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GREASE COMPOSITIONS

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Our invention relates to grease type lubricating compositions and method of using the same to lubricate various types of special equipment over wide temperature ranges, particularly low temperature ranges.

Modern military operations have created a great demand for special lubricating greases having exceptional properties, the most important of which is to provide satisfactory lubrication over a very wide temperature range. In tactical operations aircraft inevitably encounter great extremes of temperature in all parts of the world. For the best operation of the many synchronous and indicating motors, pumps, instruments, gun sights, bomb sights, gyro compasses and other similar fighting and navigation equipment, lubricants are required which will function dependably under all conditions to which they may be exposed. Also in military applications it is essential that lubricating compositions have long storage and service life with substantially complete freedom from drying and bleeding and good oxidation and rust inhibiting properties.

Many of the difficulties encountered in the use of conventional mineral oil greases in the special applications mentioned, result from the fact that conventional greases are of more or less indefinite composition and particularly are of indefinite structure. Difficulties arise when the attempt is made to use in a bearing a grease supposedly having the same composition, characteristics and structure as the one which it is intended to replace. Since greases are critical compositions comprising essentially loosely flocculated dispersions of sub-microscopic soap crystals in fluid media, slight variations in the composition on the basic ingredients can produce subtle and far-reaching changes in the resultant grease structure due to the effect small percentages of impurities have on the sizes of the crystals, their state of aggregation and their properties in flow.

An object of our invention is to provide "synthetic grease" compositions, which compositions are characterized by definiteness in formulation and reasonable precision in the nature of the ingredients of the composition so that the properties and internal structures of the compositions in every case will be reproducible.

It is another object of our invention to provide lubricating greases with high melting points, which are substantially non-caking, which do not tend to bleed base fluid over a wide temperature range and also which protect the surface to which they are applied from corrosion.

It is a further object of our invention to pro-

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vide lubricating greases which show a relatively low change in apparent viscosity over a relatively large range of very low temperatures.

It is another object of our invention to provide a method of stabilizing the compositions against bleeding and oxidation.

It is another object of our invention to provide a grease composition which is not only a good lubricant but which is capable of giving effective protection to bearing surfaces against rusting when applied thereto in thin films.

Other objects and advantages of our invention will be in part obvious and in part appear hereinafter.

Our invention accordingly comprises the lubricating compositions and greases having the properties and relation of components which will be exemplified in the compositions hereinafter described and the scope of the invention will be indicated in the claims. We have discovered that a composition comprising essentially a major portion of a branched-chain alkyl diester of dicarboxylic acids having from 5 to 12 carbon atoms per molecule or a mixture of two or more of such esters blended with a minor proportion of an alkali metal soap and stabilized against bleeding and oxidation, and when further blended with a rust inhibiting composition compatible with both fluid and the soap structure, yields a grease composition and structure which has lubricating and protective properties superior to those of conventional greases made from hydrocarbon lubricating oils and soaps. Specifically, we have discovered compositions comprising essentially greases made from branched-chain alkyl diesters of glutaric, adipic, pimelic, suberic, azelaic, sebacic, and nonane and decane dicarboxylic acids and soaps of sodium, potassium, lithium, barium, strontium, calcium, lead and aluminum have superior lubricating and physical properties.

We have found that in selecting the ester to be used as the fluid component of the grease it is preferable to use esters having the alkyl substituent in a position close to the ester linkage of the compound. By so selecting the compound it is possible, by virtue of the steric hindrance of the substituent group, to protect the ester linkage itself from water which would tend to hydrolyze the compound. In general, we have found that compounds of the class defined having the substituent in the position α , β or γ to the ester linkage are more stable against hydrolysis than the types in which the substituent is in a position more remote from the ester linkage.

For the accomplishment of the objects of our

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invention, namely, effective lubrication of instrument bearings and parts at extremely low temperatures, it is essential that the greases possess very low freezing points and low starting torques at low temperatures. They must also be free from bleeding and from evaporation of the base fluid to a much greater extent than the conventional hydrocarbon oil greases.

