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GREASE CONTAINING POLYTETRAFLUOROETHYLENE

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This invention relates to lubricating compositions and more particularly to thickened lubricants suitable for use on bearings operating at high temperatures and high rotational speeds.

The trend in design of modern engines has accentuated the need for lubricants which will lubricate anti-friction bearings operating at high rotational speeds and high temperatures. While considerable progress has been made in producing lubricants which will effectively lubricate bearings operating at high temperatures, some difficulty has been experienced in producing a lubricant which will also effectively lubricate bearings operating at high rotational speeds for prolonged periods of time. Conventional liquid lubricants because of their tendency to be thrown from a fast rotating bearing by centrifugal force have failed to meet the stringent requirements on such lubricants.

We have discovered that a lubricating composition having satisfactory lubricating characteristics for an extended period of time when used to lubricate bearings operating at an elevated temperature and a high rotational speed can be obtained by incorporating a small amount of a tetrafluoroethylene polymer into an oil thickened to a consistency of a grease with an oil thickening agent. The improved lubricating composition of our invention therefore comprises a major amount of a lubricating oil thickened to a grease consistency with an oil thickening agent and having incorporated therein a small amount of a tetrafluoroethylene polymer.

The lubricating oil in which the thickening agent and the tetrafluoroethylene polymer are incorporated is preferably a lubricant of the type best suited for the particular use for which the ultimate composition is designed. Since many of the properties possessed by the lubricating oil are imparted to the ultimate lubricating composition, we advantageously employ an oil which is thermally stable at the contemplated lubricating temperature. Some mineral oils, especially hydrotreated mineral oils, are sufficiently stable to provide a lubricating base for preparing lubricants to be used under moderately elevated temperatures. Where temperatures in the order of 400° F. and above are to be encountered, synthetic oils form a preferred class of lubricating bases because of their high thermal stability. By the term "synthetic oil" we mean an oil of non-mineral origin. The synthetic oil can be an organic ester which has a majority of the properties of a hydrocarbon oil of lubricating grade such as di-2-ethylhexyl sebacate, dioctyl phthalate and dioctyl azelate. Instead of an organic ester, we can use polymerized olefins, copolymers of alkylene glycols and alkylene oxides, polyorgano siloxanes and the like.

The liquid polyorgano siloxanes because of their exceedingly high thermal stability form a preferred group of synthetic oils to which the oil thickening agent and the tetrafluoroethylene polymer are added. These polyorgano siloxanes are known commercially as silicones and are made up of silicon and oxygen atoms wherein the silicon atoms may be substituted with alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals. Exemplary of such compounds are the dimethyl silicone polymers, diethyl silicone polymers, ethyl-phenyl silicone polymers and methyl-phenyl silicone polymers.

In those instances where a mineral oil is used as the base oil, it may be a refined or semi-refined paraffinic-, naphthenic-, or asphalt-base oil having a viscosity of about 50 to 4000 SUS at 100° F. The viscosity of the oil has little effect on the dropping point of the ultimate lubricating composition, but the more viscous oils produce compositions having greater stickiness and adhesive properties than do the lighter viscosity oils. If desired, a blend of oils of suitable viscosity may be employed as the lubricating oil base instead of a single oil by means of which any desired viscosity may be secured. Therefore, depending upon the particular use for which the ultimate composition is designed, the lubricating oil base may be a mineral oil, a synthetic oil, or a mixture of mineral and/or synthetic oils. Although the lubricating oil content of the compositions prepared according to this invention preferably comprises about 80 to about 95 percent by weight of the total composition, it can be present in amounts as low as 50 percent and as high as 97 percent.

The tetrafluoroethylene polymer employed in the lubricating composition of the present invention is itself well-known in the art. Polymerized tetrafluoroethylene and a method of preparing it, for example, are disclosed and claimed in U.S. Patent No. 2,230,654 which issued on February 4, 1941, to Roy J. Plunkett. Polymerized tetrafluoroethylene is generally obtained as a white or brown powder or jelly which rapidly changes to a powder. The polymer is insoluble in the usual solvents including hot and cold water, acetone, ether, petroleum ether, ethyl alcohol, isoamyl alcohol, carbon tetrachloride, $C_2F_3Cl_3$, dichlorobenzene, ethyl acetate, pyridine, nitrobenzene, 30 percent aqueous sodium hydroxide, petroleum oil, glacial acetic acid, concentrated sulfuric acid and concentrated nitric acid. It is inert to the usual chemical reagents and does not burn. It is a crystalline material which undergoes a reversible transition at temperatures above about 325° F.

