

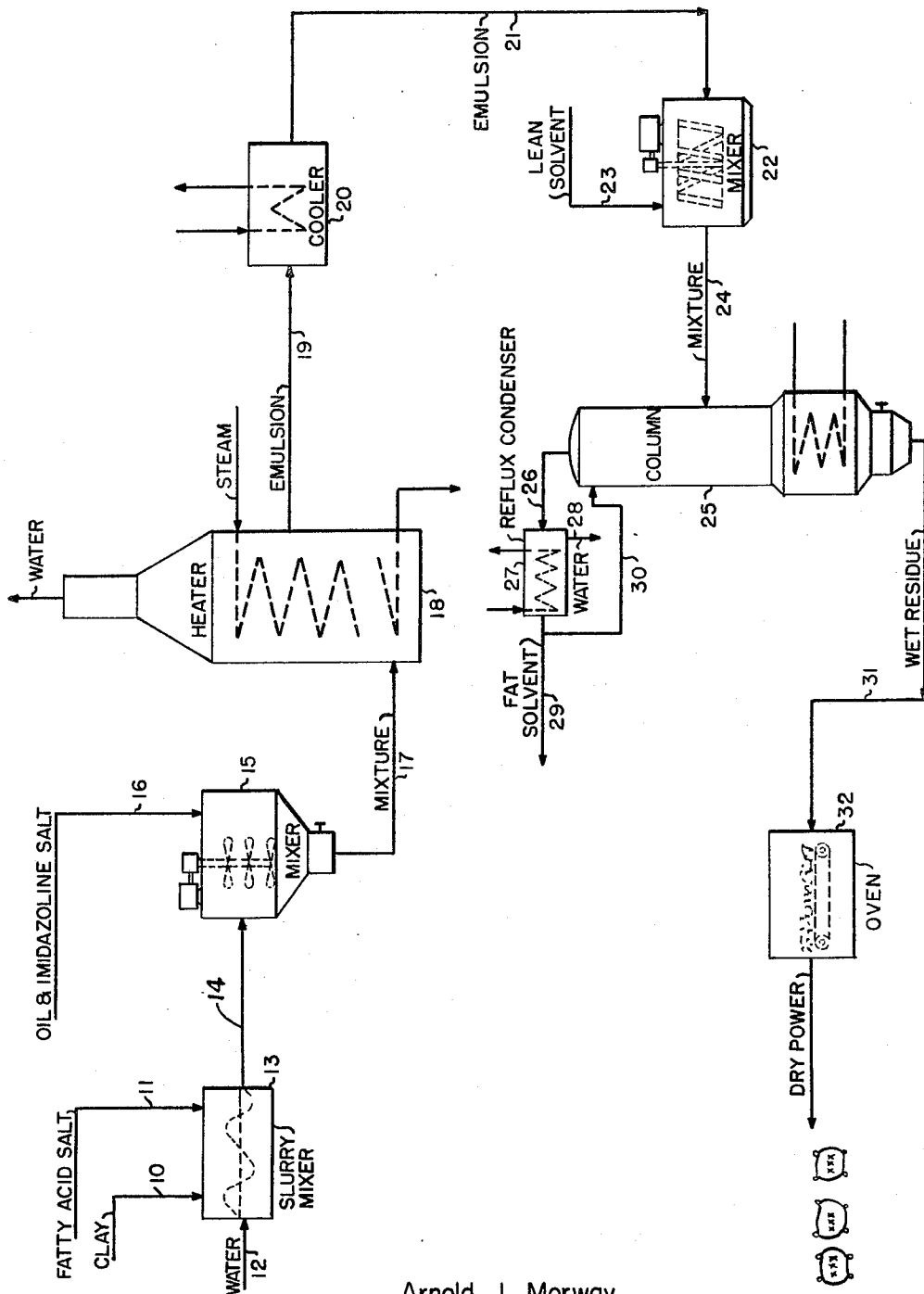
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MIXTURE OF CLAY AND FATTY ACID SALT

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MIXTURE OF CLAY AND FATTY ACID SALT
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This invention relates to mixtures of clay and metal salt of low molecular weight fatty acid, to lubricating compositions containing said mixtures of clay and metal salt of fatty acid, to methods for forming said mixtures and said lubricating compositions, and to the uses thereof. In a specific aspect, this invention relates to solid lubricating greases containing particles of clay and metal salt of C_1 to C_6 fatty acid which have been preformed by a certain technique as will be later described. These greases have good load carrying (EP) properties and are generally suitable for service at moderately elevated temperatures, e.g., 300° F. Moreover, they are water insoluble and have no dropping point (i.e., in excess of 500° F.).