Since we contemplate using organic esters of a specific class as base fluids in our grease compositions, it is essential that in the preparation of the grease composition any conditions which might tend to hydrolyze the ester should be avoided. Generally, these involve keeping the reaction mass free of water and free alkali. There is no one general method that can be prescribed for the preparation of all greases to obtain the structure which we consider the optimum. In our co-pending application, Serial No. 585,516, filed April 16, 1945, we have described a basic method and variations thereof for preparing synthetic greases which of themselves or with minor variations of the steps can be used to prepare the compositions of our invention.

In the preparation of the grease compositions of our invention described in the examples given below, we use a prepared soap, such as the substantially neutral lithium soap of stearic or palmitic acid, commercially available under brand names such as "Litholite A" (Foote Mineral Co.), and blend it with the base fluid it is desired to use for the grease.

To obtain the unique micro-crystalline soap structure, which appears to be necessary to obtain a good grease, it is desirable to interfere with the crystallization occurring during the soap precipitation process so as to produce fine soap crystals with consequent greater inter-crystalline surface area so that the fluid phase is held in equilibrium and its bleeding from the mass is prevented. We have found that polymers of the polybutene and acryloid types of approximately 10,000 to 15,000 molecular weight materially assist in the preparation of greases having the optimum crystalline structure. Not only do the polymers thus added serve as crystallization inhibitors but they also appear to enhance the anti-bleeding properties of the grease.

As oxidation and rust inhibitors we have found generally that alkyl, aryl and aralkyl substituted phenols and polyvalent metal, especially divalent metal, soaps of aryl substituted fatty acids blended with the grease compositions in amounts from about 0.1 part to about 3 parts will protect the composition against oxidation and the lubricated surface against rust for extended periods.

The method of preparing our greases will be more clearly understood by reference to the following illustrative examples:

Example I

To 85 parts of di-isoamyl adipate there was added 12 parts of lithium stearate, 3 parts of acryloid resin having a molecular weight of about 10,000 to act as a crystallization inhibitor, and about 0.2 part of diphenyl amine. The di-isoamyl adipate was substantially pure, the lithium stearate was substantially free of acid and the diphenyl amine was the chemically pure product available on the market. The components were mixed at room temperature and then rapidly raised to a temperature of 375° to 400° F. This temperature, although specifically given as 375° to 400° F. in this case, can be generally de-

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fined, for the purposes of our process, as the temperature at which all the ingredients of the composition become mutually soluble to form a clear liquid. After the soap had dissolved in the fluid, which solution was accomplished by maintaining the fluid at approximately 375° to 400° F. until clear solution was obtained, the liquid was quickly chilled by pouring it into a shallow cooling-pan which was held at a temperature of about 40° or 45° F. by circulation of water under the surface of the pan. The exact method of cooling is not critical. However, the solution should be cooled as rapidly as possible and at least sufficiently rapidly to avoid any appreciable crystallization of the soap during the cooling process.

The cooled, super-saturated solution was allowed to stand at ambient temperature for approximately 20 minutes, during which time a slow crystallization of the soap took place and produced a gel structure. The gel resulting from the crystallization process was then worked into a smooth grease by forcing it several times through a wire cloth having a mesh of about 80. Finer mesh cloth can be used satisfactorily without filtering the solid soap from the liquid phase. This working of the grease uniformly shears it to a smooth product free of lumps.

Example II

To 80 parts of substantially pure, di-2-ethyl hexyl azelate there was added 15 parts of neutral lithium stearate, i. e., the soap contained no free acid, 1 part of polybutene of molecular weight about 12,000 to act as a crystallization inhibitor, and 0.5 part 4-tertiary-butyl-2-phenyl phenol. The components were slurried at room temperature and then rapidly raised to a temperature of about 400° F. After the mixture had been held at about this temperature for about three minutes, it reached a state in which all components had gone into solution. The clear solution was then quickly chilled by pouring into a shallow cooling-pan and allowed to stand at ambient temperature for about twenty minutes to permit crystallization of the soap and formation of a gel. The resultant gel was then worked into a smooth grease by forcing it a few times through a wire cloth having a mesh of about 80.

