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## ALKENYL SUCCINIC ACID GREASE

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This invention relates to a lubricating grease and particularly to a gel-like lubricant prepared from a soap of an alkyl or an alkenyl substituted aliphatic dicarboxylic acid.

One of the principal objects of the invention is to provide a gel-like lubricating grease utilizing as part or all of the soap component a soap of an aliphatic dicarboxylic acid having a long alkyl or alkenyl side chain substituted for a hydrogen atom on one of the carbon atoms of the dicarboxylic acid chain.

Another object of the invention is to provide a dicarboxylic acid soap grease of this character having advantageously modified properties by the use of a mixture of the dicarboxylic acid with a soap-forming monocarboxylic acid for the saponification step.

Other objects and advantages of the invention will be apparent from the following description and the accompanying claims.

The use of a metal salt of an alkyl or alkenyl substituted aliphatic dicarboxylic acid as an additive in small proportions in a liquid lubricating oil, such as a motor oil, in order to improve the ring sticking and lacquer forming tendencies of the motor oil has been heretofore proposed. The present invention is distinguished by the use of particular metal soaps of the said dicarboxylic acids in sufficiently large proportion, and by a particular method of preparation involving high temperature heating to reach a gelation stage, to produce as a final product a gel-like lubricating grease; and also by the use of a mixture of the said dicarboxylic acid with a soap-forming monocarboxylic acid for the saponification step.

In accordance with the present invention, a suitable alkyl or alkenyl substituted aliphatic dicarboxylic acid having the carboxyl groups in a plane symmetrical configuration (on the same side of the carbon chain), and wherein the alkyl or alkenyl substituent group contains at least 8 carbon atoms and up to 25 carbon atoms or more to provide an oil solubilizing hydrocarbon group, is selected as part or all of the soap-forming acid. Examples of suitable acids for purposes of the present invention are the alkyl and alkenyl substituted fumaric, succinic, maleic, citraconic, glutaric and adipic acids. The alkyl or alkenyl substituent group, which generally contains about 8-16 carbon atoms and preferably 10 to 12 carbon atoms, is substituted for a hydrogen atom attached to one of the carbon atoms of the dicarboxylic acid chain. This is accomplished in known manner such as condensing an anhydride of the dicarboxylic acid with a high molecular

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weight olefin of the carbon atom content desired in the side chain, such as a propylene or butylene polymer or a selected fraction of polymer gasoline of the desired boiling range. The presence of the alkyl or alkenyl side chain of the stated carbon atom content on the dicarboxylic acid appears essential since experiments with high molecular weight dicarboxylic acids containing a similar number of carbon atoms in the acid chain but without an alkyl or alkenyl substituent group as specified, such as sebacic acid and dimerized linoleic acid, proved unsuitable in forming soaps compatible with the mineral lubricating oil or other liquid oleaginous lubricating base, and they exhibited no gelation effect when heated in the oil in substantial proportions at temperatures up to 580° F.

As representative of the dicarboxylic acids employed in accordance with the present invention and constituting the preferred acid from the standpoints of economic availability and improved results, the following description is directed to the use of a so-called alkenyl succinic acid. However, it should be understood that the invention is not restricted to this particular dicarboxylic acid since the other alkyl or alkenyl substituted aliphatic dicarboxylic acids mentioned can be employed in similar manner. The alkenyl succinic acid is obtained by condensing an olefin of the desired molecular weight with maleic acid anhydride to obtain the alkenyl succinic acid anhydride, and this may be followed by hydrolysis to produce the alkenyl succinic acid. The product produced in this manner may actually exist as an alkenyl succinic acid or an alkyl maleic acid (depending on whether the double bond remains in the hydrocarbon side chain or in the dicarboxylic acid chain), or a mixture thereof. In order to simplify the description of these condensation products and the acids produced thereby, reference will be made throughout the specification and claims to an alkenyl succinic acid or anhydride; but it is to be understood that this includes the alkyl maleic acid as well as the alkenyl succinic acid or mixtures thereof, or the corresponding anhydrides, as may be produced by this condensation reaction of an olefin with maleic acid anhydride with or without subsequent hydrolysis. It is not necessary to convert the anhydride to the corresponding dicarboxylic acid before forming the soap since the anhydride will also saponify with the metal oxide or hydroxide in the presence of the water used in the saponification step to form the soap.

By way of example, a C<sub>10</sub>-C<sub>12</sub> alkenyl succinic



acid anhydride was prepared by the condensation of maleic acid anhydride and a C<sub>10</sub>-C<sub>12</sub> fraction of propylene polymer by heating with agitation for 20 hours at a temperature of about 350-390° F. under gentle reflux. The reaction product was then allowed to cool and fractionated under diminished pressure to remove unreacted polymer and low boiling reaction products. The resulting alkenyl succinic acid anhydride was employed directly to produce certain of the soaps hereinafter described. On the other hand, the alkenyl succinic acid anhydride can be heated at about 200° F. in the presence of an equal volume of water to affect hydrolysis to the alkenyl succinic acid and until the excess water has evaporated. Products containing a C<sub>8</sub>-C<sub>10</sub> alkyl side chain and a C<sub>12</sub>-C<sub>16</sub> alkyl side chain were prepared in a similar manner except that a different fraction of the propylene polymer of the specified carbon atom content was employed in each case.

