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3,537,994

ORGANOPHILIC CLAY GREASES

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ABSTRACT OF THE DISCLOSURE

Greases prepared from a lubricating oil vehicle, thickened with an organophilic clay, and optionally containing further additives of known types frequently lack thermal stability, suffering loss of consistency upon prolonged working at high temperatures. In accordance with the invention, this defect is overcome by the inclusion in such a grease of a modicum of tris(hydroxymethyl)amino methane, such as from 1/2 percent to 2 percent by total weight of grease. A particular use of the invention is in connection with organophilic clay greases containing in addition finely divided asbestos.

This invention relates to organophilic clay-thickened greases, and more particularly, to an improvement of the thermal stability of such greases; and to novel asbestos-organophilic clay greases exhibiting thermal stability.

Whereas in past decades lubricating greases have comprised for the most part, hydrocarbon oils thickened with a soap, in recent years a number of non-soap thickening agents have been introduced which offer considerable advantages over the soaps theretofore used. Also, the range of useable lubricating vehicles has been extended to include liquids other than hydrocarbon oils such as various esters, silicone oils, and the like. Greases of the newer types just mentioned are generally known as non-soap-thickened greases. An important sub-group thereof comprises those thickened with clay minerals, such as montmorillonite and hectorite, which have been made organophilic by complexing with a long-chain compound. Greases of this type are described in Jordan Pat. No. 2,531,440 and in various articles in the technical literature, such as that entitled "Bentonite Greases," by C. M. Finlayson et al., The Institute Spokesman, May 1950, pp. 13-23; and in chapter 17 of the book, Lubricating Greases, by C. J. Boner, New York, 1954. Such greases, in common with other greases, may contain further additives such as anti-corrosion additives, extreme pressure additives, finely divided solid lubricants, fluorescence additives, and the like.

It has been found that in the general case, greases of the type described are not always ideal in their behavior upon prolonged working at elevated temperatures. Such action may bring about a loss of consistency, evident in the laboratory tests as an increase in penetration. This may not always be of such a nature that it renders the grease inoperative, but it is clearly desirable to have a grease which retains its physical characters unchanged throughout use.

An object of the present invention is to provide an organophilic clay-thickened lubricating grease containing a modicum of additive so that it has increased stability on prolonged working at high temperatures.

Another object of the present invention is to provide such an additive which is free from deleterious effects on other properties, such as corrosion, response to water contamination, and the like.

A further object of the invention is to provide novel greases containing asbestos which exhibit good thermal stability.

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Other objects of the invention will appear as the description thereof proceeds.

Generally speaking and in accordance with illustrative embodiments of my invention, I incorporate with an organophilic clay-thickened grease a modicum of tris(hydroxy methyl)amino methane. The manner of incorporation, as more fully explained below, may be highly variable, and indeed, the tris(hydroxy methyl)amino methane may be added at any desired stage of preparation of the grease. Again, as more fully explained below, the amount of tris(hydroxy methyl)amino methane is variable within fairly wide limits, but generally will be found to be more than 1/2 percent up to about 2 percent by weight of the grease. The invention has particular use in greases where the thickening effect of the organophilic clay is augmented by the inclusion of asbestos, as will appear more fully hereinbelow.

The lubricating oil forming the base of the grease to which the invention is applicable may be any of those generally employed in the manufacture of lubricating greases wherein the thickener is an organophilic clay. This covers, indeed, the full and wide range of liquid lubricants broadly, and includes, by way of example but not by way of limitation, lubricating oils obtained from petroleum, sometimes called mineral lubricating oils; lubricating oils derived from petroleum by various polymerization and reforming processes, such as the Fischer-Tropsch, Synthol, Synthine, and related processes; lubricating oils produced by the Bergius process as applied to the hydrogenation of coal, peat, and the like, and of asphalts, petroleum residues, and the like; synthetic lubricants produced by the volatilization process, for example, from fatty oils, petroleum hydrocarbons and the like; the so-called ester lubricants, which may be alkyl esters of organic acids, such as dioctylphthalate, ethyl ricinoleate, and the like, or which may be alkyl or alkyl-aryl esters of inorganic acids such as alkyl-aryl phosphorus esters such as tricresyl phosphate; synthetic lubricants made by the polymerization of alkylene oxides and glycols such as pentamethylene glycol; and the silicone polymers known generally as the silicone oils.

