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LUBRICATING COMPOSITION COMPRISING POLYTETRAFLUOROETHYLENE

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ABSTRACT OF THE DISCLOSURE

A lubricating grease and oil composition consisting of 3.75 to 15.0 percent of moderate molecular weight polyethylene, an equal amount of high molecular weight polytetrafluoroethylene, and the balance of lubricating oil.

This application is a continuation in part of application Ser. No. 618,253, filed Feb. 1, 1967, and now abandoned, of the same title.

This invention relates to lubricating grease compositions and to the process for their manufacture.

In particular, the invention relates to lubricating grease compositions having outstanding structural stability and protective action in severe bearing services. Still more particularly, the invention relates to a method for compounding the ingredient compositions to produce a stable homogenous grease material.

A principal object of the invention is to provide new and improved lubrication oil and grease.

Another object of the invention is to provide new and improved lubricating oil and grease including 3.75 to 15.0 percent polyethylene and an equivalent amount of polytetrafluoroethylene.

Another object of the invention is to provide new and improved lubricating oil and grease including a percent of polyethylene and polytetrafluoroethylene.

Another object of the invention is to provide a new and improved method for making lubrication oil and grease.

Lubricating greases are specially compounded mixtures in which a base oil is modified by thickeners selected from among fatty acid soaps, mineral diatoms, organic polymers, and by numerous other additives serving to prevent phase separation, as antioxidants, rust inhibitors and other specific corrective or enhancing additives. For certain lubricating purposes the lubricating grease compositions require structural stability in order to withstand high shear stresses, prolonged oxidation or hydrolytic activity which can break down the homogenized, uniform structures. In this breakdown the greases lose their viscosified structure whereupon the thickener and oil phase out or separate, thus depriving the metal interface of the needed protection. Usually the thickeners are either metal salts or fatty acids such as aluminum stearate and lithium hydroxystearate, which are nominally expensive additives or inexpensive mineral diatoms like bentonite clay or inexpensive polymers like polyethylene..

The selection of the thickeners is dictated by the type of lubricating service that is involved including economy. Hence, many greases adopt mixtures of different kinds of thickening agents such as proportionate ratios of metal soaps with bentonite clay, bentonite with organic base compounds described in U.S. Patent 3,033,856, toluene-soluble polyethylene with cross-linked toluene-insoluble polyethylene as described in U.S. Patent 3,310,695, and polytetrafluoroethylene with bentonite-organic base as described in U.S. Patent 3,159,577. All of these combinations provide an effective improvement in the required

specifications of structural stability as prescribed by ASTM test D217–52T, high dropping point as prescribed by ASTM test D566–42, high temperature performance life in a proximated test, and several other qualifying test standards.

However, grease compositions embodying these thickening agents fail in prolonged or excessive services in some respects when it comes to performance, storage, and preparations, which require adjustments in the ratios of the selected thickening agents. The metal soaps in some bearing systems can be corrosive to the metallurgical entities and can cause stress cracking in plastic bearings. The bentonites are frequently hygroscopic and can induce hydrolytic breakdown of the oil base and undergo bleed-out, a phenomena whereby the physical saturation or adsorption changes under bearing stress. Polyethylene while substantially resistant to hydrolytic reaction undergoes slow but relentless oxidation and crystallization under frictional wear and stress. Polytetrafluoroethylene similarly used as a thickener is most resistant chemically and thermally, but it has yet to be compounded effectively for a stable and homogeneous mixture and requires several critical polymer specifications and preparative details to provide a stable and service durable lubricating grease composition. It is, therefore, the object of this invention to describe the ingredient composition including their detailed characteristics that provide improved and uniquely different grease endowed with significantly greater endurance and to describe a preparative method for making a homogeneous mixture of uniform consistency rather than a mixture of separated phases.

The principal thickeners of this invention comprise polytetrafluoroethylene and polyethylene at a specified critical ratio added to an oil base. The polymers are most effective as mutually-complementing thickeners when selected from well defined physical characterization since as polymers they cover broad, infinite variations. In the first place their molecular weights can range for several orders of magnitude. Polytetrafluoroethylene is available in a wide range of molecular weights and according to ASTM description 1457–62T which describes this molecular weight variability and particulate physical characteristics and assigns Types I, II, III, and IV in relation to a standard specific gravity range as a measure of molecular weight, referred to in a publication by Sperati and Starkweather, Advances in Polymer Science, vol. 2, pp. 465–495, 1961.