Metal soaps of the resulting alkenyl succinic acid anhydride or the alkenyl succinic acid were then prepared by heating the former with a metal oxide or hydroxide in the presence of water and a portion or all of the mineral lubricating oil or other liquid oleaginous vehicle at a temperature of about 175-240° F. for a period of about 1-2 hours. Following this saponification period, the product was dehydrated by heating at a higher temperature up to about 300-320° F. for a further period of about ½-1 hour. The resulting dehydrated saponified product then had to be heated to a still higher temperature, with any further oil addition to obtain the desired consistency and with continual stirring, to reach a gelation temperature in excess of 450° F. and generally about 500° F., this additional heating and stirring usually requiring about 1-2 hours. The product was then allowed to cool to room temperature. Products were prepared containing 20% soap each of the following metal soaps of the C<sub>10</sub>-C<sub>12</sub> alkenyl succinic acid in a naphthene base lubricating oil having a S. U. S. viscosity at 100° F. of 307 with the results shown in Table I below.

Table I

Type of Metal Soap	Characteristic of Product
Sodium.....	Soap insoluble—separate oil and soap phases.
Potassium.....	Do.
Lithium.....	Do.
Calcium.....	Liquid—not uniform.
Barium.....	Soap insoluble—separate oil and soap phases.
Strontium.....	Do.
Magnesium.....	Dry amber gel-like grease.
Beryllium.....	Rubbery elastic dark amber gel grease.
Lead.....	Soap insoluble—separate oil and soap phases.
Tin (stannous) <sup>1</sup> ..	Do.
Zinc <sup>1</sup> .....	Do.
Titanium (ous)...	Do.
Titanium (ic)....	No reaction to form soap.
Aluminum.....	Transparent tacky amber gel grease.

<sup>1</sup> 10% soap.

The foregoing table illustrates an unusual and unpredictable feature of these particular dicarboxylic acid soaps in that only the polyvalent metal soaps of magnesium, aluminum and beryllium formed gel-like greases, and the latter only when the dehydrated saponified product was heated in the presence of the liquid lubricating base to a high temperature in excess of 450° F. Most of the other metal soaps tested were insoluble in the lubricating oil and gave products that separated into two phases during manufacture or during storage. The calcium soap even

in 20% concentration formed a liquid non-uniform product; while the titanate oxide did not react with the alkenyl succinic acid anhydride.

The type and viscosity of the mineral lubricating oil employed in the grease also affects its properties. This is illustrated in the following Table II which sets forth the characteristics of magnesium C<sub>10</sub>-C<sub>12</sub> alkenyl succinic acid (referred to as "ASA") greases prepared from different types of paraffin base and naphthene base lubricating oils and mixtures thereof.

Table II

Liquid Lubricating Base	Soap, Per Cent	Characteristic of Product
Paraffin base lubricating oil SUS Vis. at 100° F. of 101 sec.	20	Gel-like.
Paraffin base lubricating oil SAE 10 motor oil grade—SUS Vis. at 100° F. of 168.	20	Do.
Paraffin base lubricating oil SAE 20 motor oil grade—SUS Vis. at 100° F. of 336.	20	Do.
Paraffin base lubricating oil SAE 40 motor oil grade—SUS Vis. at 100° F. of 803.	20	Soft—mixture of oil and gel particles.
Residual paraffin base lubricating oil—Kinematic Vis. at 210° F. of 196 cs.	20	Viscous liquid—no gelation.
Naphthene base lubricating oil SUS Vis. at 100° F. of 307 sec.	15	Hard; gel-like.
Paraffin base lubricating oil SUS Vis. at 100° F. of 66 sec.	32.5	Soft stringy gel.
Paraffin base lubricating oil SAE 20 motor oil grade.	15	Soft sandy gel.
Mixture of 2.9% naphthene base oil of SUS of 307 with 97.1% of paraffin base oil of SAE 20 grade.	10	Tacky translucent gel.

As shown in the foregoing table, the lighter and medium grades of paraffin base and naphthene base lubricating oils of the distillate type all provide excellent grease structure. However, the distillate lubricating oils of heavier grade generally having an SUS viscosity at 100° F. in excess of about 800 and the residual lubricating oils result in products which are either viscous liquids or are too soft with non-homogeneous texture. Moreover, the naphthene base lubricating oils of comparable viscosity require less soap content than the paraffin base lubricating oils to produce greases of the same consistency or penetration. The grease listed in the last item of the table was prepared by saponifying the acid in the presence of the naphthene base oil, and following dehydration the paraffin base oil was added to bring the product to the desired consistency and soap content. In general, the soap content varies from somewhat in excess of 5% to less than 50% on the weight of the grease composition, depending on the type of lubricating oil as well as the type of soap employed, to produce gel-like greases meeting the specifications for the various grades of grease.

In addition to the distillate mineral lubricating oils mentioned, the various types of synthetic liquid oleaginous lubricating bases having comparable viscosities can also be employed as part or all of the lubricating base with these particular soaps. Among the types of synthetic liquid oleaginous lubricating bases which can be employed are the oil soluble high boiling high molecular weight aliphatic ethers, aromatic esters, aliphatic mono- and dicarboxylic esters, phosphorus acid esters and halogenated aromatic compounds which possess lubricating properties and also have small change in viscosity for a given change in temperature. Of the various synthetic oleaginous compounds specified, those falling within the category of aliphatic dicar-



boxylic acid esters, and particularly the branched chain aliphatic esters, such as di-2-ethylhexyl sebacate, are preferred. In the following description and claims, the expression "liquid oleaginous lubricating base" is employed to designate both the mineral lubricating oils and the synthetic lubricating bases specified.

Typical properties of the magnesium, beryllium, and aluminum base greases prepared as outlined above from alkenyl succinic acid or alkenyl succinic anhydride are set forth in the following Table III, wherein the acid component of the soap consisted of the C<sub>10</sub>-C<sub>12</sub> alkenyl succinic acid.

