United States Patent Office 3,390,081
Patented June 25, 1968

3,390,081

RUST INHIBITED EXTREME PRESSURE GREASE

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No Drawing. Continuation-in-part of application Ser. No. 330,608, Dec. 16, 1963. This application Mar. 10, 1967, Ser. No. 622,063
7 Claims. (Cl. 252—32.7)

ABSTRACT OF THE DISCLOSURE

This application is directed to a grease showing improved physical properties, particularly dropping point, effected by the synergistic combination of a zinc alkyl dithiophosphate with an imidazoline salt of a fatty acid, such as caprylic acid.

This application is a continuation-in-part application of S.N. 330,608, filed Dec. 16, 1963 and now abandoned.

This invention relates to a grease composition and, more particularly, relates to a rust inhibited extreme pressure grease with improved physical properties.

A grease for use in lubricating heavily loaded bearings which are exposed to high humidity and water would normally be a high quality grease containing extreme pressure additives together with a rust inhibitor. The addition of extreme pressure additives to grease compositions has heretofore been known to reduce the dropping point of the grease. The present invention involves a rust inhibited extreme pressure grease composition in which the dropping point is substantially increased over the same grease composition not employing an extreme pressure additive. While the dropping point is increased in the rust inhibited extreme pressure grease of my present invention, the bleeding is reduced and the mechanical stability increased.

It is, therefore, an object of the present invention to provide a rust inhibiting additive for an extreme pressure grease which results in an improvement in the dropping point of a rust inhibited extreme pressure grease.

It is also an object of the present invention to provide a rust inhibitor for an extreme pressure grease which reduces the bleeding characteristics and increases the mechanical stability of the resulting grease.

Other objects and a more complete understanding of my present invention will become apparent from the following description of the invention taken in conjunction with the appended claims.

We have found that a grease composition formulated by using a particular rust inhibitor with an additive which has been found useful as an extreme pressure additive produces a synergism which significantly increases the dropping point of the formulated grease. The rust inhibitor additive used to produce a synergism with one extreme pressure additive is an imidazoline salt of a fatty acid. The compound found useful as an extreme pressure agent and capable of producing the synergism with the imidazoline is a zinc alkyl dithiophosphate.

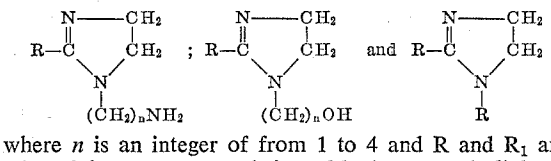
The base oil and thickening agent utilized in the grease composition of my present invention may be of the conventional type. For example, pale oils, mid-continent solvent treated paraffin base oils, western solvent treated, western refined naphthenic oils, refined Pennsylvania 100% paraffin oils, or mixtures thereof, may be utilized as base oils. The thickening agent utilized in my present grease composition may be a soap of a monocarboxylic acid having from about 14 to 22 carbon atoms per molecule, for example, lauric, myristic, palmitic, oleic, stearic,

hydroxystearic, 12-hydroxystearic methyl esters of 12-hydroxystearic acid, ethyl hexoic, behenic, etc. or their glycerides, or fatty materials containing such acids or their glycerides. The fatty materials can be vegetable, marine and animal fatty oils and hydrogenated products thereof within the above description. Hydrogenated castor oil, tallow, tallow fatty acids, cottonseed oil, stearin and hydrogenated fish oils are examples of suitable fatty oils. The metal component of the soap may be an alkali or alkaline earth metal such as lithium, sodium, barium, or mixtures thereof. The preferred soap thickening agents, however, are lithium 12-hydroxystearate, lithium stearate and lithium and barium soaps of C_{16} through C_{18} monocarboxylic acids or their glycerides. The amount of soap present in the grease of my present invention varies from about 5 to 25% of the grease by weight, preferably about 5 to 14% by weight, although normally 5 to 6% average.

The greases of my present invention may be prepared by any conventional process, however, preferably the soaps are prepared in situ in the presence of at least a portion of the total oil, preferably about 10% of the total oil. Maximum temperatures of about 230 to 425° F. may be used with a maximum processing temperature of about 230 to 350° F. being preferred to form the proper physical characteristics of the soap fibril. Complete saponification usually takes place in about 15 to 20 minutes after maximum temperature is obtained.

