United States Patent Office 3,251,774 Patented May 17, 1966

3,251,774

LUBRICANT GREASE

Arthur C. Borg, Chicago, Ill., and Stephen J. Zajac, Whiting, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Filed Mar. 5, 1962, Ser. No. 177,151
The portion of the term of the patent subsequent to Dec. 3, 1980, has been disclaimed
9 Claims. (Cl. 252—51.5)

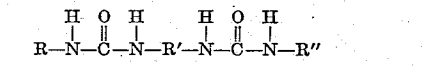
This invention relates to novel lubricant grease compositions, and more particularly concerns the provision of greases characterized by having exceptional mechanical stability characteristics.

Recently, a series of greases composed of liquid lubricants thickened with certain ureido compounds has been discovered (Robert J. Rosscup and Hubert J. Liehe, U.S. application S.N. 750,050, filed January 21, 1958, now U.S. Patent 3,015,625) which possesses unusual high temperature characteristics and mechanical stability as measured by all conventional tests. These greases are far superior to most common greases and as a result are extensively used in both civilian and military applications.

However, a newly developed laboratory test of grease performance has revealed that ureido-thickened greases are somewhat susceptible to "whip." "Whip" tests, such as the General Electric Whip Test, test the ability of a grease to maintain its consistency in overpacked ball bearings run at high speeds. At these extreme conditions of rapid churning under pressure, even greases which exhibit good performance in the ASTM worker and the Roll Stability test tend to become semi-fluid and hence leak out of the bearing.

It has now been discovered, according to the invention, that the Rosscup-Liehe ureido greases, i.e. those greases thickened with the reaction product of abietyl amines and polyisocyanates, are dramatically improved with respect to leakage characteristics and mechanical stability in overpacked bearings by incorporating in the grease a small amount of an organic carboxylic acid. Acids of widely diversified type have been tested, and while there is some variation in performance, all appear to improve grease consistency under whip conditions.

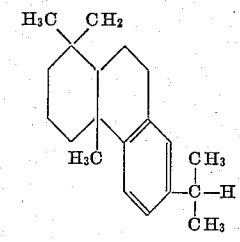
The ureido compound thickeners have the general formula



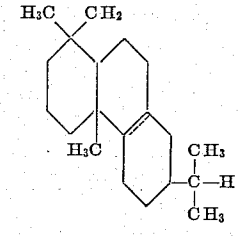
where R and R'' are the same or different abietyl radicals selected from the group dehydroabietyl radical, dihydroabietyl radical, and tetrahydroabietyl radical and mixtures thereof, and R'' is an alkylene radical or substituted alkylene radical of from 1 to about 30 carbon atoms or an arylene radical or a substituted arylene radical. The radicals R, R' and R'' can contain substituents such as, for example, alkyl, alkoxy, cyano, aryl, hydroxy, carboxy, halogen, nitro and other substituent group. The alkylene radical can be straight and/or branched chain, and the arylene radicals can be mononuclear or polynuclear such as phenylene, biphenylene, naphthylene, anthrylene and phenanthrylene radicals. The terms "alkylene and arylene radicals" as used herein and in the appended claims includes substituted alkylene radicals and substituted arylene radicals.

These thickeners, their preparation, and their use in lubicant greases are described in application S.N. 750,050, by Robert J. Rosscup and Hubert J. Liehe, filed July 21, 1958.

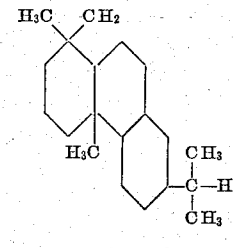
The general structural formula of the abietyl radicals are:



Dehydroabietyl (II)



Dihydroabietyl (III)



Tetrahydroabietyl (IV)

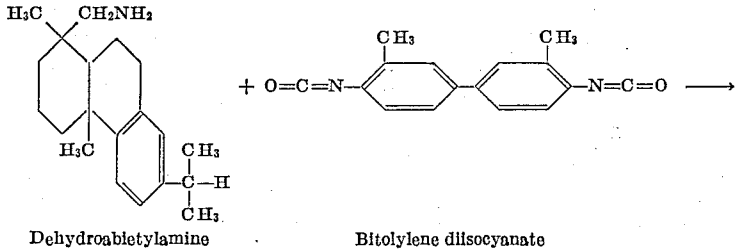
The ureido compound can be prepared by heating a mixture of an abietyl amine and a polyisocyanate in the equivalent weight ratio of 1:1, at a temperature within the range of room temperature (about 70° F.) to about 450° F.