Table III

Soap, Per Cent	Type of Oil	Dropping Pt. ° F.	Penetration ASTM at 77° F.	
			Un-worked	Worked
Mg 5%-----	Naphthene SUS at 100° F. of 307.	over 500	365	too soft
Mg 10%-----	do-----	over 500	228	320
Mg 15%-----	do-----	over 500	133	273
Mg 15%-----	Paraffin SAE 20.	over 500	252	341
Be 20%-----	Naphthene SUS at 100° F. of 307.	over 500		
Be 8.3%-----	do-----	300	359	334
Al 20%-----	do-----	over 500		
Al 11.4%-----	do-----	over 500	too soft	369

The foregoing table shows that the greases of the present invention have exceptional characteristics including melting or dropping points above 500° F., even in the lighter grades employing the lower soap contents. Moreover, these greases are obtained with excellent yields which further makes this type of dicarboxylic acid grease attractive. It will be noted that the greases discussed above consisted of the dicarboxylic acid soap as the entire soap content. While these are satisfactory for certain uses, it is to be understood that the foregoing data has been listed primarily to illustrate the properties of the dicarboxylic acid soap grease, and that other types of soap will frequently be included, as well as various other additives, to improve the properties thereof for specialized uses. Thus the magnesium, beryllium and aluminum soaps of the dicarboxylic acids enumerated above can be employed in conjunction with the ordinary soaps in various proportions to produce mixed base, as well as mixed acid type, greases. Among the soaps which can be added to the greases of the present invention may be mentioned the sodium, calcium, barium, lithium, strontium, zinc and lead soaps of the ordinary saturated and unsaturated soap-forming fatty acids and fats including the hydrogenated fats and fatty acids, such as hydrogenated fish oil acids. Also, soaps of soap-forming hydroxy fatty acids and their glycerides, such as hydrogenated castor oil, naphthenic acids and sulfonic acids can be employed. Ordinarily, to obtain the desirable properties of the dicarboxylic acid grease including extremely high melting or dropping point, the magnesium, beryllium, or aluminum soap of these dicarboxylic acids is employed in about an equal or major proportion with respect to the conventional soap used, except where the conventional soap also possesses similar properties.

As an example of a suitable mixed base grease of this character, which has been prepared with an extreme pressure additive to meet specialized service for ball bearing lubrication, the following is mentioned:

Table IV

Composition of grease:		Per Cent By Weight
Mg. C <sub>10</sub> -C <sub>12</sub> ASA soap-----		10
Lead soap of menhaden (fish oil) acids		10
Sulfurized sperm oil-----		10
Paraffin base lubricating oil SAE 20 grade-----		70
Tests of grease:		
Dropping point, °F.-----		496
Penetration ASTM 77° F.-----		
Worked-----		236
Unworked-----		165
Timken Test pounds:		
OK-----		20
Score-----		25
Torque Breakdown Machine:		
Timken bearing 80° F.-----		fair
Timken bearing 80-250° F.-----		fair
Federal bearing 80° F.-----		excellent

The Timken test referred to above employs the well known Timken machine used for testing extreme pressure lubricants, except for replacement of the usual liquid lubricant reservoir, gravity flow line to feed the liquid over the test specimens, and the scavenging pump which removes the used lubricant from the sump and returns it to the reservoir, with a special air pressure grease feed system. The latter involves a grease reservoir cylinder fitted with a piston and cap. Air pressure between 20 and 50 p. s. i. is applied to the top of the piston to force grease from the bottom of the reservoir to the test pieces. The flow of grease is maintained between 0.1 and 0.2 pound per minute by a regulating valve in the feed line. The conditions of the test are the same as for liquid lubricants except that the grease is not heated. The weights indicated in the foregoing table are those which are applied to the lever arm which forces the test block against the hardened steel cup mounted on the end of the horizontal spindle rotated at 800 R. P. M. in conventional manner. This test is thus a measure of the load carrying capacity of the grease.

The Torque Breakdown Machine test is designed to evaluate the lubricating properties of greases used for the lubrication of anti-friction bearings. Two standard 3.9370 inch Timken tapered roller bearings packed with about 25 g. each of the grease under test, and a standard Federal Precision Ball Bearing No. 1211 packed with about 32 g. of the grease are employed, the packed bearings being weighed before test. In the test of each bearing, the bearing is assembled on a motor driven shaft supported by pillow blocks within a bearing housing mounted within an insulated chamber with a system of levers connected to register any movement of the bearing housing in grams on a platform scale, whereby both the starting torque and the running torque can be measured. The insulated chamber is equipped with a copper coil tubing for the circulation of a cooling or heating medium, and also with an insulated cover equipped with an electric heater and a motor driven fan, whereby the temperature of the chamber and bearing under test can be accurately controlled. The test of the Timken bearings at 80° F. is made at 900 R. P. M., and the test of the Federal bearing at 80° F. is made at 1750 R. P. M., each for a period of two hours. The instant the motor driving the test bearing is started, the first torque reading is recorded as the starting torque. Then running torque and temperature readings of the bearing



are recorded at one minute intervals for the first 30 minutes, and at 10 minute intervals for the remaining 1½ hours, while the temperature within the chamber is adjusted to maintain the temperature within 2° of 80° F. At the end of the run, the bearing is removed from the housing and weighed, whereby the weight of the grease remaining on the bearing can be computed. The weight of the grease on the housing is also determined; and grease leakage (grease escaping from both the bearing and housing) is determined by actual weight measurement or by difference. A visual inspection is made of the grease remaining on the bearing to ascertain whether any structure or texture change has taken place; and the penetration of a sample of the grease taken from the bearing after test is compared with the original penetration of the grease. A second test procedure is conducted on the same machine in this manner, except that in this case the temperature of the chamber and of the bearing is raised gradually from an initial 80° F. to a temperature of 250° F. at the end of an hour. The test is then run at 250° F. for an additional two hours before terminating the test. Similar readings are made, as previously described. The results thus obtained are compared with those secured in the same tests on a standard premium ball and roller bearing grease of known excellent performance; and overall lubricating performance of the test grease is generally reported on the basis of this comparison as excellent, good, fair or poor.

