs which appear hereinafter exhibit the advantages to be gained by the process of the present invention as related to the effect of storage upon the pertinent grease characteristics. It has been found that the effect of the present process is variable dependent upon the specific lubricating base employed, the equilibration time and the presence or absence of stirring during cooling from homogenization or during equilibration. These subjects will be discussed in greater detail in the course of the following examples:

Example I

About 8.5% by weight of lithium stearate was dispersed at ambient temperatures in a portion of a solvent-treated petroleum hydrocarbon raffinate having a boiling point range of from about 270° C. to about 400° C. and the mixture heated with stirring to form a slurry. The temperature of the mixture was increased to 250° C. to 260° C. and the balance of the mineral oil (which may be preheated if desired), was blended with stirring into the oil-soap mixture. When a homogeneous mass was formed about 0.025% by weight of triethanolamine and about 0.25% of 2,4-methyl-6-butyl phenol were added to the grease. The hot grease was then slowly cooled, while stirring, by suitable control means such as an oil bath or the like so that it is required from 30 to about 50 minutes for the temperature of the grease to drop from about 210° C. to about 100° C. which in the instant case is the equilibration temperature at which a lithium stearate grease forms a firm non-bleeding product of desired consistency and stability. The grease was then isothermally tempered at 100° C. for about 2 hours and then rapidly chilled to room temperature (20° C. to 60° C.) by suitable means such as cooling the grease in thin layers. The grease was allowed to remain undisturbed over-night and then milled. The grease thus formed was an improved non-bleeding lithium soap grease.

Example II

In order to demonstrate the necessity of isothermally tempering a grease at a chosen equilibration temperature, the following test was made: A lithium stearate grease as described in Example I was slowly cooled from about 210° C. to a temperature at which a phase transformation in the grease structure does not occur. In the instant case the temperature was around about 130° C. and the grease was isothermally tempered at this temperature for about 2 hours and rapidly chilled and processed as described above. The grease thus produced was soft and a great deal of oil was noted to have separated from the product on standing.

Example III

To demonstrate the desirability of slow cooling of the grease from the solution temperature to the equilibration temperature a grease as described in Example I was rapidly cooled, by pouring the grease into metal trays to a depth of about ¼ inch, the trays being floated on cold water, from 210° C. to about 100° C. and isothermally tempered at 100° C. for 2 hours and then processed in the manner described above. The grease thus formed bled freely.

Example IV

To demonstrate the advantages of slow cooling and isothermal tempering at equilibration temperature a grease as described in Example I was rapidly chilled from 210° C. to 60° C. in 2.5 to 3 minutes and then milled. The product thus formed bled freely on standing.

Example V

To demonstrate that greases produced by the process of this invention can be made using smaller amounts of soap and still possess desired consistency and stability, a grease was prepared in accordance with the teaching of Example I except that only 6.5% lithium stearate soap was used. The properties of this grease together with those described above are set forth in Table II.

TABLE II

Composition and Process	Equilibration Temperature, °C.	Penetration (A. S. T. M.) Worked 60 Strokes	Percent Bleed
Example I	100	240	2.8
Example V	100–110	260	2.7
Example IV	------------	318	6.1
Example III	100	242	8.7
Example II	130	------------	(1)

[1] Bleeds freely.

It should be noted that the two lowest phase transformation points occurring above about 50° C. for the grease used in the foregoing examples occur at 94° C. and 120° C., but it should not be assumed that these temperatures are fixed irrespective of the grease composition concerned. The precise nature of the composition influences the points at which the various phase transformations take place with the consequence that the phase transformation points for one particular grease can serve only as an approximate guide to the corresponding points for another grease. The phase transformation points can, however, be determined for any particular composition by thermal analysis.

Example VI

A grease comprising 93.5 parts by weight of the mineral oil specifically described above, 6.05 parts by weight of lithium stearate and 0.45 part by weight of lithium hydroxy stearate was found to have a series of phase transformation points at 199° C., 188° C., 111° C. and 91° C. on cooling from 210° C. to room temperature. The grease is therefore prepared by mixing the above-mentioned ingredients at 210° C. and pouring the mixture into a suitable container and cooling at the rate of 2 to 2.5° C. per minute until 108° C. is reached. The grease is allowed to stand at this temperature for two hours and then rapidly cooled to room temperature and finally homogenized by milling.