Examples of abietyl amines, i.e. aliphatic amines attached to an alicyclic structure, which can be used in the preparation of the above described ureido compounds are dehydroabietyl amine, dihydroabietyl amine and tetrahydroabietyl amine or mixtures of such amines. A particularly well suited amine is a product marketed by Hercules Powder Company as "Rosin Amine D." This product is prepared by the catalytic hydrogenation of "Rosin Nitrile D" prepared by the action at elevated temperatures of ammonia on hydrogenated rosin. Distilled and undistilled grades are available as "Amine 750" and "Amine 751." The "Rosin Amine D" is a mixture of abietyl amines in the following approximate proportion:

	"Rosin Amine D," percent
Dehydroabietyl amine	60
Dihydroabietyl amine	30
Tetrahydroabietyl amine	10

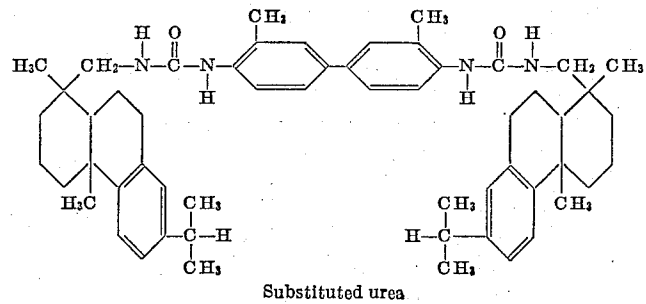
Examples of suitable polyisocyanates are tolylene diisocyanate; p,p'-diisocyanate biphenyl; 1,4-diisocyanatebenzene; p,p'-diisocyanate-diphenylmethane; 1,6-diisocyanate-hexane; 1,12-diisocyanate-dodecane; 1,3,5-benzenetriisocyanate; naphthylene diisocyanate; bitolylene diisocyanate; tris-p-isocyanate-phenylmethane; etc.

The following is illustrative of the apparent thickener-forming reaction which takes place:



Dehydroabietylamine

Bitolylene diisocyanate



Substituted urea

The grease can be prepared by forming the ureido compound in situ in the oleaginous vehicle, or a concentrate of the ureido compound in an oleaginous vehicle can be preformed and the preformed thickener then mixed with the necessary amount of the lubricant vehicle to give a grease product containing the required concentration of the thickener.

In the in situ method of preparing the grease, the desired amount of the polyisocyanate is placed in a high temperature grease kettle, or other suitable heating equipment, containing a major proportion of the liquid lubricant vehicle to be used and the mixture heated to effect solution. To the heated solution is added the abietylamine in a ratio of roughly two moles of amine per mole of polyisocyanate and the balance of the oil, or a solution of the abietylamine in the balance of the liquid lubricant vehicle, and the mixture heated to a temperature of about 200° F. to 450° F. and maintained at said temperature until the product increases to the desired consistency. The acid is then desirably added at this stage, before or after substantial setting up. The temperature at which the mixture sets-up depends largely upon the nature of the liquid lubricant vehicle employed. When using a hydrocarbon oil such as a petroleum oil the mixture sets-up or reaches the desired consistency when the temperature reaches 350°–400° F., while when using a synthetic oil, such as a dialkyl ester of a dibasic carboxylic acid, such as diisooctyl azelate, a dialkyl sebacate, etc., the desired consistency is obtained by heating to 200° F.–320° F. The grease product is then finished by cooling and colloid milling.

Oleaginous lubricant vehicles which can be thickened with the herein described ureido compounds to form greases of the present invention can be silicone polymer oils, mineral lubricating oils, synthetic hydrocarbon lubricating oils such as polybutenes or hydrogenated polybutenes, synthetic lubricating oils such as polyalkylene glycols and their derivatives, high molecular weight esters of dicarboxylic acids such as di-2-ethylhexyl adipate or o-phthalate, polyfluoro derivatives of organic compounds such as the trifluorovinyl chloride polymers known as "Florolube" (made by Hooker Chemical Company) and the trifluorochloroethylene polymers, known as "Kel-F-40" (made by the M. W. Kellogg Company), certain specialty lubricant fluids such as trimethylol propane pelargonate or pentaerythritol hexanoate, and other lubricant vehicles.