In a similar fashion greases can be prepared from any of the class of fluids we have identified using common soaps of lithium, sodium, and aluminum. Generally the temperature to which the mixture is heated for bringing the ingredients into solution will be controlled by the fluid and soap used in the grease. It should be within the solvation temperature range of the soap. In general we have found that the solvation temperature ranges of the soaps mentioned permit employment of temperatures of about 400° F. for lithium soaps, about 300° F. for sodium soaps and about 200° F. for aluminum soaps.

The temperature to which the solution is chilled to form the supersaturated solution is preferably about ambient temperature, but may be as high as 100° F. or 150° F. as an upper limit. The purpose of the step is to cool the solution rapidly, and, since the fluids are poor heat conductors, this is best done in a shallow chill-pan held at a low temperature in order to apply to the solution a sharp temperature difference of 200 or 300° F.

The nature of the lubricating grease compositions and the scope of our invention will be more clearly understood by reference to the fol-

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lowing examples in which the compositions are given in parts by weight:

Example III

Lithium stearate.....	12
Polybutene (12,000 M. W.).....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Di-2-ethylhexyl sebacate.....	34.8
Di-2-ethylhexyl adipate.....	52

Example IV

Lithium stearate.....	12
Polybutene (12,000 M. W.).....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Di-2-ethylhexyl azelate.....	86.8

Example V

Lithium stearate.....	12
Polybutene (12,000 M. W.).....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Di-2-ethylhexyl sebacate.....	86.8

Example VI

Lithium stearate.....	12
Polybutene (12,000 M. W.).....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Calcium xylol stearate.....	2
Di-2-ethylhexyl sebacate.....	33.5
Di-2-ethylhexyl adipate.....	50.5

Example VII

Lithium stearate.....	12
Polybutene (12,000 M. W.).....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Calcium xylol stearate.....	2
Di-2-ethylhexyl sebacate.....	85

Example VIII

Lithium stearate.....	12
Polymethyl methacrylate (10,000 M. W.).....	2
Para hydroxy diphenyl.....	0.3
Zinc xylol stearate.....	0.2
Di-2-ethylhexyl azelate.....	85

Example IX

Lithium stearate.....	12
Polybutene.....	1
4-tertiary-butyl-2-phenyl phenol.....	0.2
Sorbitan mono-oleate.....	2
Di-2-ethylhexyl sebacate.....	84.8

In the above series of examples we have shown grease compositions containing optimum proportions of soap and fluid for obtaining desirable plasticity or low temperature torque of the finished product. The grease compositions given above have all been exhaustively tested according to methods prescribed in "Army-Navy Aeronautical Specifications for Grease AN-G-3a" for lubricating performance, life, bleeding, evaporation, apparent viscosity, plasticity and low temperature torque. Since all were of similar proportions, a statement of results on the composition given in Example III should suffice to show the properties which can be expected:

Data for Compositions of Example III

Temperature	Apparent Viscosity, Poises, 10/sec., 12/1 capillary	Plasticity No. (gm.-cm.-sec.)
-100° F.....		33,000
-90° F.....	10,200	8,500
-80° F.....		2,870
-67° F.....	5,000	
-40° F.....	2,800	

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The grease gave eminently satisfactory lubrication at high speeds and low temperatures and also at high speeds at high temperatures. For example, after 2,200 hours of operation, in 8 hour cycles, at 10,000 R. P. M. at 250° F. in the Navy high speed-high temperature test, it retained satisfactory lubricating quality and body.

We have found that variation of the soap content of the grease from about five to about twenty per cent is feasible and will give greases with properties approaching those indicated but the optimum soap proportion appears to be about twelve per cent, as we have shown. Other soaps such as sodium, potassium, calcium, strontium, barium, lead and aluminum can be used in the fluids to form satisfactory greases of various degrees of plasticity.

In all cases illustrated in Examples III through IX, and a great many variations thereof, we have found that the compositions gave satisfactory lubrication in such applications as aircraft gyro instruments, optical instruments, gun mechanisms and similar installations. The amount of bleeding, according to Navy standard specification tests, was less than four percent and evaporation less than one percent; evaporation can usually be kept below one half of one per cent.

The freezing points of the greases were all very low and in those instances where mixtures of fluids were used as the bases, the freezing points were lowered according to the relative proportions of the fluids. The freezing point of the base fluid generally is a function of the number of carbon atoms in the chain and the amount of branching of the chain. In general, we have found that the acids having odd numbers of carbon atoms esterified with branched chain alcohols have the lowest freezing points, that is freezing points lower than homologous esters using acids having even numbers of carbon atoms in the chain.

