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LIME BASE GREASE

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This invention is directed to the provision of lime base greases of improved stability under conditions of storage and use, and is directed particularly to the improvement of grease compositions of the type set forth in Carmichael and Hain, U. S. Patent 2,197,263.

The patent above noted is concerned with the provision of lime base greases stabilized against deterioration at relatively high temperatures by the incorporation therein of significant amounts, up to about 5% usually, of the calcium salts of monobasic fatty acids having not over 6 carbon atoms specifically acetic acid.

The purpose of the present invention is to provide a grease of this character in which certain properties have been improved. One of the properties thus improved is that phenomenon known as "skin hardening," i. e., a hardening of the surface of the grease when exposed to combinations of moderate temperature and high humidity. Another property improved is that demonstrated by what is herein referred to as the "Sett" test, wherein the grease is held for a period of hours at a temperature of 300° F., which conditions have been found generally to bring about perceptible hardening of the presently available greases. A third property improved is that of long time storage stability, it having been noted that present greases tend to become harder when stored for long periods of time. While these properties of the present greases are not highly objectionable and have not greatly militated against wide and ready acceptance of the greases as a premium product, they are nevertheless of a nature that should be eliminated, if possible, in working toward a more perfect product.

This invention is based upon the discovery that worthwhile improvements in such greases can be effected by the replacement of a portion of the short-chain fatty acid modifier by phosphoric acid, giving rise to a grease containing a

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lime soap, a lime salt of a short chain fatty acid, and, probably, a lime salt of an acid of phosphorus.

In general, to arrive at such modification of the grease, we prefer to use orthophosphoric acid, but we may use any acid of phosphorus which, under the conditions of grease manufacture will hydrate or hydrolyze with the production of orthophosphoric acid. Such acids are herein indicated as phosphoric acid.

An exemplary composition is the following:

	Percent (weight)
Tallow	13.45
Candelilla wax	4.00
Lime flour	5.25
Glycerine	2.00
Acetic acid	3.20
Phosphoric acid	0.30
Solar Red oil	71.30

This formulation was compounded in the conventional compounding procedure, followed by dehydration, driving off moisture while the grease was being stirred. Dehydration is carried out to a substantial extent, sufficient to give the grease the desired structure and temperature stability.

While the exact reaction into which the phosphoric acid enters has not been studied, it is believed that the result of the neutralization of the phosphoric acid is formation of a calcium phosphate or of a calcium compound of a partial ester of phosphoric acid. It suffices to say that the results desired are obtained by partial substitution of the short-chain fatty acid with phosphoric acid and such language is used for purposes of definition in the claims.

The improved characteristics obtained by this formulation may be observed by consideration of the following table of formulae and test results.

TABLE

Lime base, acetate modified grease, further modified with phosphoric acid

	A	B	C	D	E
Tallow, Per Cent (by wt.)	13.45	13.45	9.85	12.50	10.1.
Candelilla Wax, Per Cent	4.00	4.00	2.93	3.60	2.9.
Lime Flour, Per Cent	5.25	5.25	3.84	4.70	3.8.
Glycerine, Per Cent	2.00	2.00	1.46	1.80	1.4.
Acetic Acid, Per Cent	3.20	3.60	2.63	3.30	2.7.
Phosphoric Acid, Per Cent	0.80	0.40	0.29	0.20	0.2.
Solar Red Oil, Per Cent	71.30	71.30	79.00	73.90	78.9.
Ratio of Phosphoric Acid to Acetic Acid.	1:4	1:9	1:9	1:16	1:13.
Analysis:					
Alkalinity, CaO, Per Cent	0.5	0.45	0.3	0.34	0.3.
Saponified Fat, Per Cent	12.2	12.40	9.9	12.80	10.4.
Unsaponified Fat, Per Cent	0.9	1.10	0.7		
Water, Per Cent	Trace	0.25	0.2	0.50	0.4.
Glycerine, Per Cent	1.2	1.10	1.0	2.80	1.2.
Dropping Point, ASTM, °F		500+	500+	500+	500+.
Tests:					
Penetrations, ASTM @ 77° F.—					
Unworked	436	258	322		
Worked	376	220	294	300	303.
Sett Test 16 hrs. @ 300° F.	Slightly Hardened.	Relatively Soft.	No change	Slightly Hardened	No change in consistency.
Sett Test @ 300° F. for 40 hours.		do	Remained relatively soft.		
Skin Hardening (Humidity Cabinet).	None in 7 days.	No detectable hardening 48 hours.	Slight in 72 hours.		
Storage Stability, Days Stored	890, No hardening.	90, No hardening.	84, No hardening.	303, Slight hardening.	227, No hardening.	440, Slight hardening.