Other oleaginous vehicles which may be employed herewith are, for example, mineral oils in the lubricating

oil viscosity range, i.e. from about 50 S.S.U. at 100° F. to about 300 S.S.U. at 210° F. These mineral oils may be suitably solvent extracted, with phenol, furfural, B,B'-dichlorodiethylether (Chlorex), liquid SO_2, nitrobenzenes, etc. Synthetic lubricating oils resulting from polymerization of unsaturated hydrocarbons or other oleaginous materials within the lubricating oil viscosity range such as high molecular weight polyoxyalkylene compounds such as polyalkylene glycols and esters thereof, aliphatic diesters of dicarboxylic acids such as the butyl, hexyl, 2-ethylhexyl, decyl, lauryl, etc., esters of sebacic acid, adipic acid, azeleic acid, etc., are thickened by the ureido compounds to produce excellent greases. Polyfluoro derivatives of organic compounds, particularly hydrocarbons, and dibasic acid esters of $H(CF_2)_2CH_2CH$ in the lubricating oil viscosity range can be thickened. Other synthetic oils, such as esters of aliphatic carboxylic acids and polyhydric alcohol, e.g., trimethylolpropane pelargonate, pentaerythritol hexanoate, can be used as suitable oil vehicles.

As indicated earlier, all organic carboxylic acids are suitable for use herewith. Ordinarly, the acid is present in a concentration ranging from as little as 0.001 weight percent on total grease, or less, to as much as 2.0 weight percent or even more, with the particular concentration depending on acid efficacy and the degree of improvement desired. Concentration ranges of about 0.01–1.0 appear to be optimum.

A number of organic carboxylic acids suitable for the present purposes are listed in Kirk and Othmer's "Encyclopedia of Chemical Technology," vol. 1, pp. 139–157 (Interscience), under the titles "Acids, carboxylic," and "Acids, dicarboxylic." The acid may be aromatic, aliphatic, alicyclic, or heterocyclic; may be saturated or unsaturated, and may contain non-hydrocarbon substituents which do not interfere with grease performance. Similarly, monocarboxylic or polycarboxylic acids (or their anhydride forms) may be used, and while there is some preference for monocarboxylic acids of 1–20 carbon atoms per carboxyl group, with but one carboxylic group per molecule, the invention is not restricted to these. Further, the saturated hydrocarbon carboxylic acids such as acetic acid appear to be the most effective.

Illustrative of the acid types which may be used are: aliphatic unsubstituted such as formic, acetic, propionic, n-butyric, i-valeric, methylethylacetic, trimethylacetic, caproic, heptoic, caprylic, pelargonic, capric, undecylic, lauric, tridecyclic, myristic, pentadecylic, palfitic, margaric, stearic, undecyclic and arachidic; aliphatic substituted such as chloracetic, glycolic, lactic, malic, pyruvic, and throglycolic; alicyclic such as hexahydrobenzoic and camphoric; heterocyclic such as picolinic, furoic, and 2-thro-

penecarboxylic; aromatic nonsubstituted such as benzoic o-toluic, o-phthalic (or its anhydride), phenylacetic, and naphthoric; aromatic substituted such as anisic, gallic, and p-aminobenzoic; aliphatic polycarboxylic such as tartaric, citric, etc. It will be appreciated that the foregoing list is neither exhaustive nor exclusive, and hence a variety of other acids may be used.

A particularly useful acid, both by reason of its effectiveness as well as its rust-inhibiting properties, is a polymerized unsaturated fatty acid, preferably one which is oil-soluble and has a molecular weight in the range of from about 300 to about 2000.

The polymerized fatty acids or polymerization products of the unsaturated fatty acids are those such as may be obtained by the polymerization of natural or synthetic mono-carboxylic acids which generally will have 16 to 26 carbon atoms, most frequently 18 carbon atoms, but if synthetic unsaturated fatty acids are used they may have a lesser or greater number of carbon atoms. Examples of the natural fatty acids are those such as linoleic, linolenic, ricinoleic (which upon heating forms linoleic acid), linoleaidic, elaido-linolenic, eleostearic, arachidonic, eicosatrienoic, cetoleic, docosatrienoic and the like. The free fatty acids can be polymerized either thermally or with the assistance of catalysts. A method of thermally polymerizing free fatty acids (see U.S. 2,482,761) consists of hydrolyzing a fat or an oil, adding a small portion of water, and heating in a pressure vessel until substantially all of the di-and tri-unsaturated fatty acids present polymerize. The resultant product is then heated at a reduced pressure to distill off vaporizable constituents, leaving behind the polymerized unsaturated fatty acids. The polymerization reaction is carried out at a temperature of about 300° to 360° C. for about 3 to 8 hours at a pressure varying between 75 and 500 p.s.i.g. The polymerization product may consist of monomers, dimers, trimers, and higher polymers of the unsaturated fatty acids. The various fats or oils which may be hydrolyzed to product the free fatty acids used in the above thermal polymerization are those such as sardine oil, linseed oil, soybean oil, castor oil, peanut oil, palm oil, olive oil, cottonseed oil, sunflower seed oil, and the like.