For example, the fatty materials and starting oil may be heated in a kettle until a substantially complete solution is formed. A hot solution of a metal hydroxide such as lithium hydroxide may then be added to the kettle mixture agitated vigorously while the mixture is heated slowly to evaporate water. During the saponification and the dehydration further quantities of the starting oil may be added to limit foaming and maintain the mixture in at least a semifluid state. After the water of reaction and the water in which the hydroxide was dissolved is eliminated by evaporation, it is advantageous to raise the temperature of the mixture to about 230 to 350° F. for a period of about 1 to 2 hours. At the end of this period the grease is allowed to cool and cooling may be facilitated by the further addition of base oil. The grease additives such as extreme pressure agents, oxidation inhibitors and rust inhibitors may then be added and the grease milled in the usual manner, for instance in a colloid mill at a clearance of about .001 to .005".

The rust inhibitors useful in my present invention which gives the synergism with the extreme pressure additive are reaction products of an imidazoline with a fatty acid having a carbon chain length of about 5 to 22 carbon atoms. Examples of such fatty acids are caproic, caprylic, capric, lauric, palmitic, stearic and oleic acid. Examples of the imidazolines useful in producing a rust inhibitor useful in my present invention are shown by the following formulae:

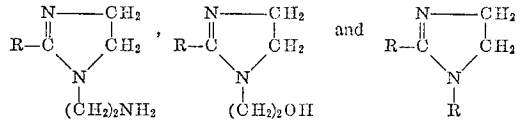


where n is an integer of from 1 to 4 and R and R_1 are selected from group consisting of hydrogen and aliphatic hydrocarbon having from about 5 to 17 carbon atoms.

The imidazolines useful for making the imidazoline salt of my present invention may be prepared by the reaction of a fatty acid with polyamine, for example, the ethylene polyamines, such as ethylene diamine, diethylene triamine, diethylene tetraamine pentamine, etc. at temperatures of about 500 to 570° F. these imidazolines are of a cyclic tertiary amine type, either the monoamine or the diamine.

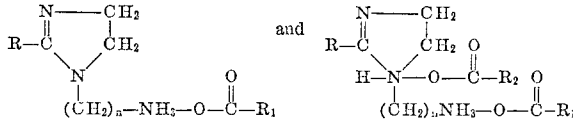
Rust inhibitor additives useful in my present invention

are described more fully in my copending application Ser. No. 147,486, filed Oct. 25, 1961 and now abandoned. These additives are effective in amounts of about 0.75 to 2.0%, preferably about 1% of the grease by weight for the imidazoline salt and about 1% by weight of the zinc dithiophosphate. For example, the type of imidazolines useful in my present invention may be of the type shown by the following formula:

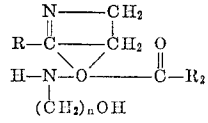


which are respectively 1-(amino ethyl)-2-alkyl-2-imidazoline and 1(2-hydroxy ethyl)-2-n-alkyl-2- imidazoline, and 1-alkyl-2-n-alkyl-2-imidazoline, where the alkyl substitutents are aliphatic hydrocarbons having from about 5 to 17 carbon atoms, such as, for example, pentyl, nonyl, tridecyl, heptadecenyl, hendecenyl, heptadecyl, heptadecenyl, heptacedadienyl, coco, pentadecenyl, etc., derived from relatively long-chain fatty acid materials, such as oleic and tall oil fatty acids, etc.

The reaction product of the fatty acid and the substituted imidazoline in the case of the amine substituted imidazoline may be represented as follows:



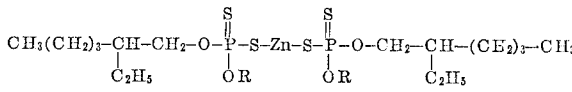
and in the case of the hydroxylated imidazoline is as follows:



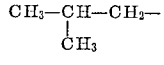
where n is an integer of from 1 to 4 and R, R_1 and R_2 are selected from the group consisting of hydrogen and an aliphatic hydrocarbon having a carbon chain length of from about 4 to 21 carbon atoms.

The latter compound is available commercially as Nalcamines G–11 from the Nalco Chemical Company. The amine substituted imidazolines are available commercially as Nalcamines G–39M from Nalco Chemical Company, and as Cationic N–FD available from the Leyda Oil and Chemical Company of Hawthorne, Calif.