Types I, II, and IV represent high molecular weight polymers endowed with properties that render them as hard and relatively resilient polymers used specifically for molding operations. These three types, often referred to in the trade as granular powders, vary in gross particle size and internal, spongiform structure as depicted for instance in FIGURE 1 of the publication by Sperati and Starkweather referred to above. Thus, Type I is the coarsest with an average particle diameter of 600 ± 100 microns. It too forms a heterogenous, non-uniform grease in which the course particles settle out and leave an oily rather than a grease-like body. Type IV on the other hand is a much finer variation with particles than are less than 100 mesh and often available in grades below 200 mesh size. It was found in our work-up by the cooking procedures described in Example 1 that the minus 100-mesh range furnishes markedly different grease consistency than either Type I and II and that the consistency and especially smooth run-out, i.e., filming, is better as the mesh size opening decreases. In fact this is a surprising feature made more evident when a bearing surface moves over the spread of this filming. With Type IV, of less than 100 mesh, there is no forward-sweeping of the resin particles, such as the case with Types I and

II. This mesh size is thus important on this account as well as the non-sedimenting feature.

Type III, commonly referred to in the trade as lubricant extrusion powder, is a relatively lower molecular weight, fine-grade polymer uniquely suited for film casting and paste extrusion as described by Lontz and coworkers in Industrial and Engineering Chemistry, volume 44, pages 1800 and 1805 (1952). In a similar bearing test, Type III, by virtue of its filming characteristics, readily coalesces under bearing stress into fibrils and flakes which deprive the cooked grease preparation of its prepared consistency. Indeed, on short stressing in a bearing, the Type III component flows away and is pushed away from the bearing surfaces thus leaving the lubricant oil exposed to the working surface and thus deteriorates as an oil rather than a protective grease. Thus, the phase separation here fails as a grease and the unthickened oil soon seeps out causing excessive wear on the bearing surfaces. The simple spread filming test most pointedly demonstrates the inoperable feature of the low molecular weight Type III polytetrafluoroethylene even though its particle size as depicted in the publication by Sperati and Starkweather is substantially below that of high molecular weight Type IV as specified by the SSG value. The ASTM specification D1457–62T for Type IV specifies SSG of 2.13 to 2.19.

In the practice of this invention it has been found that an unsuspected marked difference in grease consistency, compounding, and structural stability is evident depending upon which ASTM type is used. Of the preferred high molecular weight resins, specified by their respective standard specific gravity values, the coarse Types I and II resins produced stable greases but with gross spongiform particles and the fine Type IV furnished an even more uniform and homogenous grease. The lower molecular weight Type III compositions were less preferred by reason of intractable mixing and compounding and marked tendency to phase out as fibrils and flakes during use as a grease composition thus rendering the composition significantly less effective in extreme and/or prolonged bearing service. This invention is based on this surprising discovery and clearly reflects the preference of a high molecular polytetrafluoroethylene polymer in combination with a particle size less than 100 mesh screen size as an essential ingredient.

The polyethylene as a thickening agent serves two useful functions and is a necessary adjuvant to the above-mentioned heat-resistant and chemically-resistant polytetrafluoroethylene. The first function is to provide a viscosifying or bodying effect so that the stiffened quality and the useful dropping point (DP) as measured by the ASTM D566–42 are attained to the level suited for grease applications. This function is not fulfilled by the insoluble polytetrafluoroethylene alone and to achieve it, it has been discovered that low molecular weight polyethylenes with minimal of one percent by weight solubility in the oil is necessary. The second function, as discovered in experiments leading to the preferred aspects of this invention, has been to provide micro-crystalline structures that do not coalesce under stress or frictional heat for which a specified grade of polymer is preferred, one that either totally or in part will provide the microcrystalline structure following the critical high-temperature compounding of ingredients as described in subsequent discussion. These functions limit the selection from the infinite variations of known forms of polyethylene to low molecular weight, and well-formed morphological characteristics.

