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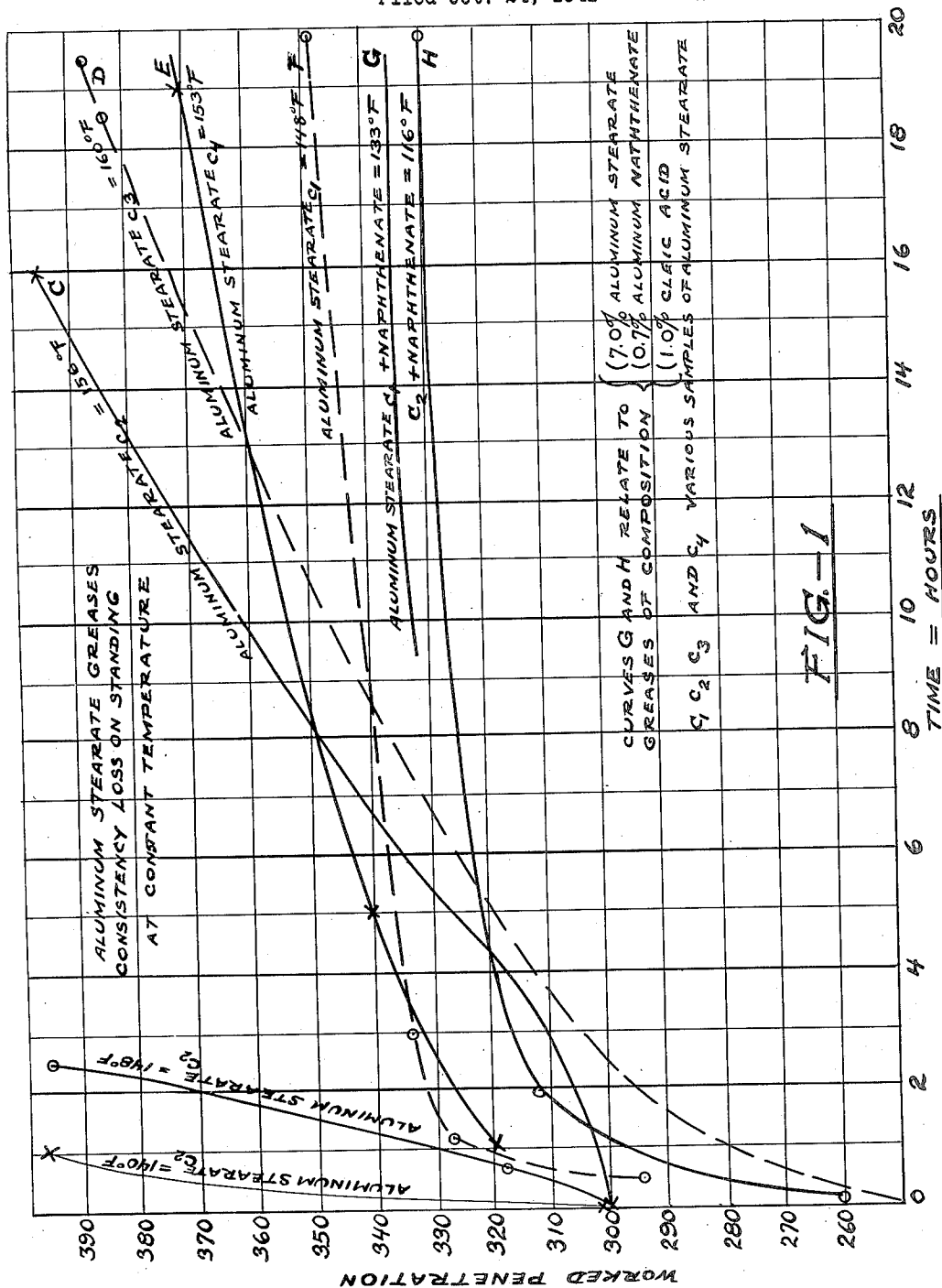
J. C. ZIMMER ET AL

2,365,037

PROCESS FOR PREPARING ALUMINUM SOAP GREASES

Filed Oct. 24, 1941

2 Sheets-Sheet 1



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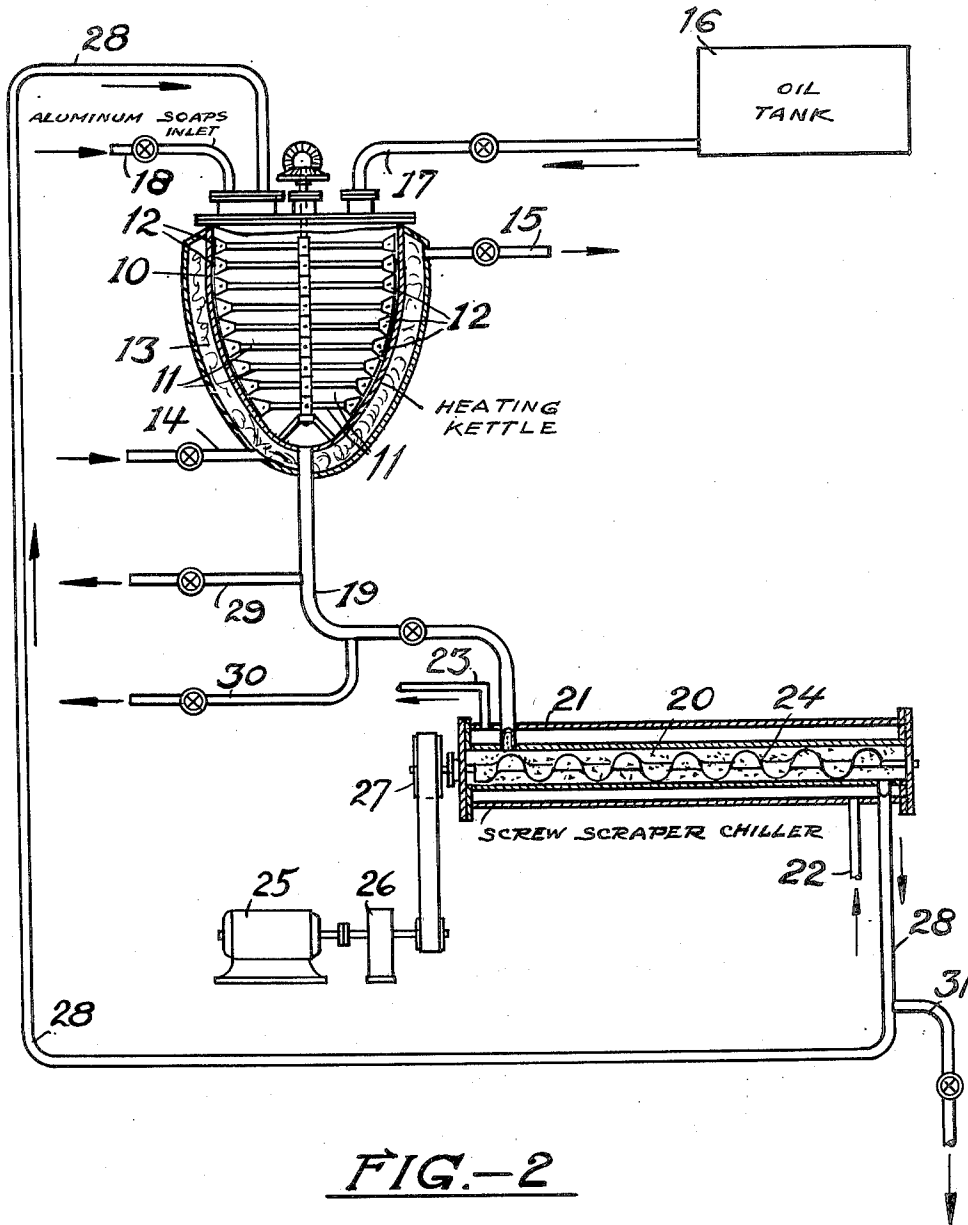


FIG.-2

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UNITED STATES PATENT OFFICE

2,365,037

PROCESS FOR PREPARING ALUMINUM SOAP GREASES

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Application October 24, 1941, Serial No. 416,314

7 Claims. (Cl. 252—35)

This invention relates to a continuous and rapid method for preparing aluminum soap greases and more especially to a method for preparing aluminum soap greases containing aluminum stearate as the main soap constituent and of semi-fluid consistency adapted for the lubrication of the chassis parts of automobiles and crawler type tractors. The present application is a continuation-in-part of our co-pending application Serial No. 255,452, filed on February 9, 1939, now Patent No. 2,264,353, and also is related in subject matter to our copending application, Serial No. 416,313, also filed on October 24, 1941.

Criteria of quality of grease compositions are specific ranges in value of consistency as indicated by the work penetration test (A. S. T. M. D217, 33T), and the S. I. L. Mobilometer (Ind. Eng. Chem., An. Ed., May 15, 1940, pages 285-7), of body density, of adhesiveness to metallic surfaces, of internal cohesion and of melting points. These characteristics depend upon the physical and chemical relationship of the ingredients in the composite and the reaction of the composite to the effects of speed, pressure and heat during service. In many commercial greases a relationship between the various constituents is desirably attained so that a composite is formed consisting of a minor portion of a colloidal dispersion of metal soaps in a relatively stable emulsion of a major portion of a colloidal dispersion of other and different type metal soaps in a mineral oil of suitable consistency. It is considered particularly important that the colloidal phase be relatively stable and form a satisfactorily adhesive lubricating film on the bearing surfaces and that the colloidal phase offers substantial resistance toward heat conduction from the surface film into the mass so as to minimize the effect of friction, speed and load during service upon the bulk of the grease composition.

The present invention relates particularly to stabilized aluminum soap grease compositions, containing aluminum stearate as the main metal soap ingredient. It has been known for some time that when aluminum stearate in an amount of about 8% by weight is admixed and heated with a mineral oil and the mass cooled, the desirable transition in structure of the mass, from being a stringy liquid to a consistency of a relatively solid gel, does not usually satisfactorily occur. The cause of the failure has not been definitely determined, but it would seem from

photomicrographs to be due to a recrystallization of the aluminum stearate at a temperature below about 150° F. If the mineral oil-aluminum stearate mixture is rapidly cooled to a temperature of about 150° F. or below, the aluminum stearate crystallizes and there is obtained a mixture of oil and coarsely dispersed soap granules.

In the prior art the cooling from 140° F. to 160° F. to permit the transition from the liquid to the gel structure was usually effected by pouring the hot liquid mixture from the heating equipment into shallow pans holding between about 50 and 100 pounds and having a depth of several inches and allowing the mass to cool overnight. The cooled mass from this pan cooling, as it is termed, was then passed to settling equipment which was usually the kettle equipment in which the mixture was previously heated, then stirred or reworked, as it is commonly termed, to develop a uniform consistency, and then filtered into containers. This slow pan cooling and reworking procedure was found to be the only satisfactory method of cooling the grease mixture to effect the desired transition in structure and developing therein a desirable consistency. In other type cooling equipment, such as the shipping containers, the grease mixture after cooling to atmospheric temperatures is found to be of a heterogeneous character, the center being a relatively liquid oil, while the outer portion is relatively hard and upon reworking a uniform desirable consistency is seldom obtained.

Prior are procedures for preparing aluminum greases are thus time and labor consuming and require extensive floor space and, due to the reworking required after such cooling, there is also involved a consistency loss based upon the quantity of aluminum stearate employed. In our copending application, Serial No. 255,452, now Patent No. 2,264,353, a formula and method for the preparation of satisfactory aluminum soap greases without the laborious and costly method of pan cooling were disclosed. Also disclosed in that application was that the addition of small quantities of free stearic acid to the grease mixture improved the stability of the composition during storage especially as regards the development of increased consistency.

In our copending application, Serial No. 255,452, now Patent No. 2,264,353, it was disclosed that by adding to the aluminum stearate about 10% by weight of either aluminum naphthenate or

aluminum oleate admixed with about 20% free stearic acid, this difficulty was overcome and a lower transition temperature was obtained upon the composite than upon a mixture having the same metal soap content but consisting of aluminum stearate only. It was also disclosed that many commercial supplies of aluminum stearate vary in the percentage of free acidity from about 5% to 15% but that such free acidity was insufficient to have the desired lowering effect upon the transition temperature and to have the stabilizing effect during storage upon consistency. Thus, many processing difficulties in the manufacture of aluminum soap greases were overcome by adding to the aluminum stearate small quantities of either aluminum naphthenate or aluminum oleate.

It has now been found that compounds other than aluminum naphthenate and aluminum oleate admixed with free stearic acid have the ability to lower the transition temperature of aluminum stearate-mineral oil mixtures and that acids other than stearic acid improve the stability of aluminum soap grease compositions during storage. The newly discovered effective compounds are naphthenic acids and fatty acids in general containing between about 10 and 20 carbon atoms in the molecule, especially oleic acid, in amounts of about 10% by weight of the aluminum stearate. It has been found that with these compounds the total soap admixture to the oil may be reduced and that the transition

aluminum naphthenate and 1% oleic acid in addition to the 7% aluminum stearate blended in the oil can, after heating, be cooled very satisfactorily to a temperature of 116° F. to effect the desirable structural transition to a gel; whereas, in the absence of these compounds, an aluminum stearate-mineral oil grease of less satisfactory consistency is obtained by cooling to 156° F. and very unsatisfactory compositions are obtained by cooling to temperatures of 148° F. and 140° F. Comparison of the four curves C, D, E and F shows that the impurities associated with the aluminum stearate in commercial supplies determine for the composition the transition temperature and instability as regards consistency during storage. Comparison of curves G and H shows that the extent of the effect of aluminum naphthenate and oleic acid upon the transition temperature of aluminum stearate is dependent upon the impurities associated with the aluminum stearate but that otherwise the effect upon aluminum stearate in mineral oil is substantially the same as indicated by the related consistency values for both compositions after ten hours' storage.

The further effects of the newly discovered active compounds in blending with aluminum stearate in mineral oil to give greases of desirable highly stabilized consistencies containing lower soap contents and of permitting rapid cooling to the lower transition temperatures are shown by the following tabulation of data:

Soap composition		Transition		Worked pene- tration	Remarks
Percent content	Type	Temp.	Time		
9.0	Commercial aluminum stearate C ₁ only.....	° F. 145/160	Hours 8/12	330	Satisfactory (pan cooling). Grainy fluid unsatisfactory, if quickly chilled be- low the transition temperature but if held and slowly cooled by pan cooling the grease is satis- factory.
7.0	do.....	145/160	8	350/370	
7.7	90% commercial aluminum stearate C ₂ +10% aluminum naphthenate.	116	20	330	Satisfactory.
6.6	do.....	115	12	340	Do.
6.6	do.....	124	20	365	Do.
6.6	do.....	115	1	345	Do.
6.6	6% commercial aluminum stearate C ₄ +1% nap- hthenic acid.	92	2	357	Do.

¹ Maintaining the grease composition at 115° F. for an additional 22 hours had negligible effect on the properties.

temperature of the composite may be reduced from the temperature range of between 150° F. and 160° F. for mineral oil-aluminum stearate mixtures to between 110° F. and 120° F. and even as low as between 90° F. and 100° F. when the naphthenic acids are employed. Furthermore, the grease compositions containing aluminum naphthenate or aluminum oleate or oleic acid or naphthenic acids in amounts of about 10% by weight of the aluminum stearate can be quickly cooled to the temperature at which transition occurs without any substantial recrystallization or partial recrystallization of the aluminum stearate and there is obtained, after such cooling, that is, without reworking, a smooth, unctuous product having no grainy structure.

In this regard, attention is directed to Figure 1. In Figure 1 there is presented a series of curves showing the effect of maintaining at relatively constant atmospheric conditions various grease compositions containing aluminum stearate in an amount of 7% by weight relative to the mineral oil as obtained by plotting worked penetration data and time in hours. Comparison between four of the curves, namely, A, B, C and H shows that a grease mixture containing 0.7%

In preparing the aluminum soap grease compositions of this invention, the oil employed is preferably derived from the naphthene base crude as, for example, oils of the Coastal type. The viscosity of the oil is usually above about 85 seconds Saybolt at 210° F. and preferably from 75 to 220 seconds Saybolt at 210° F. The aluminum soaps are added to the oil at a temperature of between 280° F. and 300° F. and the mixture heated in the usual type heating kettle to obtain a relatively homogeneous mixture. The heating kettle is furnished with close fitting scrapers, for example, small steel scrapers attached to the outer edge of the sweep, and kept at close scraping relation by means of adjusting screws. The particularly close scraping insures thorough mixing of the mass, reduces the formation of a grease composition of lumpy consistency, increases the transfer of heat into the mass and thus reduces the time of cooking.

The mass of aluminum stearate usually employed is between 3 and 8% and preferably about 5% by weight of the oil. It is to be understood that in this blending aluminum soaps of saturated fatty acids containing between about 10 and 20 atoms in the molecule other than stearic

acid may be employed and that aluminum stearate is but a preferred compound. The admixture of the aluminum naphthenate or aluminum oleate or free fatty acid or naphthenic acids in amounts of about 10% by weight of the aluminum stearate overcomes the tendency of the stearate to set upon cooling to a hard gel and permits the mixture to be cooled quickly in any device of suitable form capable of rapidly and uniformly cooling the mixture. Usually in incorporating the soap additives in the mineral oil, the mixing is made first with about 10 to 20% of the total quantity of the oil to be used and the mixture worked into a thick paste. The paste is then stirred into the balance of the oil which is heated during stirring to a temperature between 280° F. and 350° F. and held at that temperature until all the soap is thoroughly incorporated into a smooth, homogeneous mixture. The aluminum naphthenate of commerce varies considerably according to its oil content and if it is very well de-oiled, it generally requires a higher temperature in order to bring it into solution. In such a case it is found preferable to add aluminum naphthenate to the oil and to heat up the mixture to a temperature of between 350° F. and 450° F. while stirring and then to add the aluminum naphthenate-oil concentrate to the aluminum stearate-oil mixture at a temperature between about 280° F. and 350° F.

The mass after heating in the kettle is then rapidly cooled by passing through any type of cooling equipment capable of rapidly and uniformly cooling the mixture. The cooling is effected to a temperature of about the transition temperature or even slightly below. Suitable means of cooling the mass are the pan cooling as in the prior art or the use of any jacketed equipment in which the mass is relatively uniformly cooled. Of the various methods for cooling the greases, the straight pipe type coolers are generally considered less satisfactory than the helical screw scraper type. In the pipe coolers a reduction in heat transfer develops as the operation is continued due, presumably, to the formation of a thin skin of grease on the inside wall of the pipe. In the helical screw scraper type cooler the grease is continually stirred and scraped from the surface by the screw and fresh grease is brought into contact with the heat exchange surface, thus permitting rapid and uniform cooling of the mass. It has been found that with coolers of the wax chiller scraper type, the mass can be quickly cooled to approximately 10° F. below the transition temperature, especially when the flow of the grease through the cooler is opposite to the effect of the screw and countercurrent to the cooling water in the jacket. The efficiency of the wax chiller scraper type cooler is indicated by the following heat transfer data of 3 to 6 B. t. u./hr./sq. ft./°F. for streamline flow through pipe coil, 10-12 B. t. u./hr./sq. ft./°F. for scraped kettles, and 25-30 B. t. u./hr./sq. ft./°F. for the helical screw scraped wall tube such as in the wax chiller scraper equipment.

When a jacketed kettle is employed as the cooling equipment, the cooling may be effected in either of two ways. In the first procedure, the grease is left in the kettle which has been previously heated to a predetermined temperature and then allowed to cool with the grease overnight as a result of radiation and convection. The grease so prepared is seldom completely homogeneous due to the variation in the cooling rate throughout the mass. Usually with this manner of cooling, the center is relatively

liquid while the layers near the cooling surface are relatively grainy. A means of overcoming the irregular cooling has been to employ the second procedure, namely, to circulate water having the temperature of about the transition temperature for the mass during the entire cooling operation. In utilizing this means of cooling the grease and effecting the transition, the graphical representations presented in Figure 1 are worthy of note since they indicate the relationship between the amount and nature of the soap content upon the transition temperature. While the grease material is being cooled to about the transition temperature the mass is agitated. When the temperature of about transition is reached the agitation is discontinued and the mass allowed to cool further in order to permit the desirable change in texture of the mixture to occur.

After the grease has been cooled, the mass is usually allowed to stand until it attains the desired consistency. Sometimes, however, the grease is recycled to the mixing kettle until the entire contents of the kettle is reduced to about the transition temperature. When the desired temperature is reached in the mass the product is allowed to settle until transition in structure has occurred. When the naphthenic acids are incorporated in the grease composition, it has been found that the mass may be cooled below the transition temperature and pumped directly to the shipping containers maintained at atmospheric temperature to effect the change from the liquid to the gel structure.

The grease so obtained is fluid enough to have the capacity of just flowing under its own weight at room temperatures and has an A. S. T. M. penetration of between 300 and 400 at 77° F. A grease of this type can be dispensed readily from a grease gun of the ordinary type available at commercial outlets at temperatures as low as 10° F. At the same time the grease composition is possessed of a high degree of adhesiveness to metallic surfaces. The grease composition may also contain other ingredients as desired. For example, the viscosity of the grease may be considerably increased by the addition of oil thickeners such as polymers of olefins especially of the iso-olefins and particularly of isobutylene and the isoamylenes. For this purpose the polymers having molecular weights of between 30,000 and 200,000 are preferred and they are ordinarily used in amounts from about 0.05% to 0.25%, depending upon the molecular weight of the polymer employed. Oxidation inhibitors of various types may be added to the oil as well as dyes, anti-corrosion or extreme pressure agents and the like which may be employed to impart other desirable qualities.

A procedure preferably employed in the preparation of the greases of this invention is indicated by the following description of a manufacturing process which should be read in conjunction with the drawings presented in Figure 2.

Figure 2 shows a jacketed kettle 10 fitted internally with paddles 11 having scraper terminals 12 which can be finely adjusted to work upon the inner surface of the kettle. The motion of the paddles in the kettle insures very complete and thorough agitation within the kettle. The jacket portion 13 of the kettle 10 is adapted for the passing in through line 14 and the passing out through line 15 of steam either under normal or superatmospheric pressure as temperatures within the kettle 10 require. Under the conditions of such means of agitation and of a temperature

between about 280° F. and about 300° F. sufficient oil of suitable character as a mineral oil base for the preparation of the grease composition is supplied from storage tank 16 to the kettle 10 through line 17 and admixed with the aluminum soaps supplied through opening 18 to make a thick paste. Further quantities of oil to make the grease of desired consistency are then supplied through line 17 and the mass agitated until a smooth homogeneous composition is obtained.

When the mass in the kettle has become smooth and homogeneous the mixture is passed from the bottom of the kettle through line 19 to a screw scraper chiller 20. The chiller 20 has an outer jacket 21 through which a cooling medium, usually water, passes in through line 22 and out through line 23. The screw 24 within the chiller is usually operated countercurrently to the direction of the flow of the grease from line 19 and countercurrently to the direction of the cooling fluid in the jacket 21. The scraper screw is operated by the motor 25 through gears 26 and transmission 27. The cooled grease passes from the chiller through line 28.

In batch operation the cooled grease is recycled through line 28 to the kettle 10. By such recycling the entire quantity of grease composition is brought to about the transition temperature at about the same time. When this temperature within the mass is reached, agitation within the kettle is discontinued and the mass is allowed to settle and to cool further until the transition in structure has been satisfactorily effected. The gel composition is then removed from the kettle through a T 29 on line 19 and passed to shipping containers.

In continuous operation it is usual to employ a series of kettles similarly equipped to that designated by the numeral 10 and to pass the hot mixture to the chiller in a relatively continuous stream from the various kettles through the T 30 on line 19. In this manner of operation the cooling effected in the chiller 20 is more complete than that in batch operation, namely, the cooling in the chiller is effected to about the transition temperature. The cooled grease in such operation is passed directly through a T 31 on line 28 to the shipping containers wherein settling and further cooling to atmospheric temperature are effected.

Example I

An aluminum stearate grease product was prepared by adding 5.0 parts by weight of aluminum stearate, 0.5 part of aluminum oleate, and 1.0 part of naphthenic acids to about 20 parts of a naphthene type lubricating oil which had an initial viscosity of 160 seconds Saybolt at 210° F. The ingredients were stirred together to a thick paste, all lumps of aluminum stearate being carefully worked out. 72.5 parts of the same naphthene type oil as previously used were now added and the mixture heated while stirring to about 280-300° F. Stirring was continued for approximately one hour or until the mixture was found to be completely homogeneous. One part of a 6.0% oil solution of a linear polymer of isobutylene, the isobutylene having a molecular weight of about 40,000 to 60,000, was added. This material was pumped out of the kettle and through a Carbondale type chiller in which the flow of the grease through the chiller was opposite to that of the motion of the screw and to the direction of the cooling water in the jacket. Operation of the chiller in this way adds be-

tween 20 and 40 p. s. i. to the back pressure. The most satisfactory screw rotation for the particular type Carbondale chiller employed was 150 R. P. M. from the standpoint of cooling efficiency. The grease was cooled in one pass through this chiller to 95° F. and drawn directly to the containers of the size desired.

The resulting grease had a worked A. S. T. M. penetration of 360, was exceptionally smooth and transparent and was highly adhesive. It could be readily dispersed through the usual grease guns available at commercial outlets and was found to flow under its own weight at temperatures above 30° F.

Example II

A chassis lubricant was made by adding 3.6 parts by weight of aluminum stearate containing 10% of free fatty acid, 1.0 part of oleic acid and 0.4 part of aluminum naphthenate (the naphthenic acid obtained from Venezuelan gas oil) to about 20 parts of a naphthene lubricating oil which had an initial viscosity of 175 seconds Saybolt at 210° F. The ingredients were stirred together in a thick paste and after thorough incorporation, 74 parts of the same lubricating oil previously used were added and the mixture was heated while stirring to about 280° F. The stirring continued for about two hours and the mixture was found to be completely homogeneous. While still fluid one part by weight of a 6.0% oil solution of a linear polymer of isobutylene having a molecular weight of about 40,000/60,000 was added for the purpose of thickening the oil. On cooling, the mixture set into a soft solid body which was then worked into a smooth, semi-fluid grease which was just soft enough to flow under its own weight at room temperature.

The semi-fluid grease had an A. S. T. M. penetration of 390/400 at 77° F. It was highly adhesive and showed little or no tendency to splatter or to drop from the shackles or spring bolts of an automobile chassis. The composition was readily dispensable at 0° F. from a grease gun commonly available at commercial grease outlets. The following table shows the effect of the free fatty acid upon consistency during storage:

A. S. T. M. penetration

Free fatty acid in the aluminum stearate	Grease freshly prepared, as described above	After two weeks' storage at 75° F.
Per cent		
0.0	390	310
15.0	390	350
20.0	390	385

As a comparison of the lubricating quality, grease of similar consistency and of the following compositions were prepared:

	Composition A	Composition B	Composition C
Aluminum stearate.....	4.0	3.6	3.3
Aluminum oleate.....		0.4	
Aluminum naphthenate.....			
Oleic acid.....			0.4
Stearic acid.....			1.0
Oil solution polybutene.....	1.0	1.0	
Mineral lubricating oil.....	95.0	94.0	94.3

¹ Over the free stearic acid already contained in the aluminum stearate.

The three greases were tested in crawler-type tractor with the following results:

an unsaturated fatty acid containing between about 10 and 20 carbon atoms in the molecule.

[Number of days run on test, 7; air temperature, 25°-30° F.; ground, frozen.]

	Composition A	Composition B	Composition C
Average temperature of rollers	150/170° F.	120/150° F.	90/110° F.
Number of roller failures	4	2	0.
Temperature at failure	500+	500+	
Condition of rollers after tests	Brass bushing tended to swell against shaft. Shaft blue colored and brass swollen tight against shaft in case of failure.	Same as Composition A.	Like original—well lubricated.
Initial quantity of lubricant used	Rollers filled. 12 ozs. in bottom rollers; 3 ozs. in top rollers.	Same as Composition A.	Same as Composition A.
Average consumption	The grease could be added only at temperatures above 30° F. and the usual grease gun equipment could not be used because the grease would not flow to the pump. Complete refilling of the upper rollers every day and sometimes twice a day was necessary due to the improper feeding of the grease in the track rollers. Fats running hot and the grease running out through the seal. This generally necessitated three lubrications per day.	Complete refilling of upper rollers every day. Lower rollers had to be refilled twice each day. Sometimes necessary to relubricate rollers three times per day when running very hot. Noticeable leakage through seals.	1½ ozs. of grease every two days to upper rollers. 4 ozs. of grease added every two days to bottom rollers.

The present invention is not to be limited by any theory of a method of manufacture, or to any particular type of aluminum soaps, but only to the following claims or their equivalent.

We claim:

1. A process for preparing an aluminum base lubricating grease for the chassis and other parts of machinery which comprises thoroughly mixing in grease forming proportions in a pressure kettle a viscous hydrocarbon oil, an aluminum soap of a saturated fatty acid containing between about 10 and 20 carbon atoms in the molecule, and a relatively lesser amount of an unsubstituted carboxylic acid compound containing between 10 and 20 carbon atoms in the molecule of the class consisting of unsaturated fatty acids and naphthenic acids and their aluminum derivatives as a crystallization inhibitor compound for said soap in mineral oil, rapidly cooling the heated mixture to a temperature at which the grease changes from a rubbery mass to a gel by passing through heat exchange equipment and allowing the mass to settle.

2. The process according to claim 1 in which the compound inhibiting the crystallization in mineral oil of an aluminum soap of a saturated fatty acid containing between 10 and 20 carbon atoms in the molecule is a petroleum naphthenic acid.

3. The process according to claim 1 in which the compound inhibiting the crystallization in mineral oil of an aluminum soap of a saturated fatty acid containing between 10 and 20 carbon atoms in the molecule is an unsaturated fatty acid containing between about 10 and 20 carbon atoms in the molecule.

4. The process according to claim 1 in which the compound inhibiting the crystallization in mineral oil of an aluminum soap of a saturated fatty acid containing between 10 and 20 carbon atoms in the molecule is an aluminum soap of

5. A process for preparing aluminum soap greases which comprises thorough mixing in grease forming proportions in a pressure kettle of a viscous mineral lubricating oil, about 3% to 8% of aluminum stearate and from about 0.25% to 1.5% of an unsubstituted carboxylic acid compound containing between 10 and 20 carbon atoms in the molecule of the class consisting of unsaturated fatty acids, naphthenic acids and their aluminum derivatives as a crystallization inhibitor compound for said quantity of aluminum stearate in mineral oil, rapidly cooling the heated mixture to a temperature at which the mixture changes from being a rubbery mass to a gel by passing through a helical screw scraper type cooling equipment and allowing the mass to settle.

6. Process for preparing aluminum soap grease according to claim 5 in which the rapid cooling is effected by passing through a helical screw scraper type cooling equipment in which the flow of the heated mixture is in the opposite direction to that of the motion of the screw and counter-current to the fluid in the cooling jacket.

7. Process for preparing a semi-fluid aluminum soap grease for the lubrication of chassis parts of crawler-type tractors which comprises thorough mixing in a pressure kettle of a viscous mineral lubricating oil, about 3% to 8% of aluminum stearate, and from 0.25% to 1.5% of a petroleum naphthenic acid, rapidly cooling the heated mixture to a temperature at which the mixture changes in texture from being a rubbery mass to a gel by passing through a helical screw scraper type cooling equipment in which the flow of the heated mixture is opposite to the effect of the motion of the screw and counter-current to the fluid in the cooling jacket and then allowing the mixture to settle.

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