In the above tabulation, the upper portion gives several exemplary formulae, the middle portion gives analyses of the resulting greases, and the bottom portion gives tests of the resulting greases.

In the tests, the "Dropping Point ASTM" and "Penetrations, ASTM @ 77° F." are the standard tests as specified by the American Society for Testing Materials.

The "Sett Test" comprises holding a sample of the grease at the specified temperature for the specified time, and observing the consistency of the grease after such exposure.

The "Skin Hardening" test is conducted by coating a panel of small size with the grease, followed by storing in a humidity cabinet at 100° F. and 100% relative humidity for a specified period, after which the grease is observed. The absorption of water vapor by the grease frequently results in the formation of a perceptible skin or crust upon the grease.

Both the above tests are related, as accelerated tests, to the actual performance of the grease in storage, as reported under "Storage Stability" which merely reports the condition of the grease after specified periods of storage under conventional conditions.

It will be observed by reference to the table that the above greases underwent no significant change of consistency in the "Sett Test," showed no significant skin hardening, and showed no hardening in storage, even under periods ranging up towards two and one-half years.

In contrast to this, a conventional acetate-modified line base grease, compounded in accordance with the formula of column A of the table, excepting that no phosphoric acid was used and the acetic acid was increased to 4.00 weight per cent will give the following results. It will show perceptible hardening after a sixteen hour "Sett Test," it will show perceptible skin hardening after twenty-four hours of exposure in the humidity cabinet, and will, normally, both in laboratory and commercial experience, show a hardening in one year of storage of the order of about 30–40 points of penetration, (sometimes 60 points), (150 gm. load, 77° F., ASTM method).

These improvements in properties, while small in amount, are worthwhile in that together they define a grease more nearly free of objectionable features than the parent product, even though that parent product has enjoyed ready and wide acceptance. In other respects, such as temperature stability under conditions of use, ability to retain oil without separation under normal conditions of use, as well as during storage, and the like, these improved greases retain the same desirable qualities as exhibited by the parent grease.

While the degree of modification and improvement obtained is of course dependent upon the amount of phosphoric acid used, the improvements begin to be present in discernible degree with use of about 0.1% by weight of phosphoric acid in the formulation. The optimum amount of phosphoric acid appears to be of the order of from about 0.4 per cent by weight to about 0.7 per cent by weight of phosphoric acid in the formulation. Upon the other hand, amounts of phosphoric acid above about 2.0 per cent by weight appear to be definitely detrimental, and in higher amounts destructive. For example, a grease formulated as in column A of the table, except using acetic acid 0.8 weight per cent and phosphoric acid 3.2 weight per cent was found to be without any grease structure at temperatures of about 240° F. and above, and to carry an insoluble residue. This product definitely was not a commercial grease.

While the above exemplary data are directed to acetate-modified lime base greases, it will be remembered that the actate modification of a lime base grease is the preferred species of a series of modified lime base greases obtained by the use, as modifiers, of short-chain monocarboxylic fatty acids of not more than six carbon atoms. The improvements available by substitution, for a portion of this carboxylic acid, of phosphoric acid exist over the range of specified fatty acids.

In general, greases of this type can be achieved

by compounding together from about 5 to about 20 per cent by weight of high molecular weight fatty acids or fatty-acid-containing soap forming materials, from about 0.2 to about 5 per cent by weight of monocarboxylic fatty acids of not over 6 carbon atoms, the preferred one being acetic acid, from about 0.1 to about 2 weight per cent of phosphoric acid and corresponding amounts of hydrated lime or other reactive form of lime, the hydrated lime ranging from about 0.8 to about 7 weight per cent, the resulting grease being dehydrated sufficiently to give the desired stable structure. In general, the phosphoric acid will be regarded in formulation, as a replacement for the low molecular weight fatty acid, and the organic acid be diminished in amount as the amount of phosphoric acid is increased.