Another method of preparing the polymerized fatty acids consists of subjecting fats and oils such as have been listed supra (without previous hydrolysis) to a thermal or catalytic polymerization to cause polymerization of the esters of the unsaturated carboxylic acids to the dimers, trimers, and higher polymeriaztion products thereof followed by hydrolysis to yield the corresponding polymers of the acids. A large source of the polymerized unsaturated fatty acids are those residual acids obtained by methanolysis (see U.S. 2,450,940) of the semi-drying or drying type oils such as castor oil, soybean oil, and others listed supra, polymerizing the methyl esters, removing unpolymerized compounds, saponifying the residual esters and freeing polymerized acids therefrom. The products of catalytic polymerization of semidrying oils such as the BF_3 polymerization products of soybean oil, cottonseed oil, or the like also produce polymers suitable for use in the invention.

It should be understood that while various polymerized unsaturated fatty acids may be used, they do not all provide the same effect. A highly preferred source of the polymerized unsaturated fatty acids is obtained as a by-product still residue in the manufacture of sebacic acid by the dry distillation of castor oil in the presence of sodium hydroxide. A method of obtaining such by-product still residues in the manufacture of sebacic acid is described in U.S. 2,470,849 issued to W. E. Hanson May 24, 1949. The mixture of high molecular weight unsaturated fatty acids comprises monomer, dimer, trimer and higher polymers in the ratio of from about 45% to about 55% of a monomer and dimer fraction having a molecular weight in the range of from about 300 to 600 and from about 45% to about 55% of a trimers and higher polymer fraction having a molecular weight in excess of 600. The fatty acid polymers result in part from a thermal polymerization of fatty acid type constituents of the castor oil, and in part from other reactions such as the intermolecular esterification of such acid to form high molecular weight products. The acid mixture, which is mainly a mixture of polymeric long chain polybasic carboxylic acids, is further characterized by the following specifications:

Acid No.	150 to 164
Saponification No.	175 to 186
Free fatty acids, percent	75 to 82
Iodine value	44 to 55
Non-saponifiables, percent	2.5 to 5

A fatty acid mixture such as above described is marketed under the trade name Hardesty "D–50 Acids" and also as "VR–1 Acids."

The polymerization products of the unsaturated fatty acids may have a molecular weight between about 400 and 2000. Those polymers having a molecular weight higher than about 500, and especially those having molecular weight averaging about 800 or higher are particularly preferred for use in this invention. The polymerization products may consist primarily of dimers and trimers of linoleic acid, for example Emery 955 dimer acid which contains 85% of the dimer, 12% of the trimer, and 3% of the monomer of linoleic acid may be used. Especially preferred polymerized unsaturated fatty acids are the polymerization products of acids such as linoleic acid having a molecular weight between about 300 and 2000, wherein the polymerization products consist predominantly (50% or more by weight) of the dimer, with lesser amounts of monomer, trimer, etc. A commercially available predominantly-dimer polymerized linoleic acid is Empol 1022, manufactured by Emery Industries, Inc.

The following is illustrative of the preparation of acid-containing lubricating greases in accordance with the present invention:

Preparation of grease

110 grams of bitolylene diisocyanate was mixed with a large proportion (about 90%) of the total amount of a solvent extracted base petroleum oil to be used, and the mixture heated to about 210° F. to effect solution of the isocyanate in the oil. To the heated solution were rapidly added 276 grams of dehydroabietyl amine, and the mixture maintained at a temperature of 210° F. The mixture was heated to about 390° F.; heating was then terminated, and the mixture stirred for about 1 hour. At 250°–225° F. the balance of the oil and the acid were added. The grease product was then finished by passage through a colloid mill. The final grease contained 8.5% thickener.

To illustrate the exceptional mechanical stability of the ureido-thickened greases when treated according to the invention, a series of tests is conducted by preparing several greases with widely differing acids and measuring their physical properties. The following inspections are made.

(1) *Penetration.*—ASTM D1403-56T. A measure of grease hardness or consistency is obtained by measuring the distance a falling weighted ¼" cone enters a cup of grease.