In the case of the polyethylene additive, the molecular weight, expressed as weight average, is limited to a range of 5,000 to 30,000 with a preferred range of 10,000 to 20,000. For the optimal morphology of polyethylene it has been found that the cooking or dissolution schedule should be below the melting point of the polymer in order to attain the maximum polymer crystallization which provides the colloidal or micellular consistency to the prepared grease. Their limits are dictated by (a) the high molecular weight side to provide adequate solubility or compatibility with the base lubricant, on the one hand, and by (b) the low molecular weight side to provide a gelled, stable structure. Too high molecular weight, beyond 30,000 as determined by conventional methods and especially melt flow index, defined by ASTM D1238–65T, fails to provide the necessary dissolution to a gel with the microcrystalline micells. Too low molecular weight, below 5,000, causes gross crystallization into hard, gritty solid phase separation.

EXAMPLE 1

Based on numerous variations in ingredient addition sequence, warm-up schedules up to melting range of polyethylene, agitation rate, and cooling procedure, the following composition was developed for optimal structural stability and high dropping point.

Ingredient	Weight, grams	Grade and/or specification
Mineral oil	8.6	U.S.P. Heavy duty—Drukal No. 35. Pennsylvania Refining Company.
Polyethylene	7.0	Weight average molecular weight, 23,800
Polytetrafluoroethylene.	7.0	"Teflon" 7A (ASTM Type IV). E. I. Du Pont de Nemours & Co. Inc. (SSG, 2.137; particle size, average 37 microns).

(1) The mineral oil with the added polyethylene is warmed to 140° C. in a 250 ml. Pyrex beaker equipped with a stainless steel paddle type stirrer operated between 250 and 500 r.p.m. (2) The mixture is held for 30 to 90 minutes during which time the polyethylene assumes partial, quasi-solution with attendant thickening of the mixture. (3) The micro-pulverized polytetrafluoroethylene is then added with continued 15 minutes agitation following which (4) the agitated mixture is maintained at temperature for a minimum of 30 minutes, and then allowed to cool to ambient temperature to produce a stiff, coherent, homogenous gel. Each of these steps in conjunction with specified characteristics of the thickeners, polyethylene and polytetrafluoroethylene, serve a specific function in changing the characteristics of the raw polymers into distinctly different constitutive forms peculiar to the basic hydrocarbon oil of paraffinic nature. Based on extended series involving combinations of thickeners of varying molecular weight and particulate characteristics, the following tabulation of grease consistency and stability via dropping point indicates the critical balance that has to be adjusted.

Ingredient	Molecular Weight	Proportionate level 1–3	Proportionate level 3–10	Weight Percent 10–30
Polyethylene	Low 10,000	Low DP	Low DP	Low DP.
	Intermediate	Mod. High DP	High DP	High DP.
	High 25,000	Low DP	Sl. gritty	Gritty.
Polytetrafluoroethylene	Low ASTM Type III	Stringy, fibrous	Stringy, fibrous	Stringy, fibrous.
	High ASTM Type IV	Sl. gelling	Gelled	Flakes out in bearings (20).

DP=Dropping Point.

When the cooking temperatures and times are shifted, then a new set of consistencies, gel structure and stability features ensue, some of which are unsuited for grease compositions by reason of either phasing out of the ingredient thickeners, balling, and other qualitative defi-

ciencies. For instance, if the initial hold temperature, (2) above, is less than 30 minutes, the polyethylene maintains its initial, raw gritty feel. The gritty material becomes converted during bearing stress into sloughs and, moreover, if the hold cooking temperature is above the melt temperature by more than 10 degrees C. from the initial melting point, then the polymer slags out as irreversibly fused cruds that are intractable for reprocessing once the recipe is overcooked. The following Example 2 furnishes a tabulation of the effect of cooking temperatures at various hold times in relation to the ASTM penetration test.

EXAMPLE 2

The same formulation as was used in Example 1 above was applied to modified, progressive series of cooking temperatures ranging from 100° to 160° C. in step (1) with a 30 minute hold time at 100° C. to allow for uniform mixing. The penetration values are summarized in the following tabulation.

	ASTM D217-52T Penetration Processing Temperatures, °C.			
	100°	120°	140°	160°
Time (min.):				
5	400	400	400	400
15	400	360	340	315
30	400	330	*305	305
60	400	300	285	330
90	400	295	285	380

*Example 1 conditions.