The properties of this grease together with those of greases of similar composition made by techniques outside the scope of this invention are shown in Table III.

TABLE III

Process	Batch No.	Equilibration Temperature (°C.)	Penetration (A. S. T. M.) Worked 60 Strokes	Percent Bleed
As in Example VI	10	108	230	1.6
As in Example VI but with equilibration temperatures outside the correct range	11	130	295	10.7
	12	160	275	8.9
Rapid cooling from 210° C. to room temperature	13	------------	295	11.2

Example VII

93.5 parts by weight of mineral oil as specified below and 6.5 parts by weight of lithium stearate are mixed together at 210° C. until a homogeneous solution is obtained, and then cooled at the rate of 2° C. per minute with slight intermittent stirring to break up the gel which forms. When the temperature reaches 110° C. the grease is maintained at that temperature for two hours and then rapidly cooled to room temperature and milled.

Example VIII

Greases were prepared containing 8.5% lithium stearate and 0.25% 2,4-dimethyl-6-tertiary butyl phenol in a lubricating base composed of three parts by weight of bis(2-ethylhexyl) sebacate and one part by weight of a low viscosity lubricating oil. This grease was found to have critical phase transformation points at 88°, 127°, 155°, 169°. A grease prepared by the process as described in Example I, but using an equilibration temperature of 120° C. had a penetration of 335. A corresponding grease prepared by heating the ingredients to homogenization and subsequent chilling to room temperature without any equilibration period had a penetration of 342.

Example IX

A grease was prepared by the process of Example I using 20% of lithium oleate in a mineral lubricating oil. This grease showed phase transformation points at 72°, 140°, 186° C. The grease was isothermally tempered between 72° and 140° C. It exhibited substantially no bleeding.

Example X

Greases were prepared in an Edeleanu raffinate oil which contained 8.0% by weight of mixed lithium stearate and lithium 12-hydroxy stearate. These greases contained 0.25% 2,4-dimethyl-6-tertiary butyl phenol. When such greases are tested for critical phase transformation points results are obtained as given in Table I. When these greases are prepared according to the process described in Example I but isothermally gelled at a temperature between the two transformation temperatures given above, greases are obtained having maximum yield and minimum bleeding values.

Example XI

When greases are prepared according to the process described in Example I but containing lithium palmitate as the soap, it is found that optimum isothermal gelling temperatures lie between about 94 and 120° C. Optimum results are also obtained within this temperature range when using the mixture of lithium soaps derived from hydrogenated fish oil.

Example XII

In order to demonstrate the effect of variations in the slow cooling rate, the process according to Example I was repeated except that an equilibration temperature of 110° was employed. Greases so prepared are compared in the following table showing that a rapidly gelled sample was relatively soft while samples cooled slowly to the equilibration temperature exhibited much better yield values.

Rate of Cooling, °C./min.	A. S. T. M. Penetration at 25° C.
Chilled	273
0.95	232
2.0	221
2.9	223
4.0	230

Example XV

The procedure of Example XIV was repeated using a second mineral lubricating oil base. The table given below gives in detail the data plotted in Figures II and III. As the data and figures prove, the same order of magnitude of advantage is gained by isothermally gelling the grease within the preferred temperature range 100° to 120° C. When the greases were gelled at higher temperatures or gelled without isothermal gelling the initial high bleeding values and penetrations held their relatively inferior positions to the greases over periods of storage up to six months when the test was stopped.

Months' storage	Percent Bleeding					Penetration				
	Chill	160° C.	120° C.	110° C.	100° C.	Chill	160° C.	120° C.	110° C.	100° C.
0	15	11.5	3	2	2	285	300	245	242	237
2	14	10.5	2.5	2	1.5	305	320	243	243	239
4	16	14	3	3	3	--------	--------	--------	--------	--------
6	13	13.5	3	2	2.5	--------	--------	--------	--------	--------

Example XIII

The above process as described in Example XII was repeated with variation in the equilibration time. The table below demonstrates the advantage gained by the use of equilibration times of at least one hour. Two different oil stocks were employed in these tests.