In preparing the lubricating composition of the invention, we can use either powdered polymerized tetrafluoroethylene or aqueous polytetrafluoroethylene dispersions containing from about 25 percent to about 75 percent by weight of polytetrafluoroethylene. Suitable concentrated aqueous colloidal dispersions and a process for preparing them are disclosed and claimed in U.S. Patent No. 2,478,229, which issued to Kenneth L. Berry on August 9, 1949. According to the patent concentrated aqueous colloidal dispersions of polytetrafluoroethylene may be obtained by polymerizing tetrafluoroethylene in the presence of water, adding a surface-active agent to the dilute suspension, flocculating the polymer by insolubilizing the surface-active agent, separating the flocculated polymer and a small proportion of the aqueous phase from the bulk of the aqueous phase and then peptizing the flocculated polymer. While the polytetrafluoroethylene may comprise about 0.5 to about 45 percent by weight of the total composition, we prefer to use amounts in the order of about 0.5 to about 10 percent by weight. It should be understood, however, that depending upon the properties desired in the ultimate composition less than 0.5 percent or more than 45 percent of the polytetrafluoroethylene can be employed.

The thickening agents which we can employ to thicken the lubricating oil to the consistency of a grease are them-

selves known in the art and do not, per se, constitute a part of the invention. These agents, for example, are exemplified by soaps of fatty acids and organophilic siliceous materials. The amount of the oil thickening agent employed may vary over wide limits depending upon the thickening agent which is used, the particular oil with which the thickening agent is blended and upon the properties desired in the ultimate composition. While the oil thickening agent may comprise about 0.5 to about 45 percent by weight of the total composition, we prefer to use amounts in the order of about 2 to about 25 percent by weight. In any case, the thickening agent is dispersed in the oil in an amount sufficient to produce a composition having the consistency of a grease.

The weight ratio of thickening agent to polytetrafluoroethylene is advantageously between about 0.5:1 and about 20:1. In some instances the ratio of thickening agent to polymer may be as much as 50:1. However, for optimum improvement the ratio of thickening agent to polymer in any particular case depends upon the characteristics of the oil used and the characteristics desired in the final composition. When the oil thickening agent is an organophilic siliceous material such as, for example, dimethyldicetyl ammonium bentonite, a particularly advantageous lubricating composition results when the weight ratio of the bentonite compound to polytetrafluoroethylene is between about 1:1 and about 4:1. Thickened lubricants having superior performance lives in bearing tests are obtained when the weight ratio of the bentonite compound to polymer is about 2:1 to about 3:1.

Typical soap-type thickening agents include the metal soaps of fatty acids such as, for example, the sodium, lithium, copper, magnesium, calcium, zinc, strontium, barium, aluminum and lead soaps of fatty acids having 12 to 24 carbon atoms. The acids may be saturated or unsaturated and may contain substituents such as hydroxyl groups. Aliphatic acids are generally preferred. Examples of the aliphatic acids are lauric, myristic, palmitic, stearic, hydroxystearic, oleic, linoleic, linolenic, arachidic, behenic, lignoceric and selacholeic acids. Mixtures of these acids or mixtures obtained by saponification of natural fats such as cottonseed oil, lard, tallow, castor oil, fish oil, hydrogenated fatty oils, especially the fatty acids derived from hydrogenated animal, vegetable and marine oils known commercially as the "Hydrofol" acids may be used. The soap is formed by saponifying the acid or the fat with a base such as, for example, sodium, lithium, calcium, barium or strontium hydroxide.

Typical non-soap oil thickening agents which can be employed in the lubricating composition of the invention are exemplified by bentonite-organic base compounds known commercially as "Bentones" and finely divided organo-siliceous solids such as the esterified siliceous solids known commercially as "Estersils."