The results reveal two salient or critical aspects. First, with the particular grade of polyethylene used, the 100° C., the low end of the temperature series, the processing gave poor penetration resistance. Second, at the high end of the processing temperature and above the polymer melting point, the penetration optimum was reached at about 30 minutes beyond which the composition showing increasing penetration with crud formation. It is seen that the use of intermediate temperatures, 120° and 140° C. gave penetration value that remained reasonably constant. This critical feature has not been recognized in any known practice in the art of grease compounding based strictly on some physical conversion of the raw polyethylene to the mineral oil admixture. Density measurements, by means of a density gradient tube as described in ASTM on precipitates of the composition obtained by addition of cold ether-acetone mixtures to dissolve the mineral oil revealed high density microcrystals unlike that of the raw polymer.

EXAMPLE 3

The following series of formulations were made according to the cooling procedures of Example 1 using various proportions of two grades of polytetrafluoroethylene with 7.5 percent level of polyethylene, having an average molecular weight of 23,400 as determined from meet viscosity by reference standards. The resulting grease compositions were emplaced in a series of encased 8-ball bearings in a continuously operated ½-horsepower air-conditioning blower motor to measure oil loss rate as indication of oil-retention of the polytetrafluoroethylene during prolonged, up to 720 hour service. The test results are summarized as follows:

ASTM Polymer	Molecular characterization	Time Running	Oil loss rate, Percent/24 hour: Wt. Percent in Formulation 0	3.75	7.5	15.0
III	Low mol. wt. (dispersion) (SSG, 2.195) ASTM D1457-62-T.	72	11.2	5.6	5.9	5.8
		144	24.6	5.6	5.9	5.8
		288	39.5	*9.2	*7.6	*7.5
		720	*65.1	*18.4	*12.8	*12.7
IV	High mol. wt. (SSG, 2.148) ASTM D1457-62-T.	72	.....	2.7	1.8	1.7
		144	.....	2.9	1.8	1.8
		288	.....	2.7	2.1	2.2
		720	.....	3.1	2.6	2.6

*High titrable acidity.

The above results indicate the markedly superior oil retentivity of the high molecular weight powder in comparison to that of the low molecular weight polytetrafluoroethylene Type III polymer, which also showed marked change into shredded structure, with correspondingly lessened oil-retention power. There are indications that beyond 7.5 percent level there has been little change in oil retentivity for the particular oil base used in this and Example 1.

The control compositions, without the polytetrafluoroethylene and using only 15.0 percent polyethylene, revealed marked oil loss due to some breakdown of this hydrocarbon polymer. At the same time there is considerable, incipient increase in titratable acidity suspected as being due to oxidation of the polyethylene. The concomitant use of both polyethylene and polytetrafluoroethylene provide a surprising advantage for reasons not entirely clear. Microscopic inspection of the bearings indicate that there is some initial, preferential conditioning of the metal bearings with some monomolecular layer or layers of polytetrafluoroethylene thus excluding the polyethylene from the reactive, stress-laden metal-bearing surface.

EXAMPLE 4

A formulation according to the preparative, cooking schedule described in Example 1 with a 10 percent level of polyethylene having an average molecular weight of 23,800 was made using one case an equivalent, 10 percent level of Type I polytetrafluoroethylene (SSG 2.139) with an average particle size of 540 microns and in the other case 10 percent Type IV polytetrafluoroethylene (SSG 2.137) having a particle size less than minus 100-mesh seive with an average size, as determined by air porosity determination, of 37 microns. Applying the same 8-bearing lubrication test as described in Example 3, the oil loss or weep after a 288 hour test run was as follows:

Percent

(a) With Type I polytetrafluoroethylene ____ 15.0
(b) With Type IV polytetrafluoroethylene __ 0.8

When the two composition test runs were continued for 17 days, the bearing with the Type I formulation grease was practically dry with sloughs of flaked Type I particles accumulated and clogged in between the bearings and the bearing operated with an audible squeek and vibrations. The bearing with Type IV grease formulation ran noiseless and with no perceptible vibrations. This practical but highly discriminating test clearly demonstrated the merit of the fine particulate form of the high molecular weight polytetrafluoroethylene. The test further emphasizes, though in a practical way, the gross phase separation of the ingredients which is highly undesirable for bearing mechanics.