The zinc alkyl dithiophosphates used in my present invention are conventionally used as an oxidation inhibitor in motor oils and also has been useful as antiwear antiscuffing additives. It has been found that these additives are useful as extreme pressure agents in greases and when used with the rust inhibitors mentioned above impart improved dropping point, bleeding and mechanical stability properties to the grease. An example of a suitable zinc alkyl dithiophosphates useful in the synergistic combination of my present invention is the zinc di (alkyl dithiophosphate) sold by the Lubrizol Corporation as Lubrizol 1395 and identified by the structural formula:



where R is



This zinc alkyl dithiophosphate product has a viscosity at 20° C. of 1539.6 centistoke and a specific gravity of 1.1684.

My present invention will be described further in conjunction with the following specific examples which are given merely by way of illustration and should not be construed as limiting the invention to the details thereof.

EXAMPLE 1

385 grams of hydrogenated castor oil and 67.94 grams of hydrogenated fish fatty acids (Hy Fac 430) were melted in a grease kettle and 679 grams of western refined naphthenic oil having a viscosity of 70 SUS at 210° F. (W6–70) added to the kettle to dissolve the melted fats. The mixture was heated to about 195° F. and stirred until the solution was accomplished. 92 grams of 55.11% LiOH (aqueous solution) was heated to 197° F. and added to the kettle and the mixture thickened. 3171 grams of oil was then added to the thickened mass and the temperature raised to about 350° F. The mixture was cooked for an hour and seventeen minutes until the grease mass was substantially completely dehydrated. 3487 grams of finishing oil was added to the kettle and 74.3 grams of zinc dithiophosphate (Lubrizol 1395), 74.3 grams of chlorinated paraffin HV, 74.3 grams of an imidazoline salt of caprylic acid, and 297.3 grams of sulfurized sperm oil were added and the mixture milled at .001" at 162° F. in a Charlotte Colloid Mill. The grease was tested and found to have a penetration at 77° F. of 314, unworked, and an ASTM of 302. The grease was returned to the kettle and 3.9 grams zinc dithiophosphate (Lubrizol 1395), 3.9 grams chlorinated paraffin HV, 3.9 grams of the imidazoline salt of caprylic acid and 15.7 grams of sulfurized sperm oil were added to the grease and the grease again milled at .001" clearance at 170° F. The unworked penetration at 77° F. was 305 and the ASTM 296. Additional oil and additives were added to bring the additive composition to the total shown in Table I and the grease milled again at .001" clearance at 170° F.

TABLE I

Composition	Grams	Wt. percent
(Formulation Batch 276-28-G581) Lithium 12-Hydroxystearate Soap	376.62	4.48
Lithium-Hy Fac 430 Soap	69.34	0.82
W6-70 Base Oil	7,379.10	87.70
Zinc Alkyl Dithiophosphate (Lubrizol 1395)	84.20	1.00
Chlorinated Paraffin HV	84.20	1.00
Sulfurized Sperm Oil (9% S)	336.60	4.00
Rust Inhibitor RI 152-59 (imidazoline) salt of caprylic acid)	84.20	1.00
	8,414.27	100.00

Inspection tests

Unworked penetration at 77° F.	309
ASTM penetration at 77° F.	303
ASTM dropping point ° F.	459
Shear stability, 4 hour Shell roll test, penetration change percent	+6.6
Timken test at 35 lbs.	Pass
Copper corrosion test, 24 hours at 212° F.	1B
ASTM D 1743–60T rust test	Pass
Alkalinity as LiOH, wt. percent	0.031

EXAMPLE 2

A grease made according to the procedure of Example 1, having essentially the same composition was prepared without incorporating therein an imidazoline salt additive. The data obtained from inspection tests made on the finished grease is shown in Table II.