The organophilic clay which is employed as a thickener in my invention is a well-known material available in a variety of forms and indeed is an article of commerce and well-described in the book by Boner cited hereinabove. Organophilic clays which are particularly applicable in the invention are primary, secondary, tertiary, and quaternary substituted ammonium salts of montmorillonite, hectorite, attapulgite, and sepiolite, in which the substituted ammonium cation contains at least one carbon chain of 12 or more carbon atoms in length. Thus, I may use the montmorillonite, hectorite, attapulgite or sepiolite salts whereof the cation is dodecylammonium, octadecylammonium, didodecylammonium, dihexadecylammonium, tetradecylbenzylammonium, methyl dioctadecylammonium, dibenzyl dodecylammonium, dimethyldioctadecylammonium, methylbenzyl dihexadecylammonium, and the like.

The tris(hydroxy methyl)amino methane is the ordinary commercial form thereof, and is available under the trade name "Tris Amino."

The asbestos which may be included in the greases to which the invention is applied may be any chrysotile or tremolite which is reasonably free of non-asbestos dross and which has been mechanically or chemically treated so as to separate the fibers to such an extent that individual fibers are not readily seen by the unaided eye. Many procedures are available for carrying this out and need not be described in detail here. Reference may be made to the books, Asbestos Fundamentals, by Berger and Oesper, New York, 1963, and The Colloid Chemistry of Silica

and Silicates, by Iler, Ithaca, 1955, which describe both chemical and mechanical methods of fiber separation.

A specific illustrative example of my invention follows:

EXAMPLE I

A grease was prepared by making a concentration of 13.725 kilograms of a lubricating oil designated as "Conoco 5740," 900 grams of commercial dimethyldihydrogenated-tallow ammonium montmorillonite, and 375 grams acetone, this was dispersed in a laboratory blender to form a very firm gel, which was then diluted with additional oil, with and without the inclusion of tris(hydroxy methyl)amino methane in varying concentrations, so that the final greases contained 5 percent of the organophilic clay, 2.08 percent acetone (which was a dispersing aid for the organophilic clay), and the selected amount of the Tris Amino. These greases were milled in a laboratory grease mill having a clearance of 0.001 inch, and tested for mechanical stability and for thermal stability. The results are given in the table below in which the mechanical stability is shown in standard A.S.T.M. penetration units, and the thermal stability in quarter-scale penetration units.

TABLE 1

Grease	Additive, percent	Mechanical stability ASTM penetration, mm.×10				Thermal stability ¼ scale penetration			
		0×	60×	10,000×	Δ	Initial		250° F., 72 hrs.	
						0×	60×	0×	60×
A1-----	None-----	265	265	326	61	61	63	82	¹ T.T.
A2-----	do-----	265	275	315	40	62	72	76	¹ T.T.
A3-----	T.A. ² ; 0.5-----	252	259	325	66	57	62	71	102
A4-----	T.A. ² ; 1.0-----	252	268	318	50	56	58	62	87
A5-----	do-----	259	272	328	56	57	65	57	76
A6-----	T.A. ² ; 1.5-----	256	266	325	59	56	61	63	82
A7-----	do-----	262	272	332	60	61	63	61	72

¹ T.T. Greater than 107, "too thin" to measure.
² T.A. Tris(hydroxy methyl)amino methane.