BACKGROUND

The manufacture of lubricants, e.g., greases, gelled with inorganic colloids and particularly clay has been disclosed in the prior art. In the absence of a hydrophobing agent, however, a clay grease will collapse and disintegrate upon contact with water. In order to maintain the water stability of such greases, it is necessary to provide the clay with hydrophobic surfaces or otherwise protect it. Numerous means for achieving this result have been proposed in the prior art, e.g., Caruso in U.S. No. 3,006,848 discloses the use of hydrophobic amido amines as surface coatings for clay and Loeffler in U.S. No. 3,036,001 discloses the use of thermo-setting resins for this purpose.

Metal salt of C_1 to C_6 fatty acid, e.g., calcium acetate, has also been disclosed in the prior art as being very desirable in the preparation of fluid lubricants and lubricating greases. Lubricants containing substantial amounts of such salts generally possess extreme pressure (EP) and anti-wear properties. These salt-containing lubricants have found wide commercial acceptance. Because of the insolubility of these salts in lubricating oils, it has generally been the practice of industry to use either conventional surfactants, e.g., metal sulfonates, or more frequently, metal salts and soaps of higher molecular weight fatty acids (e.g., C_7 to C_{30} fatty acids), as suspending agents to maintain the fatty acid salt, e.g., calcium acetate, dispersed throughout the lubricating oil. It is further known to those skilled in the art that many of the properties of a grease containing these low molecular weight metal salts may be enhanced by reduction of the particle size of such salts to as small a size as possible, e.g., below 2 microns. This size reduction has generally been accomplished by grinding, by formation in situ, etc. The in situ formation is widely employed. Here, the low molecular weight fatty acid is first mixed with a lubricating oil and then a metal base, e.g., sodium hydroxide is added to neutralize the acid. If a conventional surfactant, (e.g., barium dinonyl sulfonate) or a higher molecular weight fatty acid (e.g., stearic acid) or metal salt thereof (e.g., calcium stearate) is present in the oil when the C_1 to C_6 fatty acid is neutralized, then the resulting C_1 to C_6 fatty acid salt particles will be prevented from agglomerating, thereby producing a suspension of finely divided salt particles. Alternatively, small C_1 to C_6 metal salt particles have been preformed by various methods and then admixed with an oil together with other ingredients to form the ultimate lubricating composition.

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DISCOVERY

It has now been discovered that clay and metal salt of C_1 to C_6 fatty acid can be treated by the same process, at the same time, to achieve the results which before now were obtained only by separate techniques. By applying the process of the present invention (which is described infra in detail) it is possible to simultaneously produce a mixture of clay and metal salt of C_1 to C_6 fatty acid wherein each possesses its desired properties, i.e., the clay is made hydrophobic and the particle size of the fatty acid salt is reduced, e.g., generally below 2 microns and more usually about 0.1 to 0.8 micron. Moreover, these small particles of metal salt are also made hydrophobic. This latter phenomenon is particularly useful where it is desired to take advantage of the different properties of the various hydrated and anhydrous forms of these metal salts. For example, calcium acetate is known to exist in several hydrated forms including a mono-hydrate and a half-hydrate, as well as several anhydrous forms including an amorphous form. These properties may be obtained by controlling the bound water in the salt. This is done, for example, by proper selection of the solvent employed in forming the coated salt. The boiling point of the solvent is the key. Hexane will give the mono-hydrate of calcium acetate while Varsol or higher boiling solvents will form anhydrous calcium acetate. Varsol is a commercially available aliphatic solvent sold by the Humble Oil and Refining Company and has a boiling range of from about 320° F. to 390° F.