TABLE II

Extreme pressure grease	Wt. percent
(Formulation batch 255–1–G526) lithium 12-hydroxystearate soap	5.21
Lithium-Neo-fat 16–54 soap	0.29
W6–70 base oil	88.50
Zinc alkyl dithiophosphate (Lubrizol 1395)	1.00
Chlorinated paraffin HV	1.00
Sulfurized sperm oil (9% S)	4.00

Inspection tests

ASTM penetration at 77° F.	320
ASTM dropping point ° F.	374
Shear stability, 4 hour Shell roll test, penetration change percent	+13.92
Timken test at 35 lbs.	Pass
ASTM D 1743–60T rust test	Fail
Alkalinity as LiOH, wt. percent	0.052

EXAMPLE 3

1011 grams of a starting oil (W6–70) having a viscosity of about 70–75 SUS at 210° F., 640.3 grams of hydrogenated castor oil, about 33.7 grams of Neo-Fat 16–54 (a eutectic mixture containing 68% palmitic acid, 30% of stearic acid and 2% oleic acid—produced commercially by the Armour Company) and 125.4 grams lithium hydroxide monohydrate dissolved in 502 grams of boiling water were added to the kettle and heated (from a starting temperature of about 190° F.) while agitating the mixture. Oil was gradually added as the temperature of the mixture was gradually raised to about 350° F. until saponification was complete.

The sapinification was complete and the grease mass substantially completely dehydrated in about 1 hour and 44 minutes at a temperature of 350° F. The temperature was maintained at 350° F. for about 30 minutes. The grease was cooled by adding oil to a total of 9695 grams and at 185° F., 440.8 grams of sulfurized sperm oil, 110.2 grams of chlorinated paraffin HV and 110.2 grams of the imidazoline salt of caprylic acid (RI 152–59) were added to the mass and thoroughly mixed for about 28 minutes. The grease was then colloidally milled in a Charlotte Mill at .003" clearance at 185° F. The resulting grease was then tested, the significant results of which are included in Table III.

TABLE III

Composition	Grams	Wt. percent
(Formulation Batch 567-43) Lithium-12-Hydroxystearate Soap	626.58	5.69
Lithium-Neofat 16-54 Soap	34.46	0.31
W6-70 Base Oil	9,695.00	88.00
Chlorinated Paraffin HV	110.20	1.00
Sulfurized Sperm Oil (9% S)	440.80	400
Rust Inhibitor RI 152-59 (imidazoline salt of caprylic acid)	110.20	1.00

Inspection tests

Unworked penetration at 77° F.	324
ASTM penetration at 77° F.	318
ASTM dropping point ° F.	387

EXAMPLE 4

Another grease was prepared according to the procedure of Example 1 incorporating the zinc dithiophosphate and imidazoline salt additives by mixing into the grease at 160 to 170° F. after the addition of the finish oil just before milling at 135 to 144° F. The composition of the grease and the data obtained as a result of tests made on the finished grease are shown in Table IV.

TABLE IV

Rust inhibited E.P. grease	Wt. percent
(Formulation batch 276–15–G577) lithium 12-hydroxystearate soap	5.21
Lithium-Neo-Fat 16–54 soap	0.29
W6–70 base oil	87.50
Zinc alkyl dithiophosphate	1.00
Chlorinated paraffin HV	1.00
Sulfurized sperm oil (9% S)	4.00
Rust inhibitor RI 152–59 (imidazoline salt of caprylic acid)	1.00

Inspection tests

ASTM penetration at 77° F.	326
ASTM dropping point ° F.	434
Shear stability, 4 hour Shell roll test, penetration change percent	+2.95
Timken test at 35 lbs.	Pass
ASTM D 1743–60T rust test	Pass
Alkalinity as LiOH, wt. percent	0.076

EXAMPLE 5

A grease was made according to the procedure of Example 1 wherein 2% lead naphthenate was added as an additive to the composition. The additives of the present invention was not utilized in this grease. The composition and results of tests made on the finished grease are shown in Table V.

TABLE V

Composition	Wt. percent
(Formulation batch 241–22–G–481) lithium-hydrogenated castor oil soap	5.69
Lithium-Neo-Fat 16–54 soap	0.31
W6–70 oil	85.25
Sulfurized sperm oil (9% S)	6.00
Chlorinated paraffin HV	0.75
Lead naphthenate, 25% Pb	2.00

Inspection tests

ASTM penetration at 77° F.	321
ASTM dropping point ° F.	364
Shear stability, 4 hour Shell roll test, penetration change percent	+11.72
Timken test at 35 lbs.	Pass
ASTM D 1743–60T rust test	Not run

EXAMPLE 6

Another grease was made according to the procedure of Example 1 with 2% lead naphthenate and the zinc alkyl dithiophosphate-imidazoline salt additives. The composition and results of test made on the finished grease are shown in Table VI.