Typical bentonite-organic base compounds employed in accordance with the invention are compounds composed of a montmorillonite mineral in which at least a part of the cation content of the mineral has been replaced by an organic base. Clays that swell at least to some extent on being contacted with water and contain as a primary constituent a mineral of the group known as montmorillonites are generally referred to as bentonites. Such clays, which contain exchangeable alkali metal atoms either naturally or after treatment, constitute the raw materials employed in making the bentonite-organic base compounds used in the compositions of this invention. So far as known, all naturally occurring montmorillonites contain some magnesium and certain of them, as exemplified by Hector clay, contain such a high percentage of magnesium that they largely have magnesium in place of the aluminum content characteristic of the more typical montmorillonites.

The bentonite-organic base compounds are preferably prepared as described in U.S. Patent No. 2,033,856, issued March 10, 1936, to Claude R. Smith, by bringing together the bentonite and the organic base in the presence of aqueous mineral acid to effect base exchange. The organic bases should preferably be titratable with mineral acids. Among these reactive bases are many alkaloids, and cyclic, aliphatic, and heterocyclic amines. The bentonite-organic base compounds used in preparing the lubricating compositions of this invention are preferably those prepared by bringing together a bentonite clay and such organic bases as aliphatic amines, their salts, and quaternary ammonium salts. Examples of such amines and salts are: decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, hexadecyl ammonium acetate, octadecyl ammonium acetate, dimethyldioctyl ammonium acetate, dimethyldidodecyl ammonium acetate, dimethyldodecylhexadecyl ammonium acetate, dimethyldicetyl ammonium acetate, dimethylhexadecyloctadecyl ammonium acetate, dimethyldioctadecyl ammonium acetate, and the corresponding chlorides and quaternary ammonium chlorides. The organic bases employed should be such as to impart substantial organophilic properties to the resulting compounds. The preferred bentonite compounds are prepared from quaternary ammonium compounds in which the N-substituents are aliphatic groups containing at least one alkyl group with a total of at least 10 to 12 carbon atoms. When aliphatic amines are used they preferably contain at least one alkyl group containing at least 10 to 12 carbon atoms.

While the long chain aliphatic amine bentonite compounds are readily dispersible in practically all oil bases, dispersion of the short or single chain aliphatic amine bentonite compounds, in the oil, particularly mineral oils and synthetic oils other than ester lubricants, can be facilitated by the use of one or more solvating agents. Suitable solvating agents are polar organic compounds such as organic acids, esters, alcohols, ethers, ketones, and aldehydes, especially low molecular weight compounds of these classes. Examples of suitable solvating agents are: ethyl acetate, acetic acid, acetone, methyl alcohol, ethyl alcohol, benzoyl chloride, butyl stearate, cocoanut oil, cyclohexanone, ethylene dichloride, ethyl ether, furfural, isoamyl acetate, methyl ethyl ketone, and nitrobenzene. In cases where the use of a solvating agent is desirable for effecting more rapid and more complete dispersion of the organic bentonite compound in the oil, ordinarily only a relatively small amount of such agent may be necessary. However, as much as about 50 percent by weight based on the amount of the bentonite compound can be used.

Typical estersils employed in acordance with the invention are described in U.S. Patent No. 2,657,149, issued October 27, 1953 to R. K. Iler. The estersils are organophilic solids made by chemically reacting primary or secondary alcohols with certain siliceous solids. In brief, the estersils are powders or pulverulent materials the internal structure or "substrate" of which have an average specific surface area of from 1 to 900 square meters per gram. The substrate has a surface of silica which is coated with —OR′ groups, the coating of —OR′ groups being chemically bound to the silica. R′ is a hydrocarbon radical of a primary or secondary alcohol containing from 2 to 18 carbon atoms. The carbon atom attached to the oxygen is also attached to hydrogen.

The estersil substrates are solid inorganic siliceous materials which contain substantially no chemically bound organic groups prior to esterification. The substrates are in a supercolloidal state of subdivision, indicating that whatever discrete particles are present are larger than colloidal size. In general, the supercolloidal substrates have at least one dimension of at least 150 millimicrons. The supercolloidal particles may be aggregates of ultimate units which are colloidal in size.