Equilibration Time	Oil Number 1	Oil Number 2
0	231	267
1	215	227
2	227	227
4	228	240
6	--------	242

Example XIV

The effect of storage upon greases prepared as described hereinbefore was investigated. Greases were prepared containing 6.5% lithium stearate and 0.25% 2,4-dimethyl-6-tertiary butyl phenol in a mineral lubricating oil. The following data illustrate the advantage gained by equilibrating the greases within the preferred temperature range between 94° and 120° C. as compared with a grease gelled rapidly to room temperature from the homogenizing temperature (210° C.) and a second grease equilibrated at a temperature of 160° C., which is outside the proper equilibration range. These data are plotted in Figure I attached to the present specification.

Months' storage	Chilled	Percent Bleeding—Gelling-Temperature			
		160° C.	120° C.	110° C.	100° C.
0	12	9	2	2	3
2	9	8	3	3	2
4	10	9	2	2	3
6	8	7	2	2	2
18	9	8	4	3	2

Example XVI

The procedure of the preceding two examples was followed but the equilibration period was varied from 0 to 6 hours in order to determine the effect of such variation on the storage characteristics of the resulting greases. Figure IV contains this data and proves that a period of at least one hour equilibration within the specified temperature range between 100 and 120° C. is essential for minimum bleed values. It will be noted that between one and two hours satisfactory equilibration was obtained and that a period of six hours equilibration time provided no additional advantage.

One advantage of this invention is that it does not require any elaborate and expensive machinery and the isothermal gelling process can readily be carried out in the conventional grease kettle. The method can also be adapted to a continuous grease making process without difficulty.

Greases made by the process of this invention in contrast to those made by conventional technique have the additional advantage of showing an improved resistance to oil separation with age.

During the cooking of the grease, there may be introduced therein small amounts of any of the prior art soaps for additional benefits, and by small amounts is meant less than 2%. However, after a grease of the present invention has been once cooked and cooled, said grease can be admixed with any amount of a desirable soap grease. For example, there may be incorporated into a cold lithium base grease of this invention about 1% to 30% of either aluminum soap grease or sodium soap grease.

To stabilize greases of the type described against oxidation it is advisable to add minor amounts of oxidation inhibitors to the grease. Among the anti-oxidants which are effective with grease composition of the type disclosed are: N-alkyl para-phenylene diamine, condensed polynuclear aromatic mono-amines and alkylolamines. Such inhibitors are N-butyl para-phenylene diamine, N,N'-dibutyl para-phenylene diamine, triethanol amine, etc. Also effective as oxidation inhibitors are alpha or beta-naphthylamine, phenyl-alpha or beta-naphthylamine, alpha-alpha, beta-beta, or alpha-beta-dinaphthylamine, diphenylamine, tetra-methyl diamino diphenyl methane, petroleum alkyl phenols, 2,4-ditertiary butyl 6-methyl phenol, 2,4-dimethyl 6-tertiary butyl phenol, polyalkylene glycols, methyl cellulose, carboxy-methyl cellulose, glycols and water, etc.

Corrosion inhibitors which are particularly applicable with compositions of this invention are N-primary amines containing at least 6 and not more than 18 carbon atoms in the molecule such as hexylamine, octylamine, decylamine, dodecylamine, octadecylamine, heterocyclic nitrogen containing organic compounds such as alkyl substituted oxazoline salts of fatty acids.