In the above, greases A1 and A2 were duplicated preparations. Greases A3, A5 and A7 were made with the same

the organophilic clay has been augmented by the incorporation of asbestos. In Table 2, which follows, the results are given for a series of greases containing increasing amounts of tris(hydroxy methyl)amino methane, and containing equal quantities by weight of dimethyldihydrogenated-tallow ammonium montmorillonite, and of asbestos, viz., 4 percent by weight of each. These greases were prepared by mixing the required amounts of organophilic clay, a relatively high purity chrysotile from near Coalinga, Calif., which has been "opened" by conventional, mechanical treatment to separate the fibers, and the additive in accordance with the invention, with a lubricating oil ("Conoco 5740") for 5 minutes. Four percent by total weight of acetone was then added and mixing continued for 25 minutes. The greases were then heated to 250° F. while still mixing. The source of heat was then removed and the greases allowed to cool to 180° F. while still being mixed. The samples were then milled in a conventional laboratory grease mill "Tri-Homo-Dispenser" set at a rotor-to-stator clearance of 0.001 inch. After

cooling to room temperature, the samples were tested with the results given below.

TABLE 2

Grease	T.A. ¹ , percent	Mechanical stability ASTM penetrations, mm.×10				Thermal stability ¼ scale penetration, mm.×10					
		0×	60×	10,000×	100,000×	Initial		230° F., 168 hrs.		250° F., 72 hrs.	
						0×	60×	0×	60×	0×	60×
1-----	0.0	269	262	250	238	53	51	71	80	70	101
2-----	0.5	281	266	269	256	51	54	60	69	54	74
3-----	1.0	278	252	265	269	49	53	55	68	54	75
4-----	1.5	255	229	244	239	49	54	56	65	56	69

¹ T.A. Tris(hydroxy methyl)amino methane.

concentrate as grease A1; which greases A4 and A6 were made with the same concentrate as grease A2.

It will be noted from the results appearing in Table 1 that the incorporation of the tris(hydroxy methyl)amino methane did not significantly change the mechanical stability of the grease, although some improvement may be noted except for 10,000 strokes working. However, the greases without the additive broke down upon being aged as a thin film at 250° F. for 72 hours, whereas those containing the additive were in excellent condition, even the sample containing the lowest amount of the additive, namely 0.5 percent.

EXAMPLE II

As mentioned earlier, my invention has particular application to those greases in which the thickening effect of

It will be seen from the above tabulation that great improvement was obtained in thermal stability by use of the additive in accordance with the invention.

EXAMPLE III

Some data are given in Table 3 below for the use of the additive in accordance with the invention in a grease thickened with a slightly different kind of organophilic clay, viz, montmorillonite reacted with a mixture of dimethylbenzyoctadecyl and dimethyldioctadecyl ammonium ions. The grease samples were prepared as described for Example II, except that two different lubricating oils were used. For the first group of greases shown, a lubricating oil of SUS viscosity at 100° F. of 400 ("Conoco 400") was used, while for the second group, another lubricating oil of SUS at 100° F. viscosity of 557 ("Gas-

con C") was used. The amount of organophilic clay was 5 percent by weight, and 4 percent by weight acetone was used as a dispersant.

TABLE 3

T.A. ¹	Oil	Percent oil	Mechanical stability ASTM pene., mm.×10 strokes grease worked			Thermal stability AST worked pene., mm.×10 ¹ Hours at 250° F.	
			0X	60X	10,000X	4	72
-0-----	C-400 ²	95.0	325	326	407	397	³ T.T.
0.5-----	C-400 ²	94.5	325	330	390	342	363
1.0-----	C-400 ²	94.0	302	295	332	292	313
1.5-----	C-400 ²	93.5	311	319	346	317	321
-0-----	SGC ⁴	95.0	268	283	322	397	388
1.0-----	SGC ⁴	94.0	297	302	313	292	330
1.5-----	SGC ⁴	93.5	280	290	310	283	296

¹ T.A. Tris(hydroxy methyl)amino methane.

² Conoco 400 Oil.

³ T.T. Too thin to measure.

⁴ Sinclair Gascon "C" oil.