(2) *Mechanical stability.*—The resistance of a grease to change upon physical working is measured by determining the ASTM penetration on a grease as obtained from the mill or homogenizer, and again after working 60 strokes in the ASTM D217-52T worker. The percentage change in penetration is taken as a quantitative indication of the mechanical stability.

(3) *Leakage.*—A 10-gram grease sample in a 60-mesh screen cone is placed on a tared beaker in an oven at 212° F. Leakage is determined by weighing the amount of oil in the beaker after 24 hours testing.

(4) *Roll stability.*—The mechanical stability of a grease while working under compressive load is determined by rolling a sample of the grease in a tube containing an eleven-pound bar, in accordance with the test described in Inst. Spokesman, 6, (1943), page 2. The change in ASTM penetration before and after rolling is a measure of mechanical stability in rolling friction service under load.

(5) *General Electric Whip Test.*—The ability of a grease to perform in an overpacked high speed, sealed ball bearing is determined by completely filling the race of a clean 306 ball bearing with the test grease and running the bearing at 3450 r.p.m. for 20 hours at 105° F. At the conclusion, grease leakage is determined and the bearing is disassembled. A small sample of grease is tested for penetration ("unworked"), after which the bearing is manually rotated at one cycle per second for 30 seconds; a sample of the softest grease is removed and immediately tested for penetration ("worked").

The following results were observed:

Grease	A	B	C	D	E	F
Acid, Wt. Percent:						
Acetic	------	0.05	0.10	------	------	------
12-hydroxy Stearic	------	------	------	0.5	------	------
Dodecenyl Succinic	------	------	------	------	0.3	------
Dilinoleic	------	------	------	------	------	0.5
Penetration:						
Unworked	288	272	272	231	256	247
Worked	292	272	276	235	264	252
Leakage, Percent	0.09	0.13	------	------	------	------
Whip Test:						
Penetration:						
Unworked	(1)	268	219	288	260	247
Worked	(1)	272	215	------	252	251
Leakage, Percent	49.0	0.0	0.0	0.0	0.0	0.0
Roll Stability:						
0 Hours	------	272	------	------	------	------
4 Hours	------	264	------	------	------	------
30 Hours	------	272	------	------	------	------
47 Hours	------	292	------	------	------	------

[1] Semi-fluid.

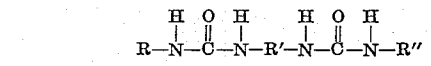
Percentages and parts given herein and in the appended claims are by weight, unless otherwise stated.

Although the present invention has been described with reference to specific embodiments thereof, the invention is not limited thereto, but includes within its scope such modifications and variations as come within the broad scope and spirit of the appended claims.

We claim:

1. A lubricating grease composition comprising a normally liquid lubricant vehicle thickened with from

about 2% to about 25%, by weight, of at least one ureido compound having the general formula



wherein R and R'' are abietyl radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, a tetrahydroabietyl radical and mixtures thereof, and R' is an organic radical selected from the group consisting of an alkylene radical of from 1 to about 30 carbon atoms, and an arylene radical, and containing a small amount, effective to improve the leakage characteristics and mechanical stability of said grease in overpacked ball bearings, of an organic carboxylic acid.

2. The grease of claim **1** in which the normally liquid lubricant vehicle is a mineral lubricating oil.

3. The grease of claim **1** wherein R' is an arylene radical.

4. The grease of claim **3** wherein said arylene radical is a ditolylene radical.

5. The grease of claim **1** wherein said small amount is in the range of about 0.001–2.0 weight percent.

6. The grease of claim **1** wherein said acid is acetic acid.

7. The grease of claim **1** wherein said acid is 12-hydroxystearic acid.

8. The grease of claim **1** wherein said acid is dodecenyl succinic acid.

9. The grease of claim **1** wherein said acid is dilinoleic acid.

References Cited by the Examiner

UNITED STATES PATENTS

2,262,773	11/1941	Lincoln et al.	252—56
2,334,158	11/1943	Von Fuchs et al.	252—56
2,349,044	5/1944	Jahn	252—56
2,611,743	9/1952	Kipp	252—56
2,647,872	8/1953	Peterson	252—56
2,788,326	4/1957	Bondi et al.	252—56
2,971,915	2/1961	Borsoff et al.	252—56
3,015,625	1/1962	Rosscup et al.	252—51.5
3,113,107	12/1963	Borg	252—56

OTHER REFERENCES

"Manufacture and Application of Lubricating Greases," by Boner, Rheinhold Pub. Corp., New York, 1954, pp. 46–49 and 142.

DANIEL E. WYMAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*

I. VAUGHN, *Assistant Examiner.*