We claim:

1. An improved lime base grease composition characterized by stability at temperatures in excess of 200° C. and by improved storage stability, comprising lubricating oil, lime soaps of fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability, of a calcium salt of a monocarboxylic fatty acid having not more than six carbon atoms, and a small proportion, sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula.

2. An improved lime base grease composition characterized by stability at temperatures in excess of 200° C. and by improved storage stability, comprising lubricating oil, lime soaps of fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability, of calcium acetate, and a small proportion, sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula.

3. An improved lime base grease composition characterized by stability at temperatures in excess of 200° C. and by improved storage stability, comprising lubricating oil, lime soaps of higher molecular weight fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability and not over about 5 per cent, of a calcium salt of a monocarboxylic fatty acid having not more than 6 carbon atoms, and a small proportion, sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula.

4. An improved lime base grease composition characterized by stability at temperatures in excess of 200° C. and by improved storage stability, comprising lubricating oil, lime soaps of higher molecular weight fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability and not over about 5 per cent, of a calcium salt of acetic acid, and a small proportion sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula.

5. Improved lime base greases characterized by stability at temperatures in excess of 200° F. and by improved storage stability formed by compounding together from about 5 to about 20 per cent of high molecular weight fatty acid soap forming materials, from about 0.2 to about 5 per cent of monobasic fatty acids of not over 6 carbon atoms, from about 0.1 to about 2 per cent of phosphoric acid, from about 0.8 to about 7 per cent of lime, all by weight, the remainder being lubricating oil.

6. Improved lime base greases characterized by stability at temperatures in excess of 200° F. and by improved storage stability formed by compounding together from about 5 to about 20 per cent of high molecular weight fatty acid soap forming materials, from about 0.2 to about 5 per cent of acetic acid, from about 0.1 to about 2 per cent of phosphoric acid, from about 0.8 to about 7 per cent of lime, all by weight, the remainder being lubricating oil.

7. An improved lime base grease composition characterized by stability at temperatures in excess of 200° F. and by improved storage stability, comprising lubricating oil, lime soaps of fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability, of a calcium salt of a monocarboxylic fatty acid having not more than six carbon atoms, and a small proportion, sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula, the resulting grease being dehydrated to a degree sufficient to give high temperature stability.

8. An improved lime base grease composition characterized by stability at temperatures in excess of 200° F. and by improved storage stability, comprising lubricating oil, lime soaps of higher molecular weight fatty acids in grease forming amounts, a small proportion, sufficient to impart said temperature stability and not over about 5 per cent, of a calcium salt of a calcium salt of acetic acid, and a small proportion, sufficient to impart said storage stability, of a lime salt of phosphoric acid, phosphoric acid having been present in the formulation of said grease in amounts of at least about 0.1 weight per cent and not exceeding about 2 weight per cent of the grease formula, the resulting grease being dehydrated to a degree sufficient to give high temperature stability.

9. Improved lime base greases characterized by stability at temperatures in excess of 200° F. and by improved storage stability formed by compounding together from about 5 to about 20 per cent of high molecular weight fatty acid soap forming materials, from about 0.2 to about 5 per cent of monobasic fatty acids of not over 6 carbon atoms, from about 0.1 to about 2 per cent of phosphoric acid, from about 0.8 to about 7 per cent of lime, all by weight, the remainder being lubricating oil, the resulting grease being dehydrated to a degree sufficient to give high temperature stability.

10. Improved lime base greases characterized by stability at temperatures in excess of 200° F. and by improved storage stability formed by compounding together from about 5 to about 20 per cent of high molecular weight fatty acid soap forming materials, from about 0.2 to about 5 per cent of acetic acid, from about 0.1 to about 2 per cent of phosphoric acid, from about 0.8 to about 7 per cent of lime, all by weight, the remainder be-

ing lubricating oil, the resulting grease being dehydrated to a degree sufficient to give high temperature stability.

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