Extreme pressure agents can be added to such grease and the preferred comprise esters of phosphorus acids such as triaryl, alkylhydroxy aryl, or aralkyl phosphates, thiophosphates or phosphites, etc., neutral aromatic sulfur compounds such as diaryl sulfides and polysulfides, e. g., diphenyl sulfide, dicresyl sulfide, dibenzyl sulfide, methyl butyl diphenol sulfide, etc., diphenyl selenide and diselenide, dicresyl selenide and polyselenide, etc., sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g., sperm oil, jojoba oil, etc., in which the sulfur is tightly bound, sulfurized long-chain olefins obtained by dehydrogenation or cracking of wax, sulfurized-phosphorized fatty oils, acids, esters and ketones, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with hydroxy fatty acids, chlorinated hydrocarbons such as chlorinated paraffins, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc., or chlorinated ester of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients which can be added are anti-wear agents such as oil-soluble urea or thiourea derivatives, e. g., urethanes, allophanates, carbazides, carbazones, etc., or rubber, polyisobutylene, polyvinyl esters, etc.; viscosity index (V. I.) improvers such as polyisobutylenes having a molecular weight above about 800, voltolized paraffin wax, unsaturated polymerized esters of fatty acids and monohydric alcohols, etc.; oiliness agents such as stearic and oleic acids and pour point depressors such as chlorinated naphthalene to further lower the pour point of the lubricant.

The above additives can be added to grease compositions of this invention in amounts of from about 0.01% to less than 10% by weight, and preferably 0.1 to 5% by weight.

This is a continuation-in-part of application Serial No. 69,412, filed January 5, 1949, now abandoned.

We claim as our invention:

1. In a process of preparing a stable non-bleeding grease comprising an oleaginous vehicle gelled to a grease structure with a lithium soap of a higher fatty acid, the steps comprising heating said oleaginous vehicle and lithium soap to a temperature between 210° and 260° C. until a homogeneous composition is formed, cooling the composition to an equilibration temperature between the temperatures of the two lowest phase transformation points which occur above 50° C., isothermally tempering the grease between said transformation points for a period between about 1 and about 6 hours and thereafter cooling and homogenizing the grease.

2. A process of manufacturing a lubricating grease which comprises heating an oleaginous vehicle mixed with a lithium soap of a higher saturated fatty acid having more than 12 carbon atoms in the hydrocarbon radical thereof to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, slowly cooling said composition to a temperature between the two lowest phase transformation temperatures above 50° C., said temperatures being between about 90° and 170° C., isothermally gelling the composition between said points for a period from about 1 to about 4 hours and thereafter cooling and homogenizing the grease.

3. A process for manufacturing a stable non-bleeding grease comprising a mineral oil and a lithium soap of a higher saturated fatty acid having more than 12 carbon atoms in the hydrocarbon radical thereof to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, cooling this homogeneous composition to an equilibration temperature between the two lowest phase transformation temperatures which occur above 50° C., said temperatures being between about 90° and 170° C., isothermally gelling the composition between said temperatures for a period from about 1 to about 4 hours and subsequently cooling and homogenizing the grease.

4. In a process of preparing a stable non-bleeding lithium stearate grease, the steps comprising agitating and cooling the grease from above about 210° C. and 260° C., to an equilibration temperature in the range of from about 94° to about 120° C., isothermally tempering the grease at said equilibration temperature for a period between about 1 and about 6 hours, and thereafter rapidly chilling the tempered grease to about 60° C.

5. A method of manufacturing a lubricating grease which comprises heating an oleaginous aliphatic diester and lithium stearate in grease forming proportions at an elevated temperature until a homogeneous composition is formed, slowly cooling said composition to a temperature between the two lowest phase transformation temperatures which occur above 50° C., said temperatures being between about 90° and 170° C., isothermally gelling the composition between said temperatures for a period between about 1 and about 4 hours and subsequently cooling and homogenizing the grease.

6. In a process of preparing a stable non-bleeding grease comprising a mineral lubricating oil and grease forming proportions of lithium stearate, the steps comprising heating said ingredients to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, cooling said composition at a rate of from about 1 to 3° C. per minute to a temperature between about 94° and 120° C., isothermally gelling the composition between said temperatures for a period between about 1 and 6 hours and subsequently cooling said grease at a rate from about 5° to about 15° C. per minute.