EXAMPLE 5

A formulation according to the preparative, cooking schedule described in Example 1 with a 10 percent level of low molecular weight (4400) polyethylene used commercially as a wax was made with 10 percent level of Type IV polytetrafluoroethylene (SSG 2.137) used in above Example 4. Apply the 8-bearing lubrication test

described in Example 3, the oil loss after a 288 hour test run was 13.4 or approximately that of case (a) in Example 4. The polyethylene sloughed off in microscopic flakes causing a looseness in the bearing run and attendant vibrations. There was evidence of degration of the polyethylene. This test emphasized the need for polyethylene higher in molecular weight than that of the wax forms. Substituting a high molecular weight (50,000) polyethylene as determined by conventional ASTM melt index with the equivalent, the equivalent formulation with Type IV gave a gritty grease composition with an incomplete solution phase that sloughed off the polyethylene long before the 288 test was reached. In commercial sense the gritty-textured grease would not be accepted on this account.

From the above example, it is evident that interaction of three components, namely (a) the base lubricant oil serving as the fluid medium, (b) the polyethylene serving as the thickening or viscosifying component, and (c) the low friction, chemically and hence oxidatively resistant polytetrafluoroethylene, has (1) either a stable, common fluid phase or (2) degenerates into an overworked mixture. In the latter instance the relatively low molecular weight polyethylene and polytetrafluoroethylene, Type III as prescribed by the SSG, are clearly undesirable for a grease composition in severe, continuous bearing service. This has been overcome by a specified use of moderate molecular weight of the viscosifying agent, polyethylene, kept within limits to ensure the proper partition between oil solubility and crystalline micelle. Also, the polytetrafluoroethylene has to be of sufficient molecular weight, as determined by the SSG range and less than that of the relatively low molecular weight Type III polymer but with an added requirement of particulate size that must be less than that of the 100-mesh screen and preferable in the range of Type IV polytetrafluoroethylene.

The fact that the compositions of this invention can have either (a) a common phase or (b) degenerate into separated components, is difficult to explain. The phenomenon here may be quite analogous to the inorganic and metallic alloy phase systems existing in the classical concepts of eutetics and solubility diagrams. However, the inorganic or metallic concept obviously cannot predict what would happen in the present base oil-polyethylene-polytetrafluoroethylene compositions in their critical ranges, i.e., ranges of molecular weight and particle sizes that makes for a static, durable grease.

The examples given are based on paraffin, mineral oils as the base ingredient thickened with two different polymers serving quite different purposes. The invention is not intended to be limited to mineral oils and can be applied to synthetic oils or lubricants such as vegetable oil esters, esters of polycarboxylic acids, and silicone oils. Thus the invention relates to grease compositions having an optimal, unique ratio or balance of structural stability, acceptably low penetration, low oil loss or excidency, and particulate forms resistant to sloughing, flaking, shredding and otherwise losing their component structure in the gel. It is understod that other additives, such as corrosion inhibition, extreme pressure additives, scavenging additives, and so on, can be added to augment the merits of the composition described above.

What is claimed is:

1. A lubricating grease composition consisting of 3.75% to 15% of polyethylene having a molecular weight in the range of 5,000 to 30,000, 3.75% to 15% polytetrafluoroethylene of high molecular weight and having a standard specific gravity from 2.13–2.19 and a particle size less than 100 mesh and the balance of lubricating oil.

2. The composition of claim 1 having polyethylene of molecular weight in the range of 10,000–20,000.

3. The composition of claim 1 having polytetrafluoroethylene of high molecular weight and having standard specific gravity of substantially 2.148.

4. The method of making a lubricating grease composition consisting of 3.75% to 15% of polyethylene having a molecular weight in the range of 5,000 to 30,000, 3.75% to 15% polytetrafluoroethylene of high molecular weight and having a standard specific gravity of 2.13–2.19 and a particle size less than 100 mesh and the balance of lubricating oil comprising the steps of:

mixing said polyethylene with mineral oil,

warming the mixture to approximately 140° C.,

holding the mixture for 30–90 minutes for thickening of the mixture,

adding pulverized polytetrafluoroethylene in amount generally equal to said polyethylene and agitating for 15 minutes,

cooking the said mixture at a temperature of approximately 140° C. for a minimum of 30 minutes,

and allowing to cool to ambient temperature to produce a stiff coherent homogenous gel.

5. The method as in claim 4 wherein the cooking range is 120–140° C.

6. The method of claim 5 wherein the polytetrafluoroethylene has a standard specific gravity of substantially 2.148.

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