The foregoing data show that this mixed base grease containing the sulfurized sperm oil EP additive provided improved extreme pressure properties and afforded fair to excellent lubrication of ball and roller bearings under the rigorous conditions of the torque breakdown test. These results, in conjunction with the high dropping point and excellent yield of the magnesium ASA type product, are indicative of the advantageous results of the present invention.

In the preparation of the mixed base greases described above, the magnesium ASA soap and the lead menhadenate were separately formed and mixed in the lubricating oil by blending at high temperatures with agitation. Thus the magnesium ASA soap was formed by saponification of the alkenyl succinic acid anhydride in the customary manner, the product dehydrated, and then further heated with addition of oil to the gelation temperature of about 500° F. The lead menhadenate and sulfurized sperm oil were then added with stirring as the product cooled from about 500 to 440° F. It will be understood

properties of the dicarboxylic acid soap greases can also be desirably modified, particularly from the standpoint of improving lubricating properties and storage stability, by saponifying a mixture of the alkyl or alkenyl substituted aliphatic dicarboxylic acid with a soap-forming mono-carboxylic acid. Various types of soap-forming saturated and unsaturated fatty acids, hydroxy fatty acids, sulfonic acids, naphthenic acids, acids from the oxidation of paraffin wax, etc., have been found effective for this purpose. In addition to desirably modifying the properties of the grease, the manufacturing procedure is also aided in some cases since the gelation temperature has been found to be lowered. These mixed acid type greases are prepared utilizing a major proportion of the dicarboxylic acid with a minor proportion of the mono-carboxylic acid generally in a ratio of about 2:1, although ratios from above approximately 1:1 up to 9:1 have been employed with good results. Increasing the proportion of the mono-basic acid in the mixture utilized for saponification up to and over an equal proportion with the dicarboxylic acid, results in a very substantial lowering of the dropping point from that of the dicarboxylic acid grease itself, and consequently the desirable properties of the latter are not effectively retained.

The procedure for manufacture of these mixed acid greases is essentially the same as previously described for the dicarboxylic acid greases. Thus the mixture of the dicarboxylic acid with the selected mono-carboxylic acid in the desired proportions is saponified by heating with an oxide or hydroxide of magnesium, beryllium or aluminum in the presence of water and a portion of the mineral lubricating oil or other liquid oleaginous lubricating base. In place of the dicarboxylic acid, the corresponding anhydride thereof can be employed. Saponification takes place at a temperature of about 180–220° F., the saponified product is then heated to about 280–320° F. for dehydration, and the resulting dehydrated material is then further heated with the necessary oil addition and stirring to a gelation temperature of about 450–500° F., followed by cooling and drawing at a temperature of about 340–100° F.

As examples of these mixed acid greases, the following Table V sets forth the gelation temperature during manufacture and the properties of certain Mg base greases prepared from a 2:1 mixture by weight of C<sub>10</sub>–C<sub>12</sub> alkenyl succinic acid anhydride with the specified mono-basic acid, the soap content of the grease in each case being approximately 10% by weight.

Table V

Mono-Basic Acid	Liquid to Gel Temperature, °F.	Dropping Pt., °F.	Penetration ASTM, 77° F.		Lubrication Grease Breakdown Test, RT–300° F.
			Unworked	Worked	
Behenic Acid .....	460	449	200	308	Good.
Stearic Acid .....	450	410	208	297	Excellent.
Myristic Acid .....	490	374	362	Soft	Do.
Snodotte Acids (hydrogenated fish oil acids) .....	460	411	241	346	Do.
12-Hydroxystearic Acid .....	470	458	199	283	Fair.
Sulfonic Acid .....	500	349	270	332	Do.
Naphthenic Acid .....	495	420	170	266	Poor.
Oleic Acid .....	500	382	312	376	Fair.
Wax Acids .....	490	350	366	Soft	Excellent.

that other types of additives, such as oxidation inhibitors, dyes and the like, can also be added during the cooling and stirring stage and prior to drawing of the grease.

In accordance with the present invention, the

The foregoing Grease Breakdown Test is used to determine the lubricating properties of ball bearing greases at various temperatures. The machine employed consisting essentially of a standard motor-driven rotating ball bearing (20 mm.



bore x 47 mm. diameter x 14 mm. width) mounted vertically and enclosed in an oil jacket containing an electric immersion coil with adjustable rheostat for temperature control. The upper face of the bearing is not covered, so that observations of performance during operation can be made. The bearing is charged with 5 grams of the grease. With the system at atmospheric temperature, rotation of the packed test bearing is started at 3450 R. P. M. and allowed to proceed for 3 minutes, during which time observations are taken of the general nature of the lubrication provided, i. e., whether or not the grease folds over the bearing, channels, slings away from the bearing, tends to "ball up," etc. Then heat is applied to the bearing as it continues to rotate at the same speed so as to gradually raise the temperature of the bearing until the grease fails to lubricate (the breakdown point) or until a temperature of 300° F. is reached in about 40 minutes from the start of the test. Beginning at a bearing temperature of 100° F., observations of performance are recorded for every 25° F. temperature rise or for any significant development such as texture change, expansion in volume, air entrainment, channeling, leakage, melting and consequent thinning, separation, discoloration, vaporization, etc. After completing the run, the bearing is removed and cooled; and grease remaining on the bearing is examined for texture and consistency change, discoloration, etc. and compared with the original grease. The results obtained are compared with those secured in the same test on a standard premium ball and roller bearing grease of known excellent performance; and the performance of the test grease is rated on a comparative basis as excellent, good, fair or poor.