EXAMPLE IV

This is an example showing the improvement in thermal stability imparted by the use of tris(hydroxy methyl) amino methane in a clay base grease in which the thickener is hectorite clay reacted with dimethyl dihydrogenated-tallow ammonium ion. One thousand gram batches of grease were prepared as follows: 50 grams of the dimethyl dihydrogenated-tallow ammonium hectorite were dispersed with stirring in 350 grams of 400 SUS at 100° F. lube oil ("Conoco 5740") and 25 grams of acetone were added. After 25 minutes stirring, the indicated percentage of tris(hydroxy methyl) amino methane was added and stirred for 5 more minutes, the balance of the oil was then added and stirring continued for about 15 more minutes. The grease was then milled through a laboratory "Tri-Homo" colloid mill at 0.4 pound-per-minute and a stator-to-rotor clearance of 0.001 inch.

After standing overnight, the grease was tested for mechanical and thermal stability, with the results indicated in Table 4.

It will be noted that the addition of tris(hydroxy methyl) amino methane was without adverse effect on the mechanical stability and greatly improved the thermal sta-

reduce corrosion is helpful, and I have found that sodium nitrite is particularly well suited for greases of the general type involved in my invention. In Table 5, which follows,

some test results are given for a grease made up of a dry mixture of, by weight, 32.6 percent dimethyldihydrogenated-tallow ammonium montmorillonite, 32.6 percent chrysotile asbestos, 23.0 percent sodium nitrite, and 11.8 percent tris(hydroxy methyl) amino methane. This was incorporated in the lubricating oil described in connection with Example I at two different concentrations of the composite thickener, just described, dispersed with the aid of 2.5 percent acetone based on the total weight of grease. The grease samples were tested in accordance with standard procedures for various types of stability and for bearing corrosion. Table 5 includes test results run in the same series of tests on a sample of a very satisfactory, commercially produced organophilic clay grease designated in the table as D-2. The superior corrosion resistance characteristics of the grease made in accordance with the invention is evident from the tabulation. It may be mentioned that in this particular grease formulation, the lower concentration 7.5 percent composite gellant produced a grease rather lighter in consistency than the comparison commercial grease. Even so, however, the characteristics of this lighter grease held up better water absorption and in various of the other tests, as may be seen from the table.

TABLE 5

Grease	Percent composite gellant	Mechanical stability ASTM penetrations, mm.×10				Water stability ASTM pene., 10% water 100,000X	Bearing corrosion	Oxidation p.s.i. drop, hours		Thermal stability 1/4 scale pene., mm.×10					
		0X	60X	10,000X	100,000X			100	500	Initial		230° F., 168 hrs.		250° F., 72 hrs.	
		0X	60X	10,000X	100,000X			100	500	0X	60X	0X	60X	0X	60X
A-----	7.5	301	299	297	310	318	2	3.5	11	66	68	70	84	65	76
B-----	9.0	276	262	268	272	296	1	4.5	14.5	58	57	64	77	56	60
D-2-----	259	271	280	279	279	423	3	13	26	58	63	66	75	62	77

Grease	Shell roll stability SMC penetrations, mm.×10			Water absorption SMC penetrations, mm.×10										4-ball	
	Initial			percent water absorbed										Mean load	
	165 r.p.m. 150° F.			0	10	20	30	40	50	60	70	80	90	Hertz	Weld
A-----	117	144	164	94	127	130	111	110	109	89	S*	28.2	112		
B-----	87	99	142	97	102	105	101	95	83	S*					
D-2-----	84	116	125	84	155	163	147	152	153	148	S*	26.8	112		

NOTE.—S* could not saturate with this much water.

bility of the grease when exposed as a thin film at 250° F. for 72 hours.

TABLE 4

Percent organic hectorite	Percent tris (hydroxy methyl) amino methane	Mechanical stability ASTM penetration, mm.×10			Thermal stability 1/4 scale pene., mm.×10 ¹ 250° F., 72 hrs.	
		0X	60X	10,000X	0X	60X
5-----	-0-	278	275	359	68	103
5-----	0.5	323	317	373	69	89
5-----	1.0	305	306	368	62	77
5-----	1.5	300	288	348	59	71

¹ 107 on this scale is too thin to measure.