The estersils which we employ are advantageously those in which the ultimate units have an average diameter of 8 to 10 millimicrons. The substrates advantageously have specific surface areas of at least 25 square meters per gram and preferably at least 200 square meters per gram.

The estersils made from most alcohols become organophilic when they contain more than about 80 ester groups per 100 square millimicrons of surface of internal structure. They become more organophilic as the ester groups increase. Thus, the products which contain 100 ester groups per 100 square millimicrons of substrate surface are more organophilic than those that contain only 80 ester groups. When the estersils contain at least 200 ester groups per 100 square millimicrons of substrate surface, the estersils not only are organophilic but also are hydrophobic. Thus, the more highly esterified products are particularly desirable where the lubricant made therefrom comes in contact with water. When C_3 to C_6 alcohols are used in preparing the estersils, the estersils may contain from 300 to 400 ester groups per 100 square millimicrons of substrate surface. Thus, a preferred group of estersils are those prepared from the C_3 to C_6 alcohols. The estersils, as noted above, are powders or pulverulent materials. The estersil powders are exceedingly fine, light and fluffy. The bulk density of preferred estersils is in the order of 0.15 to 0.20 gram per cubic centimeter at 3 pounds per square inch and in the order of about 0.30 gram per cubic centimeter at 78 pounds per square inch. The estersils are available commercially and thus the estersils per se and their preparation constitute no part of this invention.

In compounding the compositions of the present invention, various mixing and blending procedures may be used. In preparing a soap-thickened lubricant, the soap may be prepared and then added to the oil, or the soap may be prepared in situ. According to one embodiment, for example, the fats and/or fatty acids are charged to an atmospheric or pressure type vessel and intimately mixed at a temperature below 200° F. After thorough intermixture, the temperature is raised to between about 300° and about 400° F. to effect saponification. After complete dehydration of the soap base, the soap is admixed with mineral oil while cooling to a temperature of 150° to 250° F. The polytetrafluoroethylene in the desired proportion is then added to the grease composition. The product is adjusted to the desired consistency and then milled. According to another embodiment, when the soap is prepared in situ, about one third of the total oil, together with all of the acid, and metal hydroxide in an amount sufficient to react with the acid and to produce a composition which is approximately neutral, is placed in a pressure kettle. The contents of the kettle are then stirred and slowly heated to a temperature of about 300° F. under a pressure of about 80 to about 90 pounds per square inch until saponification is complete. The kettle contents are then transferred to an open kettle where stirring is continued and the temperature raised to about 400° F. over a period of about one hour. The temperature is maintained for an additional 30 minutes or until dehydration is substantially complete. The remainder of the oil and the polytetrafluoroethylene are then added and the mixture stirred and heated at about 400° F. for an additional period to remove any water introduced with the polytetrafluoroethylene. The grease composition thus formed is cooled to about 200° to about 250° F. The cooled grease is then pumped to homogenize or otherwise treated as in a colloid mill or similar device to give the desired degree of dispersion. When the soap is prepared in situ, a small amount, i.e., 1 to 3 percent by weight, of glycerin, particularly when an excess of saponifying base is employed, increases the dropping point of the final grease composition.

In preparing a non-soap thickened lubricant, the lubricating oil, the polytetrafluoroethylene and the organophilic siliceous thickener together with a solvating agent and conventional lubricant additives, if desired, are mixed together at room temperature for a period of 10 to 30 minutes to form a slurry. During this initial mixing period some thickening is evidenced. Some lumps may be formed. The slurry thus formed is then subjected to a conventional milling operation in a ball mill, a colloid mill, homogenizer or similar device used in compounding greases to give the desired degree of dispersion.

The lubricating composition of this invention can contain conventional lubricant additives, if desired, to improve other specific properties of the lubricant without departing from the scope of the invention. Thus, the lubricating composition can contain a filler, a corrosion and rust inhibitor, an extreme pressure agent, an antioxidant, a metal deactivator, a dye, and the like. Whether or not such additives are employed and the amounts thereof depend to a large extent upon the severity of the conditions to which the composition is subjected and upon the stability of the lubricating oil base in the first instance. Since the polyorgano siloxanes, for example, are in general more stable than mineral oils, they require the addition of very little, if any, oxidation inhibitor. When such conventional additives are used they are generally added in amounts between about 0.01 and about 5 percent by weight based on the weight of the total composition.

In order to illustrate the lubricating characteristics at an elevated temperature and a high rotational speed, grease compositions of the invention were subjected to the test procedure outlined by the Coordinating Research Council Tentative Draft (July 1954), "Research Technique for the Determination of Performance Characteristics of Lubricating Grease in Antifriction Bearings at Elevated Temperatures," CRC Designation L–35. According to this procedure, 3 grams of the grease to be tested are placed in a bearing assembly containing an eight-ball SAE No. 204 ball bearing. The bearing assembly which is mounted on a horizontal spindle is subjected to a radial load of 5 pounds. The portion of the spindle upon which the test bearing assembly is located is encased in a thermostatically controlled oven. By this means the temperature of the bearing can be maintained at a desired elevated temperature which in the tests reported hereinafter was 300° and 350° F. The spindle is driven by a constant belt-tension motor drive assembly, capable of giving spindle speeds up to 10,000 revolutions per minute. The spindle is operated on a cycling schedule consisting of a series of periods, each period consisting of 20 hours running time and 4 hours shutdown time. The test continues until the lubricant fails. The lubricant is considered to have failed when any one of the following conditions occurs, (1) spindle input power increases to a value approximately 300 percent above the steady state condition at the test temperature; (2) an increase in temperature at the test bearing of 20° F. over the test temperature during any portion of a cycle; or (3) the test bearing locks or the drive belt slips at the start or during the test cycle.

The lubricating oil used in preparing illustrative lubricating compositions of the invention, comprised a highly refined paraffinic mineral oil having as typical properties an API gravity of 30.2°, a viscosity of 303 SUS at 100° F. and 53.9 SUS at 210° F., a viscosity index of 107, a flash point of 420° F., a fire point of 530° F., and a pour point of +5° F. In preparing the lubricating composition with a soap-type thickening agent, the soap was prepared in situ. The polytetrafluoroethylene was then added to the grease and homogenized. In preparing the lubricating composition with a non-soap thickening agent, the oil, the polytetrafluroethylene and the thickener were mixed at room temperature for a period of 10 to 30 minutes. The slurry thus formed was passed twice through a Premier Colloid Mill set at a stator-rotor clearance of 0.002 inch. The "Hydrofol 150" which was used is marketed by Archer-Daniels-Midland Co., Minneapolis, Minnesota. "Hydrofol 150" is made up of about 10 percent C_{16} and 90 percent C_{18} straight chain fatty acids. As typical properties, "Hydrofol 150" has a titer of 64–65° C., and iodine number of 3, an acid number of 195–199 and a saponification number of 196–200. The thickened

lubricating compositions which were thus prepared had the following approximate make-up:

Table I

Composition, percent By Weight	A	B	C	D	E	F
Mineral lubricating oil	66.85	89.1	85.72	88	85.5	83
Polytetrafluorethylene powder	6.41					
Aqueous colloidal dispersion of polytetrafluorethylene (53.6% polytetrafluoroethylene)		1.0	4.76	5	7.5	10
Dimethyldicetyl ammonium bentonite		9.9	9.52	7	7.0	7
Hydrofol acids 150	21.73					
Sodium hydroxide	3.48					
Glycerin	1.53					
Approximate ratio of thickener to polytetrafluoroethylene	4:1	18:1	4:1	3:1	2:1	1:1
Inspection:						
Penetration (ASTM D217—52T):						
Unworked	220	210	207	260	275	256
Worked	300	223	255	249	282	268
Dropping Point, ° F. (ASTM D566—42)	387	450+	450+	450+	450+	450+
Performance Life, hours 10,000 r.p.m.:						
At 300° F.			808	1,596	2,544	775
At 350° F.	240	140	384	95		108

The long performance life of the compositions of the invention at high temperatures and a high rotational speed is self-evident from the data summarized in Table I. It will be noted that compositions in which the ratio of thickener to polytetrafluoroethylene is between about 1:1 and 4:1 have especially good performance characteristics and that the compositions wherein the ratio of thickener to polytetrafluoroethylene is about 2:1 to 3:1 (Compositions E and D, respectively) have superior performance lives at 300° F.

Other lubricating compositions within the scope of the invention are illustrated in Table II.

Table II

Composition, Percent By Weight	G	H	I	J	K	L	M	N
Mineral lubricating oil	93	92	91	90	88	93	91	88
Dimethyldicetyl ammonium bentonite	4	4	4	4	4	4	4	4
Polytetrafluoroethylene powder						1	3	6
Aqueous colloidal dispersion of polytetrafluoroethylene (53.6% polytetrafluoroethylene)	1	2	3	4	6			
Methanol	1	1	1	1	1	1	1	1
Octylated diphenylamines (antioxidant)	1	1	1	1	1	1	1	1
Approximate ratio of thickener to polytetrafluoroethylene	7:1	4:1	2:1	2:1	1:1	4:1	1:1	0.7:1
Inspection:								
Penetration (ASTM D217-52T):								
Unworked	314	330	309	333	338	316	313	295
Worked	328	335	309	342	356	291	301	304
Dropping Point, ° F. (ASTM-D566-42)	450+	450+	450+	450+	450+	450+	450+	450+

Other lubricating compositions within the scope of the invention are illustrated in Table III. G. E. Silicone 81717 is marketed by General Electric Company and is a water-white to amber liquid polymer of the general formula

$$[—Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2O—]_x$$

It has a viscosity at —65° F. of 3487 centistokes, at 0° F. of 390 centistokes, at 100° F. of 71.3 centistokes, at 210° F. of 22 centistokes and at 700° F. of 1.9 centistokes.

Estersil GT is marketed by E. I. du Pont de Nemours and Company and consists of an amorphous silica coated with approximately 340 butoxy groups per 100 square millimicrons of surface. The product is a white granular solid comprising 88 to 89 percent SiO_2 having an ultimate particle size of 8 to 10 millimicrons. The surface area comprises about 285 to 335 square meters per gram. The product has a pH in a 50–50 methanol-water mixture of 8.0 to 9.0 and a bulk density of 19 to 20 pounds per cubic foot.

DC 550 Fluid is a synthetic oil marketed by Dow-Corning Corporation. This fluid is a methylphenyl-siloxane polymer having as typical characteristics a viscosity at 100° F. of 300 to 400 SUS, a viscosity-temperature coefficient of 0.75, a freezing point of —54° F., a flash point of 600° F. and a specific gravity 25° C./25° C. of 1.08.

Table III

Composition, Percent By Weight	A	B	C	D	E	F	G	H	I	J
Lubricating Oil:										
DC 550 Fluid	50			80						
G.E. Silicone 81717		60			90					
Di-2-ethylhexyl sebacate			70			97				
Mineral oil							70	70	80	79
Thickener:										
Dimethyldicetyl ammonium bentonite	25									
Dimethyldidodecyl ammonium bentonite		30								
Dimethyldioctyl ammonium bentonite			25							
Dimethyldioctadecyl ammonium bentonite				10						
Estersil GT					8					
Lithium stearate						2				
Sodium stearate							24			
Calcium stearate								27		
Barium stearate									19	
Strontium stearate										20
Polytetrafluoroethylene	25	10	5	10	2	1	6	3	1	1
Ratio of thickener to polytetrafluoroethylene	1:1	3:1	5:1	1:1	4:1	2:1	4:1	9:1	19:1	20:1

While our invention has been described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claim hereinafter made.

We claim:

A lubricating composition capable of functioning at temperatures up to about 300° F. consisting essentially of a major amount of a mineral lubricating oil thickened to the consistency of a grease with dimethyldicetyl ammonium bentonite and having incorporated therein about 0.5 to about 45 percent by weight of an aqueous colloidal dispersion of polytetrafluoroethylene, said aqueous colloidal dispersion consisting of about 25 to about 75 percent by weight of polytetrafluoroethylene and about 75 to about 25 percent by weight of water, the weight ratio of the bentonite compound to the tetrafluoroethylene polymer being about 2:1 to about 3:1.

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