From the foregoing table it will be noted that behenic acid, stearic acid, hydrogenated fish oil acids and 12-hydroxystearic acid produced a substantial lowering of the gelation temperature, while at the same time maintaining the dropping point of the resultant grease above 400° F. The stearic, myristic, hydrogenated fish oil acids and the acids from the oxidation of paraffin wax provided greases of excellent lubricating properties as determined by the rigorous Grease Breakdown Test, with all the listed greases withstanding a temperature as high as 300° F. in this test. While monocarboxylic acids proved satisfactory in admixture with the dicarboxylic acids for preparation of these greases, the use of fats, such as tallow and hydrogenated castor oil, proved unsatisfactory in that liquid or viscous to unsuitably stiff grainy products were obtained.

The effect of varying the dicarboxylic acid to mono-carboxylic acid ratio in the preparation of these mixed acid greases is illustrated in the following Table VI for a magnesium C<sub>10</sub>-C<sub>12</sub> ASA:Mg stearate grease prepared with a paraffin base lubricating oil of SAE 20 grade, the soap content being 10% in each case.

Table VI

Ratio MgAMA: Mg Stearate	Gelation Temperature, °F.	Dropping Pt., °F.	Penetration ASTM, 77° F.		Lubrication Grease Breakdown Test RT- 300° F.
			Unworked	Worked	
0:1	-----	Fluid	Fluid	Fluid	-----
1:1	450	343	156	217	Poor.
2:1	450	410	208	297	Excellent.
3:1	450	440	217	298	Poor.
1:0	500	Over 500	183	236	Do.

In the foregoing table, it will be seen that an increase in the ratio of the magnesium ASA to the magnesium stearate within the limits of 1:1 to 3:1 produced a substantial increase in dropping point of the grease, while the desirable lowering of the gelation temperature to 450° F. was maintained. The best lubricating qualities were obtained with the 2:1 ratio, as very strikingly shown by the Grease Breakdown Test. The presence of the mono-carboxylic acid in all cases improved the storage stability of the grease.

The effect of total soap content in the 2:1 Mg C<sub>10</sub>-C<sub>12</sub> ASA:Mg stearate grease was found to be in line with the general behavior of soap/oil systems as illustrated in the following Table VII.

Table VII

Total Soap, Per Cent	Dropping Pt., °F.	Penetration, ASTM, 77° F.	
		Unworked	Worked
15	439	56	96
10	428	174	245

The effect of the alkyl side chain length of the ASA in the system, 10% soap of 2:1 Mg ASA:Mg stearate/paraffin base oil of SAE 20 grade, was investigated by using alkenyl succinic acid with alkyl side chains of C<sub>8</sub>-C<sub>10</sub>, C<sub>10</sub>-C<sub>12</sub> and C<sub>12</sub>-C<sub>14</sub>, respectively. The following results with respect to gelation temperature and properties of the resulting products were obtained.

Table VIII

Chain Length	Required Temperature for Gelation, °F.	Dropping Point, °F.	Penetration, ASTM, 77° F.		Appearance
			Unworked	Worked	
C <sub>8</sub> -C <sub>10</sub> ---	490	-----	-----	-----	Fluid, Uniform, gel- like. Grainy, but- tery.
C <sub>10</sub> -C <sub>12</sub> ---	450	410	208	297	
C <sub>12</sub> -C <sub>14</sub> ---	450	409	196	289	

As noted from the table, the ASA with the C<sub>10</sub>-C<sub>12</sub> side chain gave optimum results with respect to uniformity and gel characteristics. While this particular mixed soap product made with the C<sub>8</sub>-C<sub>10</sub> ASA was fluid, satisfactory gel type greases have been prepared from the C<sub>8</sub>-C<sub>10</sub> ASA unmixed with mono-carboxylic acid soap, as illustrated in the following Table IX for greases containing 10% magnesium ASA in a naphthene base lubricating oil having a S. U. S. viscosity at 100° F. of about 300.

Table IX

Alkyl Group	Gelation Temperature, °F.	Dropping Pt., °F.	Penetration ASTM, 77° F.	
			Unworked	Worked
C <sub>8</sub> -C <sub>10</sub> -----	500	over 500	291	364
C <sub>10</sub> -C <sub>12</sub> -----	490	over 500	226	320
C <sub>12</sub> -C <sub>14</sub> -----	480	over 500	146	209

The type and viscosity of mineral lubricating oil used has a similar effect in the mixed acid greases as described above in connection with the straight dicarboxylic acid greases. This is illustrated in the following Table X for the system 10% 2:1 Mg. C<sub>10</sub>-C<sub>12</sub> ASA:Mg. stearate/oil.



Table X

Type of Oil	Maximum Temperature used, °F.	Dropping Pt., °F.	Penetration, ASTM, 77° F.		Appearance
			Unworked	Worked	
Paraffin base oil SAE 10.....	450	390	176	262	Gel-like.
Paraffin base oil SAE 20.....	450	410	208	297	Do.
Paraffin base oil SAE 40.....	490				Viscous liquid.
Naphthene base oil SUS Vis. at 100° F. of 300.....	455	428	174	245	Gel-like.
Paraffin <sup>1</sup> base residuum SUS Vis. at 210° F. of 196.....	460				Gel-like fluid.

<sup>1</sup> Soap.