TABLE VI

Composition

	Wt. percent
Formulation batch 276–53–G590) lithium-hydrogenated castor oil soap	2.78
Lithium-Neo-Fat 16–54 soap	1.94
W6–70 oil	86.38
Zinc alkyl dithiophosphate (Lubrizol 1395)	0.90
Chlorinated paraffin HV	1.00
Sulfurized sperm oil (9% S)	4.00
Lead naphthenate, 25% Pb	2.00
Rust inhibitor RI 152–59 (imidazoline salt of caprylic acid)	1.00

Inspection tests

ASTM penetration @ 77° F.	307
ASTM dropping point ° F.	370
Timken test @ 35 lbs.	Fail

EXAMPLES 7–8

Two other greases were prepared according to the procedure of Example 1 incorporating the zinc alkyl dithiophosphate and imidazoline salt additives. The composition of the greases and the results of the inspection tests made on the finished greases are shown in Tables VII and VIII.

TABLE VII

Composition	Grams	Wt. percent
(Formulation Batch 276-17-G578) Lithium-Castorwax Soap	317.93	5.21
Lithium-Neo-Fat 16-54 Soap	17.47	0.29
W6-70 Oil	5,320.65	87.25
Zinc Alkyl Dithiophosphate	61.00	1.00
Chlorinated Paraffin HV	61.00	1.00
Sulfurized Sperm Oil (9% S)	243.90	4.00
Rust Inhibitor RI 152-59 (imidazoline salt of caprylic acid)	76.20	1.25
	6,098.15	100.00

Inspection tests

Unworked penetration @ 77° F.	329
ASTM penetration @ 77° F.	321
ASTM dropping point, ° F.	438
4 hour Shell roll test, penetration change, percent	0.0
Timken test at 35 lbs.	Pass
Copper corrosion test, 24 hours @ 212° F.	1B
ASTM D 1743–60T rust test	Pass
Alkalinity as LiOH, percent	0.032
AAR bleed test, bleed, do	1.3
AAR bleed test, evaporation, do	1.7

TABLE VIII

Composition	Grams	Wt. percent
(Formulation Batch 276-13-G576) Lithium-Castorwax Soap	317.93	5.21
Lithium-Neofat 16-54 Soap	17.47	0.29
W6-70 Oil	5,305.40	87.00
Zinc Alkyl Dithiophosphate	61.00	1.00
Chlorinated Paraffin HV	61.00	1.00
Sulfurized Sperm Oil (9% S)	243.90	4.00
Rust Inhibitor RI 152-59 (imidazoline salt of caprylic acid)	91.50	1.50
	6,098.20	100.00

Inspection tests

Unworked penetration @ 77° F.	324
ASTM penetration @ 77° F.	316
4 hour Shell roll test, penetration change, percent	−1.2
Timken test @ 35 lbs.	Fail
Copper corrosion test, 24 hours @ 212° F.	1B
ASTM D 1743–60T rust test	Pass
Alkalinity as LiOH, percent	1.108

Examples 2 and 3 show that greases with the rust inhibiting imidazoline salt and the extreme pressure additive zinc alkyl dithiophosphate incorporated individually but not together in combination as taught by my present invention and shown in Example 1, have a dropping point of approximately 380° F. Similar greases shown in Examples 1 and 4 *with* the additive *combination* of my present invention show dropping points of 459° F. and 434° F., respectively. This represents a substantial improvement in the base grease attributed to the additive of the present invention and illustrates the synergistic effect of the two additives in combination. It had previously been found that the extreme pressure additives normally *decrease* the ASTM dropping point of the grease slightly but when the extreme pressure additive is employed in combination with the imidazoline salt rust inhibitor in accordance with the present invention as above mentioned, a synergistic effect is obtained and the ASTM dropping point is actually increased.

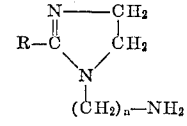
Examples 5 and 6 use a 2% lead naphthenate which is known to cause a lowering of the ASTM dropping point. It should be noted that the dropping point of the grease of Example 6 is slightly improved over that of Example 5 and required less than half the amount of lithium hydrogenated castor oil soap required for thickening the grease of Example 5. Thus, the grease of Example 6, by using about half the amount of this soap, showed a slight increase in the dropping point which clearly indicates that the additive combination of the present invention which was used in Example 6 had a substantial beneficial effect on the dropping point of the grease.