The present invention has numerous advantages over prior art techniques. It eliminates the separate processing equipment previously used to individually prepare the clay and fatty acid salt, thus reducing equipment costs as well as freeing manpower and simplifying operations. The dry product of the present process can be easily handled, stored, and transported to remote lubricant, e.g., grease making facilities which can then easily add the dry mixture to oil to form desired lubricating compositions. Used in this manner, production facilities can be greatly expanded without the usual heavy capital outlay. Moreover, greases, containing these mixtures are insoluble in water, have good extreme pressure (EP) properties, and function well at elevated temperatures. Moreover, their properties are comparable to, or better than, many commercially available materials prepared by more complex techniques and thus having a higher unit cost. Other advantages will be apparent from a reading of the following description.

THE PROCESS

The process of the present invention can best be understood by reference to the accompanying drawing which is a flow diagram illustrating a method of manufacture of the dry mixture of the present invention.

Referring now to the drawing, relatively coarse particles of clay from conduit 10 and relatively coarse particles of a normally solid fatty acid salt from conduit 11 are mixed with water from conduit 12 in slurry mixer 13. The weight ratio of clay to fatty acid salt will generally be from 0.2:1 to 5:1, more usually from 0.5:1 to 2:1, e.g., 0.8:1 to 1.2:1. The amount of water used, although not critical, will be sufficient to form a slurry containing from about 5 to 98 parts (by weight) of water per 100 parts of slurry, e.g., about 30 to 90 parts of water. The slurry from conduit 14 is mixed in mixer 15 with oil from conduit 16 in which a surface active agent of the amino imidazoline salt type has been previously dispersed. The amount of oil (including the imidazoline salt) used may vary from 0.1 to 10 parts by weight per one part by weight of combined clay and fatty acid salt

present in the slurry. More usually, from 0.2 to 5, e.g., 0.3 to 2.5 parts of the oil will be employed on the same basis. The resulting mixture is passed from conduit 17 to heater 18, which may be heated by any convenient means, e.g., steam. Heating is continued until sufficient water has been removed so that an oatmeal-like emulsion will form on cooling. The amount of water present in the emulsion will then generally be in the range of from 5 to 70 parts, more usually 30 to 60 parts, e.g., about 40 to 50 parts of water in 100 parts of emulsion. The warm emulsion from conduit 19 is then optionally cooled in cooler 20 (e.g., by means of cooling water, etc.) and passed through conduit 21 to mixer 22. Here it is intimately mixed with from about 0.5 to 20 or more volumes (based on one volume of the emulsion) e.g., from about 2 to 15 volumes of a volatile hydrocarbon solvent from conduit 23. If the total water content is reduced to about 30 to 60, e.g., about 40 to 50 wt. percent of the entire mixture before the solvent is added, then more finely divided particles are generally obtained than if the water content had been reduced to zero before the addition of the solvent, since removal of much or all of the water may cause the particles to agglomerate. The resulting mixture from line 24 is heated in column 25 by some convenient means, e.g., steam, under reflux, to remove water, oil, and finally the solvent itself. The purpose of the solvent is to aid in removing water and oil. The overhead vapors from column 25 pass through conduit 26 to reflux condenser 27, which is cooled by some convenient means, e.g., cooling water. Water present in the overhead vapors may be removed from the system by gravity separation after the vapors have been condensed, e.g., through conduit 28. Condensed solvent can be removed from the system through conduit 29. Reflux is returned to column 25 through conduit 30. A wet residue (e.g., 0.1 to 5 parts by weight of water and/or solvent per 100 parts of wet residue) substantially comprised of the finely divided fatty acid salt and hydrophobic clay is withdrawn from column 25 and passed through conduit 31 to oven 32 where the remaining solvent and water are removed. The dry mixture of finely divided fatty acid salt and hydrophobic clay is then removed from oven 32 for later use. While not completely understood, it is believed that the acid salt of the imidazoline acts as a crystal growth inhibitor and as a hydrophobic agent by coating the calcium acetate and clay, thus preventing their agglomeration into larger particles.

While the instant process has been described with reference to a continuous process, it will be realized that the process is equally applicable to single batches.

THE CLAYS

Suitable clays for use according to the present invention include those of the montmorillonite group (e.g., bentonite) and the palygorskite group (e.g., attapulgite). Of all the various clays, the attapulgites are preferred. They are less water soluble than the bentonites and do not swell as much.