The following details of preparation of a superior type of ball and roller bearing grease containing an oxidation inhibitor are set forth as a preferred example of the present invention. Five pounds of water, 24 pounds of a paraffin base lubricating oil of SAE 20 grade, 1658 grams of C<sub>10</sub>-C<sub>12</sub> alkenyl succinic acid anhydride, a slurry of 518 grams of magnesium hydroxide in 10 pounds of water, and 881 grams of triple pressed stearic acid were charged to a grease kettle in the order listed, and heating and stirring was started. The temperature was raised to 200° F. in about 1 hour and then was maintained at about 200-219° F. with continued stirring and boiling for about 6 hours, at which time saponification was completed and the product had thickened. The temperature was then raised to about 300° F. with continued stirring in about 2 hours and maintained slightly above 300° F. for another hour, when the kettle was shut down overnight. The product at this time was a soft amber-colored liquid and dehydration was substantially complete. The next morning heating and stirring of the kettle were resumed with the temperature being rather rapidly raised to about 460° F. over a period of 2½ hours, and then being held at a gelation temperature of 450-476° F. while an additional 30 pounds of the paraffin base oil were gradually added during a period of about 2 hours. The heat was then cut and the product slowly cooled down to 200° F. with continued stirring over about 4 hours, when the mix assumed a smooth glossy dark brown gel-like appearance. A sample removed for control purposes at this time had an unworked ASTM penetration at 78° F. of 309 and a worked penetration of 327. The product was allowed to continue to cool with stirring to about 90° F. when 30 pounds of the uninhibited grease were drawn. To the remaining batch of grease in the kettle a blend of 70 grams of diphenylamine in one pound of the paraffin base lubricating oil were added. Stirring of the mix was continued at about 90° F. for an hour, when the final inhibited grease was drawn as an amber gel-like tacky product, which became soft on slight rubbing. The calculated composition of this grease was:

	Per cent by weight
Mg. C <sub>10</sub> -C <sub>12</sub> ASA soap .....	6.4
Mg. Stearate soap .....	3.2
Paraffin base lubricating oil SAE 20 grade ..	89.9
Diphenylamine .....	0.5

Tests on the inhibited grease prepared as outlined above were obtained as listed in the appended Table XI.

Table XI

	Dropping point, °F.....	409
20	Penetration, ASTM, 77° F.—	
	Unworked .....	195
	Worked .....	307
	Soap, Mg, % (determined) <sup>1</sup> .....	8.6
25	Lubrication (torque breakdown and grease breakdown machine tests):	
	Small ball bearing, 80-300° F.....	Excellent
	Large ball bearing, 80° F.....	Excellent
	Large ball bearing, 80-250° F.....	Excellent
30	Roller bearing, 80° F.....	Good
	Roller bearing, 80-250° F.....	Fair
	Shear resistance, Dynamic shear, 8 hr. 225° F.:	
	Miniature penetration, original .....	90
	Miniature penetration, after test .....	86
35	Low temperature torque:	
	Minus 40° F., sec./rev.....	66
	Minus 50° F., sec./rev.....	188
	Water resistance test loss, per cent .....	20
40	Norma-Hoffmann oxidation:	
	Hours at 210° F.....	100
	Pressure drop, lb.....	5
	Oil separation, 50 hr. 210° F.:	
	Separation, per cent .....	0.5
	Evaporation, per cent .....	0.25

<sup>1</sup> Basis of weight of total fatty acid.

The Dynamic Shear Resistance test of the foregoing table is a measure of the resistance of the grease to texture change when worked under high shearing stress, the test being carried out as described in U. S. Patent No. 2,450,219, Ashburn and Puryear, in column 5, lines 6-19. A small change in miniature penetration of the sample after test in comparison with the original is indicative of excellent texture stability under high shearing stress. The miniature penetration test is described in Ind. Eng. Chem., analytical edition, vol. II, page 108, February 15, 1939.

The Low Temperature Torque test of the foregoing table is essentially a measure of the resistance of the grease to congealing and of its ability to afford proper lubrication under extremely low temperature conditions, such as are encountered in aircraft at very high altitudes. The apparatus employed for the test consists essentially of a vertically mounted hollow spindle with a No. 204K Conrad type 8-ball bearing mounted on the bottom, and a drum on which is wrapped a coiled line for applying torque mounted on the top. The bearing packed with a 60% capacity charge of the grease to be tested is clamped at the inner race to the spindle, while the outer race is clamped immovably to a stationary cup within which the bearing is inserted. The assembly is inserted with the lower bearing end in a low temperature bath containing isopropyl alcohol,



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and the desired temperature of the bath and bearing is attained by dropping dry ice in the bath. The drum and drum extension carried at the upper end of the hollow spindle and protruding from the bath are held in vertical position by a tapered roller bearing. The line coiled around the drum extends over a pulley to a container into which the desired weights are added to apply the torque load to the hollow spindle to thereby cause rotation of the spindle and inner race of the bearing with respect to the fixed outer race. A time of not less than two hours is utilized to cool the bearing to the test temperature, and an additional soaking period at the test temperature is permitted such that the test is not run until three hours from the start of cooling. The bearing is rotated one revolution in each direction during the cooling and soaking periods. When the desired bearing temperature and soaking period are attained, a 2000 g.-cm. torque load is applied in both clockwise and counterclockwise directions, and the number of seconds for one rotation in each direction is observed and the readings averaged.

The Water Resistance test of the foregoing table is that described in Army-Navy Aeronautical Specification AN-G-25, Low Temperature Aircraft Lubricating Grease, item F-4f, October 9, 1947. This measures the resistance of the grease against being washed out of the bearing in the presence of water. Briefly, the test involves the 204 ball bearing mentioned above packed with 4 grams of the grease and clamped in a tight fitting housing which allows the inner race to rotate. The latter is mounted on a horizontal shaft and rotated at 600 R. P. M. while a fine stream of distilled water is directed against the end plate of the bearing housing just above the outer opening of the bearing housing. This operation is continued for one hour, when the loss in weight of the dried bearing is then reported as grease loss; and this loss in weight divided by the weight of the grease used in packing the bearing is reported as the % loss.