EXAMPLE V

As mentioned, various additives to impart special properties to the grease may be included. An additive to

droxy methyl) amino methane, these being incorporated later with the lubricating oil in order to form the lubricating grease. Considering the thickening ability of com-

mercially practicable organophilic clays, the relative proportion of tris(hydroxy methyl)amino methane to organophilic clay, which corresponds to an amount of the former in the finished grease which is within the range heretofore stated is: from about one-twelfth to about one-third of the weight of said organophilic clay.

When asbestos is used in accordance with the invention, it is likewise in many cases convenient to make a dry mixture by blending of the organophilic clay, the tris(hydroxy methyl)amino methane, and the asbestos. Considering the relative thickening and stabilizing effects of commercially practicable organophilic clays and of asbestos, a practical range of weight of asbestos to organophilic clay in such a dry mix is from about one-half to twice the amount of said organophilic clay.

As mentioned, it is common to include an anti-corrosive agent in greases with an organophilic clay, and examples have been given hereinabove of the use of sodium nitrite as such an agent. Generally speaking, when sodium nitrite is so used, a practicable range of concentration thereof is from about 0.25 to about 1.0 times the weight of the organophilic clay used. Again, where a dry mixture lacking merely the lubricating oil is prepared in advance, it is quite practicable to include any sodium nitrite contemplated as one of the components thereof. In such a case, it will, of course, bear the same weight ratio to the organophilic clay as has been just stated for the grease.

It will be appreciated that while I have described my invention with the aid of numerous specific examples, nevertheless considerable variation in components, relative proportions, sequence of compounding operations, and the like is contemplated within the broad scope of the invention as defined by the claims which follow.

Having described my invention, I claim:

1. A lubricating grease consisting essentially of a lubricating oil, a thickening amount of an organophilic clay, and sufficient tris(hydroxy methyl)amino methane to enhance the thermal stability of such grease.

2. A grease in accordance with claim 1 wherein said tris(hydroxy methyl)amino methane is present within the range of about 0.5 to about 2.0 percent by weight of said grease.

3. A grease in accordance with claim 1 wherein said lubricating oil is a hydrocarbon oil.

4. A lubricating grease consisting essentially of a lubricating oil containing a mixture of organophilic clay and asbestos in amount sufficient to thicken said oil, and an amount of tris(hydroxy methyl)amino methane sufficient to enhance the thermal stability of said grease.

5. A grease in accordance with claim 4 wherein said

tris(hydroxy methyl)amino methane is present within the range of about 0.5 to about 2.0 percent by weight of said grease.

6. A grease in accordance with claim 4 wherein said lubricating oil is a hydrocarbon oil.

7. A grease in accordance with claim 1 in which said clay is selected from the class consisting of montmorillonite, hectorite, attapulgite, and sepiolite.

8. A grease in accordance with claim 4 in which said asbestos is chrysotile asbestos.

9. A grease in accordance with claim 1 which includes a sufficient amount of sodium nitrite to reduce the corrosion properties of said grease.

10. A grease in accordance with claim 4 which includes a sufficient amount of sodium nitrite to reduce the corrosion properties of said grease.

11. A thickener for lubricating greases consisting essentially of a mixture of an organophilic clay and tris(hydroxy methyl)amino methane in an amount of from about one-twelfth to about one-third of the weight of said organophilic clay.

12. A thickener in accordance with claim 11 which contains in addition to said organophilic clay and said tris(hydroxy methyl)amino methane, asbestos in an amount within the range of from about one-half and twice the weight of said organophilic clay.

13. A thickener in accordance with claim 11 which contains in addition an amount of sodium nitrite within the range of from 0.25 to 1.0 times the weight of said organophilic clay.

14. A thickener in accordance with claim 12 which contains in addition an amount of sodium nitrite within the range of about from 0.25 to 1.0 times the weight of said organophilic clay.

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