Attapulgite is a fibrous clay, the individual particles of which occur in nature as bundles, or aggregates of minute fibrils. It has been recognized (U.S. No. 2,784,110) that the usefulness of this material could be enhanced if it were possible to disperse attapulgite into its individual fibrils and render them hydrophobic. By treating the clay as hereinbefore described, it is possible to substantially accomplish this desired result while simultaneously forming small particles of metal salt of low molecular weight fatty acid. The particular clay used in the working examples of the present invention was Attagel 20, manufactured by Minerals & Chemicals Co., located at Phillip, Menlo Park, New Jersey. Attagel 20 is a colloidal form of the mineral attapulgite. It is neither water soluble nor does it swell such as the bentonites.

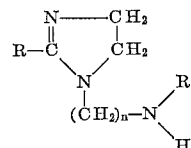
It has a surface area of about 210 square meters/gram and an average particle size of about 0.13 micron.

FATTY ACID SALTS

Suitable fatty acid salts for use according to the present invention include the alkali metal and alkaline earth metal salts of C_1 to C_6 fatty acids, viz. the Na, K, Li, Ca, Sr, Ba, etc. salts of formic, acetic, propionic, hexanoic, etc. acids. The alkaline earth metal salts, especially the calcium salts are preferred. Of the acids, acetic acid is preferred. These salts may be obtained commercially and their initial preparation, per se, does not constitute a part of the present invention. For example, a typical commercially available calcium acetate, having a particle size up to about 100 microns (an average of about 25 microns), is suitable, although finer particles are preferred. Preliminary particle size reduction of the salt may be made, if desired, by pulverizing, etc., prior to mixing the fatty acid salt with the clay. The present invention offers the advantage that the ultimate particle size of the fatty acid salt, e.g., calcium acetate, is considerably less than that of the original fatty acid salt. For example, an ultimate calcium acetate particle size of less than 2 microns can be readily achieved. Repeated laboratory tests have consistently produced needle-like calcium acetate particles having an ultimate size of about 0.1 micron in diameter and 1.0 micron in length.

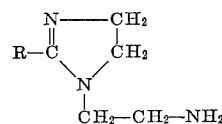
THE IMIDAZOLINE SALTS

The amino imidazolines used in the forming the imidazoline salts of the present invention include those having the general structure:



In the above formula, n represents an integer of from about 2 to 6, preferably 2 to 3; R represents a C_{12} to C_{22} , preferably a C_{14} to C_{18} , hydrocarbon group, either saturated or unsaturated, and preferably aliphatic; while R' is either hydrogen or a C_2 to C_{18} alkyl group. Preferably, R' is hydrogen and n is a small integer, e.g., 2, in order that the effectiveness of the imidazoline can be as great as possible per pound of material. In other words, the apparent effectiveness of the imidazoline in the present invention seems to depend on the ring structure and the terminal amino group, while the number of carbon atoms in the branches merely dilutes the apparent effectiveness.

A specific example of an imidazoline of the above formula, which was used in the working examples of the invention, was a commercially available imidazoline, 1-(2-amino ethyl)-2-(n -alkyl)-2-imidazoline having the formula:

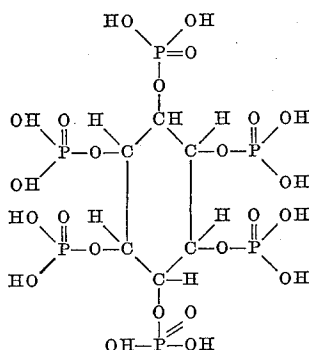


wherein R represents heptadecenyl and heptadecadienyl chains in a mole ratio of about 1:1. This product is commercially available under the tradename Nalcamine G-39M and is sold by Nalco Chemical Company, Chicago, Illinois.

The acids which can be reacted with imidazoline to form the salts, include inorganic mineral acids such as ortho, pyro and meta phosphoric acids, hydrochloric acid, sulfuric acid, nitric acid, and also phytic acid which is closely related to phosphoric acid. Phytic acid is the preferred acid.

Phytic acid is the hexaphosphoric acid ester of inositol. It is a strong acid containing twelve acidic hydrogen

groups. Its structural formula is believed to be as follows:



This material, having a molecular weight of 666 with 12 reactive hydrogen groups, has a combining weight (mole equivalent weight) of 55.