The Norma-Hoffmann Oxidation test is a measure of the resistance to oxidation of lubricating greases when stored under static conditions for long periods of time, as when coated in thin films on anti-friction bearings, motor parts, etc. In this test five four gram samples of the grease are put in flat sample dishes and placed in a stainless steel bomb sealed with a lead gasket in an atmosphere of oxygen under an initial pressure of 110 pounds per square inch at a temperature of 210° F. The pressure drop in pounds within the bomb is then recorded at 100 hours as shown in the table, or at different times up to 500 hours or until a pressure drop of 55 pounds per square inch occurs.

The Oil Separation test is described in Army-Navy Aeronautical Specification AN-G-3a, Low Temperature Lubricating Grease, page 5, March 6, 1943. This is a measure of the resistance of the grease to oil bleeding and evaporation. In this test 10 grams of the grease are placed in a weighed 60 mesh screen cone supported from the rim of a weighed 100 milliliter beaker so that the pointed bottom of the screen cone containing the grease is substantially above the bottom of the beaker. This assembly is then placed in a gravity convection oven maintained at 210° F. for a period of 50 hours. At the end of that period, the assembly is removed, cooled in a desiccator, and the beaker and cone weighed together and the beaker weighed separately. The final weight of the beaker minus the initial weight of the beaker

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divided by the initial weight of the grease sample times 100 is reported as % bleeding. The initial weight of the beaker plus cone and grease minus the final weight of the beaker plus cone and grease divided by the initial weight of the grease sample times 100 is reported as % evaporation.

The foregoing Table XI shows that this grease has excellent characteristics in regard to lubrication, low temperature torque, shear resistance, resistance to oil separation and water resistance. Comparison of this grease with a premium type of ball and roller bearing grease now on the market showed the former to be comparable or superior for this specialized type of service.

Other greases prepared in accordance with the detailed procedure outlined above but employing different oxidation inhibitors showed that the present type of grease has excellent response to oxidation inhibitors, as illustrated by the following data.

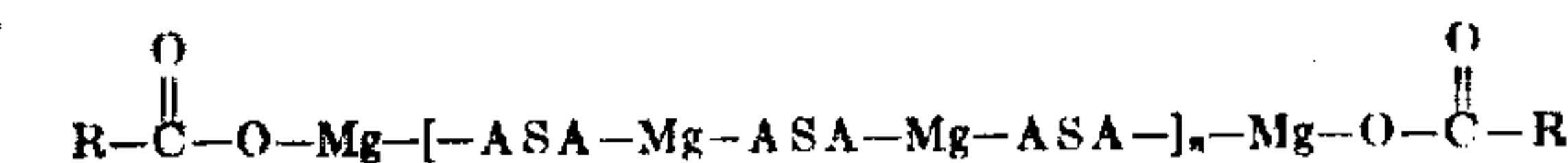
Table XII

Inhibitor (0.5% based on the grease)	Norma-Hoffmann Oxidation Test	
	Hours	Pressure Drop, Lbs.
None	20	21
Diphenylamine	100	5
Phenyl alphanaphthylamine	100	2
4-methyl 2,6-di-tertiary butyl phenol	100	2
Tetramethyl diamino diphenyl methane	100	1

It is postulated that the ASA soap grease has a chain-like structure, as illustrated below for the straight magnesium ASA grease.



where  $n$  represents a number satisfying the chain length of the polymer. Rather high chain length is believed responsible for the comparatively hard gel-like appearance, high melting point and good yield of the magnesium ASA greases. It is further postulated that the incorporation of the mono-carboxylic acid in the mixture being saponified effects a reduction in the average chain length of the magnesium ASA polymer brought about by the mono-basic radical forming a terminal group and preventing further lengthening of the chain, as illustrated below:



where  $n$  is a number indicating the chain length of the magnesium ASA polymer. Molecular weight determinations by the Staudinger viscosity method on lutidine solutions of the 2:1 Mg C<sub>10</sub>-C<sub>12</sub> ASA:Mg stearate soap gave values of approximately 2100 and 1600 respectively. Similar molecular weight determinations by this method on 2% and 1% solutions of the soap in a paraffin base lubricating oil of SAE 20 grade gave values of 1860 and 1295 respectively. The theoretical molecular weight of the 2:1 (weight ratio) magnesium ASA:Mg stearate (equivalent to a 4:1 mol ratio) soap is 1770, assuming a polymer with 4 mols of ASA and 2 mols of stearic acid per molecule. From these determinations, it is believed that the value of  $n$  in the above formula for the compound dicarboxylic-monocarboxylic acid soap may vary between about 1 and 4 including fractional increments therebetween.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations



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should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating grease comprising an oleaginous liquid lubricating base as the predominant constituent, and in excess of 5% but below 50% by weight based on the grease of a soap of a hydrocarbon substituted aliphatic dicarboxylic acid having the carboxyl groups in a plane symmetrical configuration and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl and contains at least eight carbon atoms, said soap being formed from a polyvalent metal selected from the group consisting of magnesium, aluminum and beryllium, said soap being in sufficient proportion with the mixture of soap and lubricating base heat treated at a gelation temperature to thicken said lubricating base to a gel-like consistency.

2. A lubricating grease according to claim 1, wherein the aliphatic substituted dicarboxylic acid is an alkenyl succinic acid.

3. A lubricating grease according to claim 2, wherein the soap is magnesium C<sub>10</sub>-C<sub>12</sub> alkenyl succinate.