Since certain changes may be made in the grease compositions of our invention and different embodiments could be made by varying the ester used as the base fluid, the soap, and the balancing ingredients without departing from its scope, it is intended that all matter contained in the above description and examples shall be interpreted as illustrative and descriptive of preferred embodiments and not in a limiting sense. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

Having described our invention what we claim is new and desire to secure by Letters Patent of the United States is:

1. A lubricant comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of a carboxylic acid having from five to twelve carbon atoms per molecule blended with from about 5% to about 20% by weight of a soap to produce a stable grease, the sum of the percentages of these ingredients totaling 100 percent.

2. A lubricant comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of a dicarboxylic acid having from five

to twelve carbon atoms per molecule blended with from about 5% to about 20% by weight of a lithium soap to produce a stable grease, the sum of the percentages of these ingredients totaling approximately 100 percent.

3. A lubricant comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of a dicarboxylic acid having from five to twelve carbon atoms per molecule blended with from about 5% to about 20% by weight of a lithium soap to produce a stable grease, said grease containing small proportions by weight of rust and oxidation inhibiting agents, the sum of the percentages of these ingredients totaling 100 percent.

4. A lubricating composition comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of azelaic acid blended with from about 5% to about 20% by weight of a metal soap to produce a stable grease, said grease containing an antibleeding agent, an oxidation inhibitor and a rust inhibitor, the sum of the percentages of these ingredients totaling 100 percent.

5. A lubricating composition comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of azelaic acid blended with from about 5% to about 20% by weight of a lithium soap to produce a stable grease, said grease containing about 1% by weight of a polymer selected from the group consisting of polybutene and acryloid resins of a molecular weight of from 10,000 to 15,000 and from about .2% to about 0.5% by total weight of oxidation and rust inhibitors, the sum of the percentages of these ingredients totaling 100 percent.

6. A lubricating grease composition comprising a blend of about 85 percent of di-2-ethyl-hexyl azelate, about 12 parts of lithium stearate, about 1 percent of polybutene of molecular weight about 12,000, less than three percent of a substituted phenol as an oxidation inhibitor and less than three percent of a polyvalent metal aryl substituted soap as a rust inhibitor, the sum of the percentages of these ingredients totaling 100 percent.

7. A lubricating composition comprising from about 95% to about 80% by weight of a branched-chain alkyl di-ester of adipic and sebacic acids blended with from about 5% to about 20% by weight of a lithium soap to produce a stable grease containing about 1% by weight of a polymer selected from the group consisting of polybutene and acryloid resins of a molecular weight of from 10,000 to 15,000 said grease also contain-

ing about 0.2% to about 0.5% by weight of oxidation and rust inhibitors, the sum of the percentages of these ingredients totaling 100 percent.

8. A lubricating composition comprising about 85 percent by weight of a mixture of the 2-ethyl-hexyl esters of adipic and sebacic acids, about 12 percent of lithium stearate, about 1 percent of polybutene resin of molecular weight about 10,000 less than three percent of a substituted phenol as an oxidation inhibitor, and less than three percent of a polyvalent metal aryl substituted soap as a rust inhibitor, the sum of the percentages of these ingredients totaling 100 percent.

9. A lubricating composition comprising from 95% to about 80% by weight of a branched-chain alkyl di-ester of adipic acid blended with from 5% to 20% by weight of a lithium soap to produce a stable grease, said grease containing about 10% by weight of a polymer selected from the group consisting of polybutenes and acryloid resins of a molecular weight of from 10,000 to 15,000, said grease also containing about 3% by weight of oxidation and rust inhibitors, the sum of the percentages of these ingredients totaling 100 percent.

10. A lubricating composition comprising about 85 percent of di-2-ethyl-hexyl adipate, about 12 percent of lithium stearate, about 1 percent of polybutene resin of molecular weight about 10,000, less than three percent of a substituted phenol as an oxidation inhibitor and less than three percent of an aryl substituted soap as a rust inhibitor, the sum of the percentages of these ingredients totaling 100 percent.

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