7. A method of manufacturing a lubricating grease which comprises heating a mineral lubricating oil and grease forming amounts of lithium stearate to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, cooling said grease at a rate of from about 1 to about 3° C. per minute to a temperature between 94° and 120° C., isothermally gelling said composition between said temperatures for

a period between about 1 and about 4 hours and subsequently cooling and homogenizing the grease.

8. A method of manufacturing a lubricating grease which comprises heating an oleaginous vehicle and a lithium soap of a higher saturated fatty acid at a temperature between 210° and 260° C. until a homogeneous composition is formed, agitating and cooling said composition to a temperature between the two lowest phase transformation temperatures which occur above 50° C., isothermally gelling said composition between said temperatures for a period between about 1 to about 4 hours and subsequently rapidly cooling the composition to a temperature below about 60° C.

9. In a process of preparing a stable non-bleeding lithium base grease comprising a major amount of mineral oil having incorporated therein from 6.5% to 14% lithium stearate, the steps comprising cooling while agitating the grease from between about 210° C. and 260° C. to an equilibration temperature in the range of from about 94° to about 120° C., isothermally tempering the grease at said equilibration temperature for about 2 hours, and thereafter chilling the tempered grease to about 60° C.

10. In a process of preparing a stable non-bleeding lithium base grease comprising a major amount of mineral oil having incorporated therein from 5% to 25% lithium stearate, the steps comprising agitating and cooling the grease from between about 210° C. and 260° C. to an equilibration temperature in the range of from about 94° to about 120° C., isothermally tempering the grease at said equilibration temperature for about two hours, and thereafter chilling the tempered grease to about 60° C.

11. In a process of preparing a stable non-bleeding lithium base grease comprising a major amount of mineral oil having incorporated therein from 6.5% to 14% lithium stearate, the steps comprising agitating and cooling the grease from between about 210° C. and 260° C. to an equilibration temperature of about 100° C., isothermally tempering the grease at said equilibration temperature for about 2 hours, and thereafter chilling the tempered grease in thin layers to about 60° C.

12. In a process of preparing a stable non-bleeding lithium base grease comprising a major amount of mineral oil having incorporated therein from 6.5% to 14% lithium stearate, the steps comprising agitating and cooling the grease from between about 210° C. and 260° C. to an equilibration temperature of about 100° C., isothermally tempering the grease at said equilibration temperature for about 2 hours, and thereafter chilling the tempered grease to about 60° C.

13. A method of manufacturing a lubricating grease which comprises heating a mineral oil and 6.5–14% by weight of lithium stearate to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, slowly

cooling said composition to a temperature of about 120° C., isothermally gelling the composition at about said temperature for a period between about 1 and about 6 hours and subsequently rapidly cooling and homogenizing the grease.

14. In a process of preparing a stable non-bleeding grease comprising a mineral lubricating oil mixed with lithium stearate and a minor amount of lithium salt of a hydroxy stearate, at above 210° C. and 260° C. until a homogeneous composition is formed, cooling this homogeneous composition to an equilibration temperature in the range of from about 94° to about 120° C., isothermally gelling the composition while it is at such temperature for from one to about four hours and subsequently cooling and homogenizing the grease.

15. A method of manufacturing a lubricating grease which comprises heating a mineral oil and a lithium soap of a higher saturated fatty acid between about 210° C. and 260° C. until a homogeneous composition is formed, cooling said composition at a rate between about 1 and about 3° C. per minute, substantially without agitation, to a temperature between 94° and 120° C., isothermally gelling said composition between said temperatures for a period between about 1 and 6 hours and subsequently cooling and homogenizing the grease.

16. In a process of preparing a stable non-bleeding grease comprising a mineral oil mixed with a lithium soap of a higher saturated fatty acid, the steps comprising heating said oil and soap to a temperature between about 210° C. and 260° C. until a homogeneous composition is formed, cooling said composition at a rate from about 1 to about 3° C. per minute substantially without agitation, to a temperature between about 94° and 120° C., isothermally gelling said composition between said temperatures substantially without agitation for a period from about 1 to about 4 hours and subsequently cooling the composition and homogenizing the grease.

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