4. A lubricating grease comprising an oleaginous liquid lubricating base as the predominant constituent, and in excess of 5% but less than 50% by weight based on the grease of a soap of a polyvalent metal selected from the group consisting of magnesium, aluminum, and beryllium, said soap being formed from a mixture of a major proportion of a hydrocarbon substituted aliphatic dicarboxylic acid having the carboxyl groups in a plane symmetrical configuration and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl and contains at least eight carbon atoms, and a minor proportion of a soap-forming mono-carboxylic acid, said soap being in sufficient proportion with the mixture of soap and lubricating base heat treated at a gelation temperature to thicken said lubricating base to a gel-like consistency.

5. A lubricating grease according to claim 4, wherein the substituted aliphatic dicarboxylic acid is an alkenyl succinic acid.

6. A lubricating grease according to claim 5, wherein the soap is magnesium alkenyl succinate-magnesium stearate.

7. A lubricating grease comprising a mineral lubricating oil as the major constituent, in excess of 5% but less than 50% by weight based on the grease of soap consisting of a major proportion of magnesium C<sub>10</sub>-C<sub>12</sub> alkenyl succinate and a minor proportion of magnesium stearate sufficient with heat treatment at a gelation temperature to thicken said lubricating oil to a gel-like consistency, and a small amount of an oxidation inhibitor.

8. A lubricating grease according to claim 7, wherein the soap is about a 2:1 mixture by weight of the magnesium C<sub>10</sub>-C<sub>12</sub> alkenyl succinate and the magnesium stearate respectively, and the oxidation inhibitor is selected from the group consisting of a diphenylamine, phenyl-alpha-naphthylamine, 4-methyl 2,6-ditertiary butyl phenol, and tetra-methyl diamino diphenyl methane.

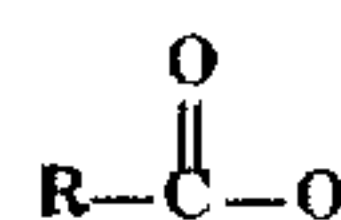
9. A lubricating grease comprising an oleaginous liquid lubricating base as the predominant constituent, and in excess of 5% and less than 50% by weight based on the grease of a magnesium polymer soap of the formula



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where ADA represents a hydrocarbon substituted aliphatic dicarboxylic acid residue having the carboxyl groups in a plane symmetrical configuration and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl and contains at least eight carbon atoms, R represents the hydrocarbon portion of terminal soap-forming mono-carboxylic acid residues, and  $n$  is a number indicating the chain length of the magnesium dicarboxylate portion of the soap polymer which may vary between 1 and 4 including fractional increments therebetween, said soap being in sufficient proportion with the mixture of soap and lubricating base heat treated at a gelation temperature to thicken said lubricating base to a gel-like consistency.

10. A lubricating grease according to claim 9, wherein ADA is C<sub>10</sub>-C<sub>12</sub> alkenyl succinate, and



is a stearic acid residue.

11. A lubricating grease according to claim 10, wherein the soap polymer has a molecular weight approximating a chain length of about four ADA groups.

12. The method of preparing a lubricating grease which comprises saponifying a hydrocarbon substituted aliphatic dicarboxylic acid or anhydride thereof having the carboxyl groups in a plane symmetrical configuration, and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl and substituent group contains at least eight carbon atoms, with an oxide or hydroxide of a polyvalent metal selected from the group consisting of magnesium, aluminum and beryllium, dehydrating the resulting saponification product, then heating the dehydrated saponified product in the presence of a predominant proportion of a liquid oleaginous lubricating base to a gelation temperature above about 450° F., and drawing the product to obtain a gel-like grease containing in excess of 5% and less than 50% by weight of said soap based on the grease.

13. The method according to claim 12, wherein the dicarboxylic acid is an alkenyl succinic acid.

14. The method of preparing a lubricating grease which comprises saponifying a mixture consisting of a major proportion of a hydrocarbon substituted aliphatic dicarboxylic acid or anhydride thereof having the carboxyl groups in a plane symmetrical configuration, and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl and contains at least eight carbon atoms, and a minor proportion of a soap-forming mono-carboxylic acid, with an oxide or hydroxide of a polyvalent metal selected from the group consisting of magnesium, aluminum and beryllium, dehydrating the resulting saponification product, then heating the dehydrated saponified product in the presence of a predominant proportion of a liquid oleaginous lubricating base to a gelation temperature above about 450° F., and drawing the product to obtain a gel-like grease containing in excess of 5% and less than 50% by weight of said soap based on the grease.

15. The method according to claim 14, wherein the dicarboxylic acid is an alkenyl succinic acid, and the mono-carboxylic acid is stearic acid.

16. A lubricating grease comprising an oleaginous liquid lubricating base as the predom-



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inant constituent, and in excess of 5% but less than 50% by weight based on the grease of a mixed base soap, said soap consisting of a major proportion of a polyvalent metal soap of a hydrocarbon substituted aliphatic dicarboxylic acid having the carboxyl groups in a plane symmetrical configuration and wherein the hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl radicals containing at least eight carbon atoms, with the polyvalent metal selected from the group consisting of magnesium, aluminum and beryllium, and a minor proportion of metal soap of a soap-forming mono-carboxylic acid, said mixed base soap being in sufficient proportion with the mixture of soap and lubricating base heat treated at a gelation temperature to thicken said lubricating grease to a gel-like consistency.

17. The method of preparing a lubricating grease which comprises heating a mixture of a distillate mineral lubricating oil containing in excess of 5% but less than 50% by weight of a polyvalent metal soap of a hydrocarbon substituted aliphatic dicarboxylic acid having the carboxyl groups in a plane symmetrical configuration wherein the polyvalent metal is selected

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from the group consisting of magnesium, aluminum and beryllium, and wherein the said hydrocarbon substituent is selected from the group consisting of alkyl and alkenyl containing at least eight carbon atoms, to a gelation temperature in excess of 450° F., and allowing the product to cool to obtain a gel-like grease.

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