Phytic acid is derived from grain, and is a byproduct from waste corn steep liquor. A description of phytic acid and its preparation is given in Chemical Engineering, January 27, 1958, under the title "Ion Exchange Now Yields Phytic Acid," published by McGraw-Hill Publishing Co., Inc., New York, N.Y.

The amino imidazoline salts may be prepared by mixing the imidazoline and appropriate acid, preferably in a small amount of inert hydrocarbon oil, e.g., 0.5 to 3.0 or more parts by weight of oil per part of combined imidazoline and acid, to form the imidazoline salt. Frequently the imidazoline is dispersed in the oil and then an aqueous solution of the acid is added to the dispersion. Reaction times will generally be from 0.05 to 1 hour, or more, usually from 15 to 30 minutes. Temperature of from 75° to 200° F. are usually employed, although other temperatures may be used. For best results, the relative amounts of imidazoline salt and oil should be sufficient to form a gel on gentle heating, e.g., 70-130° F.

THE SOLVENTS

The solvent used should be one in which the fatty acid salt and clay particles are insoluble. Suitable solvents include hydrocarbon solvents which can be aliphatic, naphthenic, aryl, alkyl, alkaryl, etc. Preferably, the solvent will be a liquid aliphatic solvent, e.g., heptane having a relative density of less than 1.0, e.g., 0.4 to 0.95, and a boiling point of from about 100 to 700° F., e.g., 120 to 500° F. The purpose of the solvent is to aid in removing water and oil from the coated particles of clay and fatty acid salt. It also serves to strip some of the bound water from the fatty acid salt.

THE LUBRICATING OILS

In preparing the mixture of dry, coated particles of clay and fatty acid salt it is preferred to use a mineral lubricating oil in combination with the imidazoline salt. This oil will usually (but not necessarily) have a viscosity at 100° F. of from 50 to 1200 SUS, e.g., 300 to 700 SUS, and a viscosity index (Dean Davis) of from about 40 to 50. In preparing the ultimate lubricating compositions containing the dry mixture, however, selection of the lubricating oil base is more closely related to the intended use of the lubricant thus prepared. Here, mineral oils, synthetic oils, etc., may be employed. Such oils include mineral lubricating oils, silanes, silicones, dibasic acid esters, fluoro esters, polyphenyl ethers, phosphate esters, complex esters, etc. Selection of an appropriate oil is well within the skill of the art.

LUBRICANTS CONTAINING THE MIXTURES OF CLAY AND FATTY ACID SALT

Lubricating compositions can be prepared by mechanically mixing the dry particles in a lubricating oil and will generally comprise from about 2 to 65 wt. percent or more, preferably 5 to 55 wt. percent, e.g., 10 to 40 wt. percent, of the coated particles. Occasionally, it may be desirable to heat the oil during the mixing step. The resulting lubricants may range from fluid lubricants to solid lubricating greases. However, the fluid lubricants are not particularly stable and the thickener tends to settle out on standing.

Various additives may be included in the lubricating compositions of this invention in amounts of from about 0.001 to 10.0 wt. percent or more each, based on the total weight of the composition. Examples of such additives include oxidation inhibitors such as phenyl-alpha-naphthylamine, tackiness improvers such as polyisobutylene, corrosion inhibitors such as sorbitan monooleate, sodium nitrite and lanolin, waterproofing agents, dyes, V.I. improvers, thickeners and the like.

The lubricant can be homogenized in a Morehouse mill, a Gaulin homogenizer, etc. If a fluid lubricant is desired, it is generally more convenient to first form an oil concentrate with the dry mixture and then dilute the concentrate with additional oil to form the final product.

The preparation of the finely divided clay/calcium acetate particles and lubricating compositions therefrom will be more clearly understood by reference to the following examples which include a preferred embodiment. All parts are by weight unless otherwise indicated.

Example 1

17.8 parts of a mineral lubricating oil (Coray 55) having a viscosity of 55 SUS at 210° F. and 10 parts of an amino imidazoline (Nalcamine G-39-M) were added to an electrically heated grease kettle and mixed together. Next, 2.2 parts of phytic acid in the form of a 50 wt. percent aqueous solution were added to the mixture. The phytic acid formed a salt with the imidazoline (Nalcamine G-39-M). A gel-like mass formed on gentle heating (125° F.).

Thirty-five parts of calcium acetate and 35 parts of clay (Attagel 20) in the form of a 15 wt. percent aqueous slurry was added to the gel. Heating was continued until the total water content had been reduced to about 46 wt. percent, thereby forming a clay/calcium acetate/imidazoline phytate/oil emulsion. Then 10 volumes of n-hexane were added to the emulsion to form a mixture. This mixture was placed in a distillation flask equipped with a reflux condenser and trap. Heating was initiated and the hexane refluxed. The water was gradually collected in the trap by gravity and removed. When substantially all of the water had been removed, the hexane was removed by distillation. The residue was oven dried at 220° F. for 30 minutes. The mixture of clay and calcium acetate thus recovered was in the form of a gray, fluffy powder.

Example 2

A solid lubricating grease was prepared by mixing and milling (without heating) 33.0 parts by weight of the dried mixture of clay and calcium acetate of Example 1, 66.0 parts of a mineral lubricating oil (Coray 55) having a viscosity of 55 SUS at 210° F. and a viscosity index (Dean Davis) of 45, and 1.0 part of phenyl alpha naphthylamine. The properties of that grease are shown in Table I.

Example 3

The formulation and procedure followed in Example 2 were repeated using a silicone fluid in lieu of the mineral lubricating oil. The silicone fluid was Dow Corning QF-6-7012 which is a medium methyl-phenyl polysiloxane having a viscosity at 100° F. of 64.3 cs., a viscosity index of 162 and a pour point (ASTM) of less than

minus 100° F. The properties of that grease are also shown in Table I.

Example 4

The technique employed in Example 2 was repeated using a synthetic oil as the base stock in lieu of the mineral lubricating oil. The synthetic oil was a polyphenyl ether manufactured by Monsanto Chemical Co. under their designation of OS-124. The properties of that grease are shown in Table I.

Example 5

Attempts to make a fluid lubricant produced negative results. While a fluid composition could be made, the thickener tended to settle out on prolonged standing and large separations occurred on centrifuging.

TABLE I

	Formulation (By Weight)	Formulation		
		Example Number		
		2	3	4
1.	Mineral Lubricating Oil (Coray-55)	66.0	66.0	66.0
2.	Silicone Fluid			
3.	Polyphenyl Ether (OS-124)			
4.	Calcium Acetate	16.5	16.5	16.5
5.	Clay	16.5	16.5	16.5
6.	Phenyl-2-naphthylamine	1.0	1.0	1.0
	Properties	Properties		
		(1)	(1)	(1)
A.	Appearance	500+	500+	500+
B.	ASTM Dropping Point, ° F.			
C.	ASTM Penetration at 77° F. (mm./10):			
	Unworked	260	315	285
	Worked 60 Strokes	265	320	280
	Worked 10,000 Strokes	300	324	282
D.	"ABEC-NLGI" Lubrication Life, Hrs. at 10,000 r.p.m. (204 bearing):			
	250° F.	2,000+	2,000+	2,000+
	300° F.	2,000+	2,000+	2,000+
	350° F.	300	418	2,000+
	400° F.		177	1,500+
E.	Timken Test (lbs.)	55		
F.	Almen Test:			
	Gradual (Weights)	15	8	15
	Shock (Weights)	15	10	15
G.	Shell 4-Ball:			
	Weld (Kg.)	300	295	310
	Scar diameter, mm. (1,800 r.p.m., 10 Kg., 75° F., 1 hour)	0.36	0.60	0.32
H.	Water Solubility at 77° F.	Nil	Nil	Nil

NOTE: Where plus signs are shown the test was discontinued (not a failure).

¹ Smooth, homogeneous.

From Table I it can be noted that all of the greases (Examples 2, 3, and 4) prepared according to the present invention had an excellent texture. They were smooth and homogeneous. They all possessed a dropping point in excess of 500° F. Lubrication lives were exceptionally long, e.g., over 2000 hours at 300° F. Results of the Timken and Almen tests are very favorable and the scar diameters obtained from the Shell 4-Ball test were good. In this respect, however, the performances of the mineral oil and polyphenyl ether based greases were superior to the silicone based grease. It should also be noted that these greases were water insoluble.

When employed in the formulation of lubricating greases, the coated particles of the present invention are particularly effective in lubricating systems wherein a lubricant is applied to the rubbing surfaces of parts having relative motion and wherein the lubricant is subjected to high pressures.

While the present invention has been described with a certain degree of particularity, it should be realized that numerous modifications and adaptations can be made within the spirit and scope of the invention as hereinafter claimed.

What is claimed is:

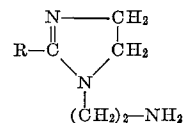
1. A method for forming a dry, coated, mixture of attapulgite clay and calcium acetate which comprises:

(I) forming an aqueous slurry of attapulgite clay and calcium acetate,

(a) said slurry containing from about 30 to 90 parts by weight of water per 100 parts of slurry, and

(b) said clay and said calcium acetate being present in a weight ratio of from 0.8:1 to 1.2:1;

(II) mixing one part by weight of the combined clay and calcium acetate in said slurry with from 0.2 to 5.0 parts by weight of a lubricating oil dispersion of the phytic acid salt of an amino imidazoline having the formula:



wherein R is a C₁₄ to C₁₈ hydrocarbon group,

(III) heating said mixture to reduce the water content of said mixture to from 30 to 60 parts by weight of water per 100 parts of said mixture thereby forming an emulsion,

(IV) admixing from about 2 to 15 volumes of a hydrocarbon solvent with one volume of said emulsion, said solvent having a relative density of from 0.4 to 0.95 and a boiling point of from 100 to 700° F.,

(V) heating, under reflux, the mixture of said solvent and said emulsion to remove lubricating oil, solvent, and water, thereby forming a wet residue consisting essentially of clay and calcium acetate,

(VI) drying said wet residue to eliminate any remaining water and solvent, and

(VII) recovering said dry mixture of coated attapulgite clay and calcium acetate.

2. As a composition of matter, the dry mixture prepared according to the method of claim 1.

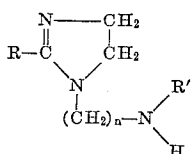
3. A method for forming a dry mixture of finely divided clay and alkaline earth metal salt of C₁ to C₆ fatty acid which comprises:

(I) mixing an aqueous slurry of said clay and said fatty acid salt with an oil dispersion of an amino imidazoline salt,

(a) said amino imidazoline salt being the reaction product of an acid selected from the group consisting of inorganic mineral acids and phytic

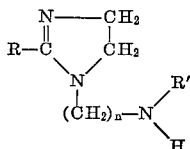
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acid, and an amino imidazoline having the general formula:



wherein n is an integer of about 2 to 6, R is a C_{12} to C_{22} hydrocarbon group and R' is selected from the group consisting of hydrogen and C_2 to C_{18} alkyl groups,

- (II) heating said mixture to reduce the total water content of the heated mixture to from 5 to 70 wt. percent,
 - (III) adding a solvent to said mixture in a volume ratio of from about 0.5 to 20,
 - (IV) heating said solvent and said mixture to remove oil, solvent and water, thereby forming a wet residue of clay and fatty acid salt, and
 - (V) drying said residue to form said dry mixture of clay and fatty acid salt.
4. As a composition of matter, the mixture of clay and fatty acid salt prepared according to the method of claim 3.
5. A method for forming a mixture of finely divided clay and fatty acid salt particles which comprises:
- (I) adding an aqueous slurry of clay and metal salt of C_1 to C_6 fatty acid to an oil dispersion of the salt reaction product of an amino imidazoline and an acid selected from the group consisting of inorganic mineral acids and phytic acid,
 - (a) said amino imidazoline having the general formula:



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wherein n is an integer of about 2 to 6, R is a C_{12} to C_{22} hydrocarbon group and R' is selected from the group consisting of hydrogen and C_2 to C_{18} alkyl groups, and

- (b) said metal being selected from the group consisting of alkali metals and alkaline earth metals
 - (II) heating said mixture to reduce the water content thereof, and
 - (III) recovering said mixture of clay and fatty acid salt.
6. As a composition of matter, the mixture of clay and fatty acid salt prepared according to the process of claim 5.

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