An improvement in mechanical stability is obtained by the use of the additive of the present invention as shown in the results of the tests run on the greases of Examples 4, 7 and 8 where the ASTM penetration change after the 4 hour Shell roll test was +2.95%, 0% −1.2%, respectively.

Although I have described my present invention with a certain degree of particularity, it is to be understood that the scope of my invention is not to be limited by the details set forth, but should be afforded the full breadth of the appended claims.

I claim:

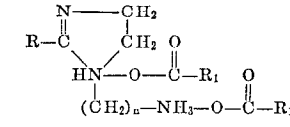
1. A grease composition comprising a mineral oil of lubricating viscosity, a soap thickening agent in amounts sufficient to gel said lubricating oil to grease consistency, and a synergistic proportion of zinc dialkyl dithiophosphate and the reaction product of caprylic acid and an imidazoline represented by the formula.



where R is selected from the group consisting of hydrogen and an aliphatic hydrocarbon having from 15 to 17 carbon and *n* is an integer of at least 1.

2. The composition of claim **1** wherein said imidazoline is 1-(2-aminoethyl)-2-n-heptadecyl-2-imidazoline.

3. The composition of claim **1** wherein the caprylic acid-imidazoline reaction product is



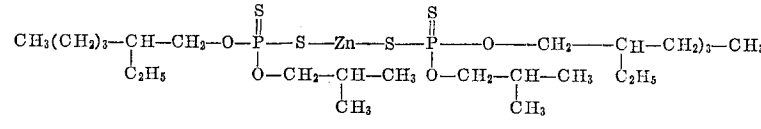
wherein R_1 is heptyl.

4. The composition of claim **1** wherein said reaction product is present in the amount of about 1.0 to 2.5 percent by weight.

5. The composition of claim **1** wherein the soap thickening agent is a lithium 12-hydroxy stearate soap.

6. The composition of claim **1** wherein said soap thickening agent is present in the amount of about 5 to 25 percent by weight.

7. The composition of claim **1** wherein said zinc dialkyl dithiophosphate is



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I. VAUGHN, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

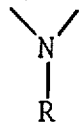
CERTIFICATE OF CORRECTION

Patent No. 3,390,081 June 25, 1968

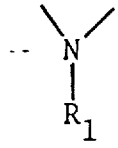
Peter E. Floeck

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

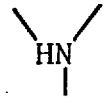
Column 2, line 31, "kettle" should read -- kettle and the --; line 60, the lower right-hand portion of the formula reading



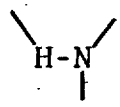
should read



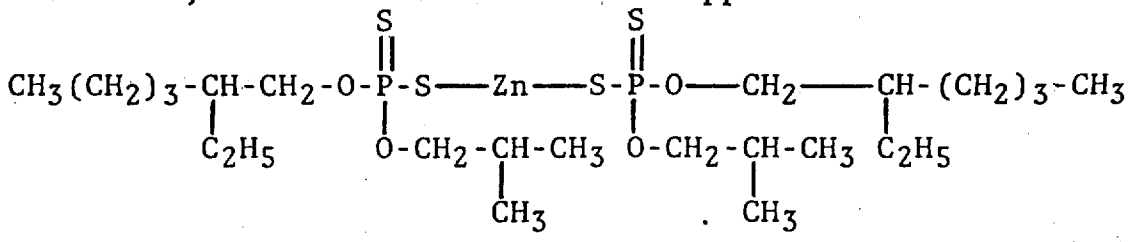
Column 3, lines 16 and 17, "substitutents" should read -- substituents --. Column 4, TABLE I, second column, line 2 thereof, "69.34" should read -- 69.35 --; same table, first column, line 8 thereof, "(imidazoline)" should read -- (imidazoline --. Column 5, line 23, "sapinification" should read -- saponfication --; same column 5, TABLE III, third column, line 5 thereof, "400" should read -- 4.00 --. Column 7, line 34, "1.108" should read -- 0.108 --; line 48, before "grease" insert -- base --. Column 8, line 9, "0%-1.2%" should read -- 0% and -1.2% --; line 31, "carbon" should read -- carbons --; lines 36 to 40, that portion of the formula reading



should read



Columns 7 and 8, the last formula should appear as shown below:



Signed and sealed this 16th day of December 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents