directly assayed by this method, but it should be kept in mind that the Emmerie and Engel reaction measures total reducing power. Therefore, other reducing substances, including carotenoids, will give false readings for tocopherol, and the method should not be applied to crude materials.

Acknowledgment: The author is indebted to Dr. J. G. Baxter, of these laboratories, for making available the tocopherols in pure form.

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Continuous Lithium and Aluminum Stearate Grease Manufacture

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THE Votator has been used extensively in the commercial manufacture of margarine, shortening and lard. More recently it has found commercial application in the manufacture of soap, crystallization of paraffin wax, pasteurization and freezing of eggs. To this list can now be added the continuous manufacture of aluminum and lithium stearate lubricating greases.

The batch method of manufacturing lithium and aluminum greases consists in heating the soap and oil to the dissolving point in an open kettle. The hot grease is then run into small pans to cool and gel. These pans hold about 35 to 50 pounds. The cooling rate is generally controlled and takes about twelve hours. The cooled grease is then transferred from the pans to some type of hopper where the grease is picked up by a pump for working the grease to a fairly constant consistency and then pumped to containers for shipment. Over-all rates of production for this batch method vary about 1,000 to 2,000 pounds per hour and this necessitates considerable handling and transferring of the grease.

In the case of lithium grease a light oil of about 300° F. flash point is used and, since the slurry needs to be heated to about 400° F. to completely dissolve the soap, this introduces a fire hazard. A completely enclosed, continuous process, therefore, provides safety, eliminates handling and transferring and provides a much closer control of operational variables.

Equipment and Operation

The continuous process for lubricating greases herein reported was carried out on a pilot plant scale at rates varying from about 30 pounds per hour to 200 pounds per hour.

Three-inch diameter Votators, equipped with a 2¼-inch diameter shaft and two stainless blades, were used. The assembly of one of these units is given in Figure 1. Cooling units were helically jacketed while the Dowtherm unit had an open jacket in order to secure low jacket pressure drops. A flow sheet of the process as finally developed is given in Figure 2.

An oil and soap slurry was placed in a slurry tank, as indicated in the flow sheet. With certain oils the slurry picked up air from the atmosphere and this slurry was, therefore, passed to a deaerator where this air was removed. The deaerated slurry was then passed to a heating Votator where the slurry was simultaneously mixed and heated to a point where the soap dissolved completely. This required temperatures in the range of 300° F. for aluminum greases and in the range of 400° F. for lithium greases.

The hot grease was then immediately cooled to a pre-determined critical value in the second Votator, and passed through a gelling section sufficiently large to allow the grease to set. This was followed by a third Votator in series where the grease structure was broken down to nearly the maximum capacity. That is, the grease leaving this unit was such, that further working changed its consistency only slightly.

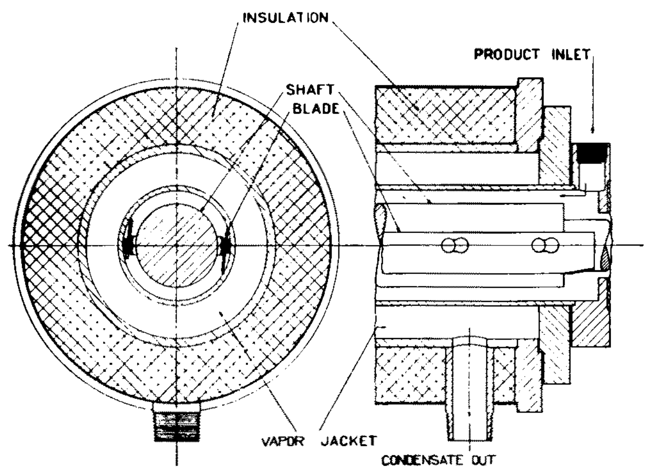

FIG. 1. Longitudinal and cross sectional view of pilot plant votator.

Variables studied included the following: (a) Grease formulation was studied in which not only the types of oils used were examined, but also the quantity of materials blended, the type of soap to give the best yields and the amount of mixing necessary to produce a fairly uniform slurry. (b) The type and design of proper evacuation equipment was studied. (c) The critical temperatures, pressures, blade velocities, through-put rates, retention times and overall heat transfer coefficients for each of the three Votators used were determined. (d) The temperature, holding times and proper design of gelling section were established. (e) The design and critical conditions necessary for the working Votator were developed.

These variations led to a wide number of combinations and permutations but have in general been quite widely covered for the manufacture of lithium and aluminum greases.

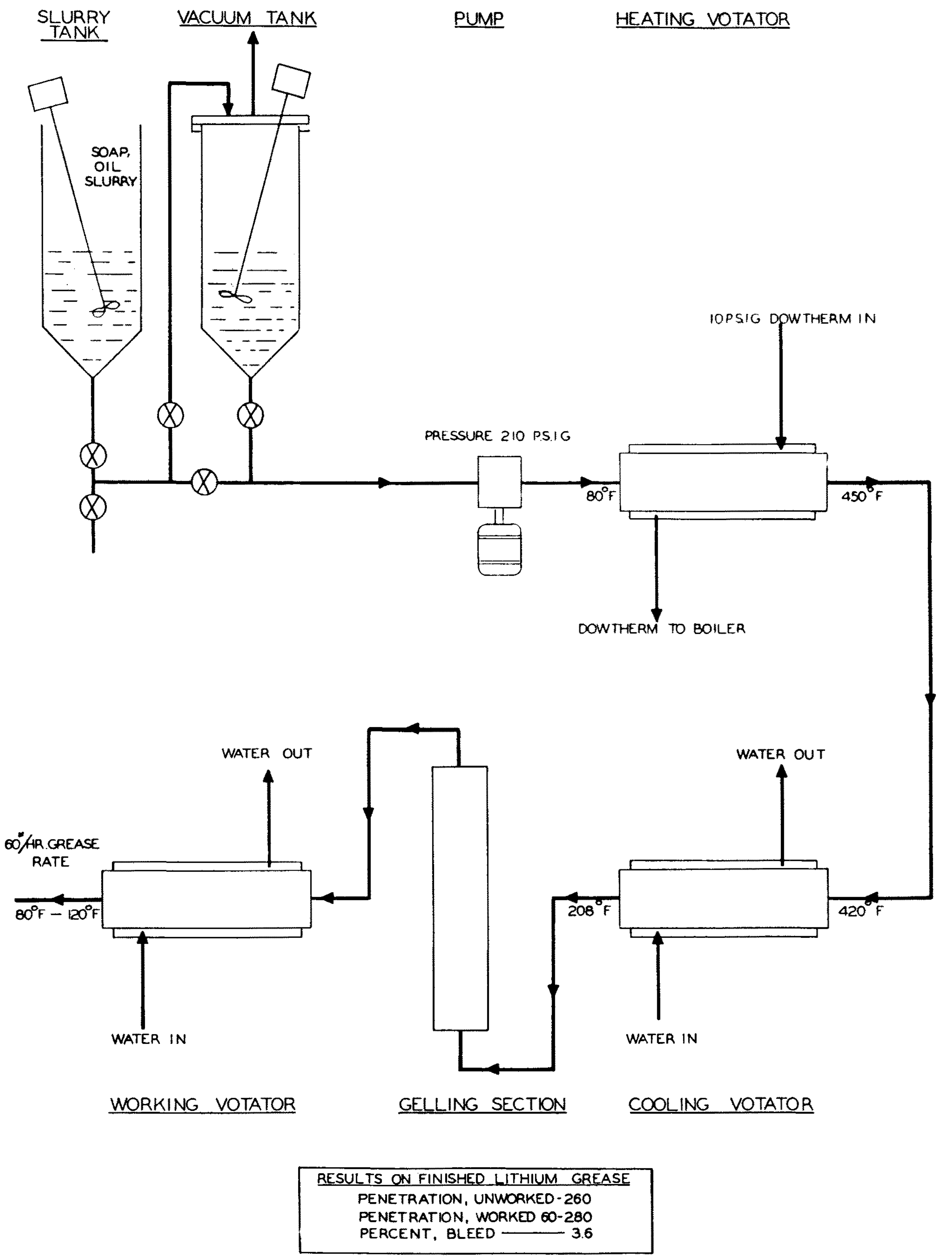

FIG. 2. Flow sheet for continuous manufacture of lithium grease.

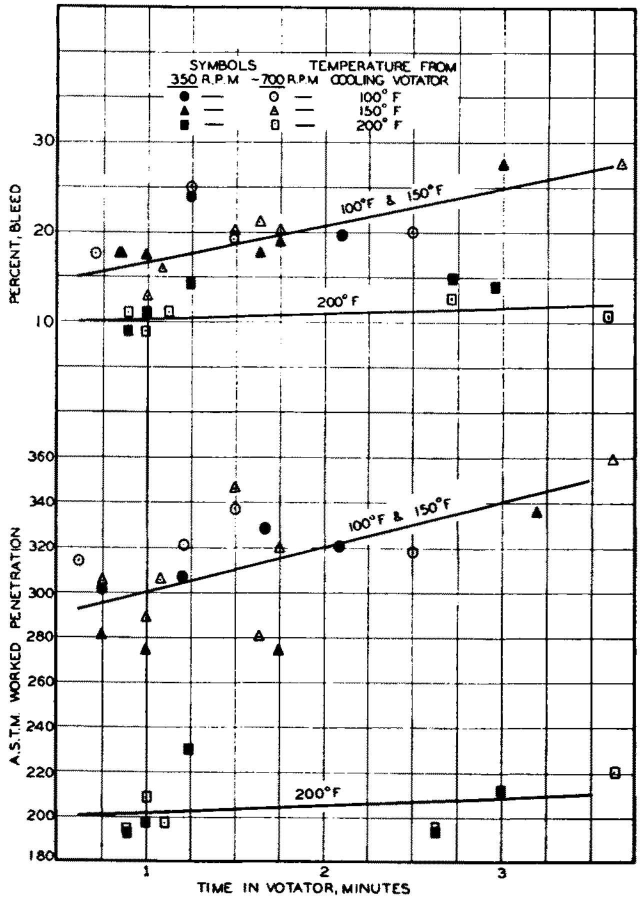

FIG. 3. Effect of retention time on properties of cooling votator lithium grease.

Lithium Grease Manufacture

LITHIUM grease as manufactured at the present time is generally made from a lubricating oil of about 50 SSU at 100° F. The final product should have a worked penetration of about 280 and a bleed less than 4%.

Process and Operation. A lithium stearate- Pennsylvania oil slurry containing oxidation and other inhibitors was made, using a "Lightnin" mixer. The deaerating equipment was found unnecessary with these low viscosity oils. The slurry at room temperature was pumped directly through a Dowtherm jacketed Votator and heated to about 400° F., then cooled with agitation to about 210° F., in the cooling Votator. The grease passed at this temperature into the gelling section where sufficient time was allowed for the gel to set after which the set gel was further cooled and worked simultaneously in the working Votator.

Heating Stage. Temperatures higher than 400° F. were found unnecessary as long as the soap went completely into solution. Dissolving the soap depended on the amount of mixing, the retention time under heat and the final temperature reached. Shorter retention times demanded higher temperatures, likewise less agitation demanded higher temperatures. Temperatures of 400° F. were found satisfactory for retention times of two minutes and shaft speeds about 1000 r.p.m. in the Votator used. The flash point of these oils was about 300° F., and since approximately 400° F. was necessary to dissolve the soap, a completely enclosed heating unit under pressure was therefore used to reduce fire hazard to a minimum.

Cooling Stage. The critical temperature for cooling was found to be about 210° F. Below this temperature simultaneous cooling and agitation of the unset gel in the Votator produced a grease exhibiting high syneresis and a mushy consistency when allowed to cool normally to room temperature. This is shown in Table I.

TABLE I

Effect of Cooling Votator Outlet Temperature on Lithium Grease Properties

Temp. °F.	% Bleed	ASTM Worked Penetration @ 77° F.
118	7.8	314
145	4.9	284
214	0.0	203

In grease making it is very important to obtain as firm a gel as possible. Consequently, the outlet temperature was selected which produced the hardest gel as measured by the penetrometer. The syneresis effect reported as per cent bleed must also be low. The lower the separation, the more stable the gel.

Figure 3 shows the effect of retention time in the cooling Votator for different temperatures. The values here are poor because of the particular formula used. The comparative results are, however, accurate and similar changes, though at a different level of values, are detected with other stocking formulas, such as used in this work. The curves show that as long as the outlet temperature is sufficiently high to produce a satisfactory grease the retention time does not appreciably affect the grease quality.

Table II shows some values of the unworked and worked penetration of grease. These samples were taken from the cooling Votator at 210° F., and allowed to cool to room temperature in the grease container.

TABLE II

Comparison of ASTM Worked and Unworked Penetrations Cooling Votator Grease

% Lithium Stearate	Unworked	Worked	Difference
11	177	258	81
11	169	244	75
10	200	268	68
10	181	248	67
Average			73

The difference in penetration is 73 units. This indicates a grease which will break down and become softer under service, e.g., when in the bearing. Table III shows still another lithium grease which has been worked to 1000 strokes in the ASTM worker. It will be noticed that the bleed also increases with working.

TABLE III

Effect of Working Lithium Grease Taken From the Cooling Votator

No. of Strokes	0	30	60	150	200	300	400	500	1000
Penetration	176	261	270	286	293	296	300	311	312
Per cent Bleed	1.7	....	....	....	....	....	....	....	10.6

Figure 4 shows how the worked penetration and bleed varied with increasing soap content in the grease from the cooling Votator. Increased soap content means increased cost. The lowest possible soap content is, therefore, selected which will produce a grease meeting the desired service conditions.

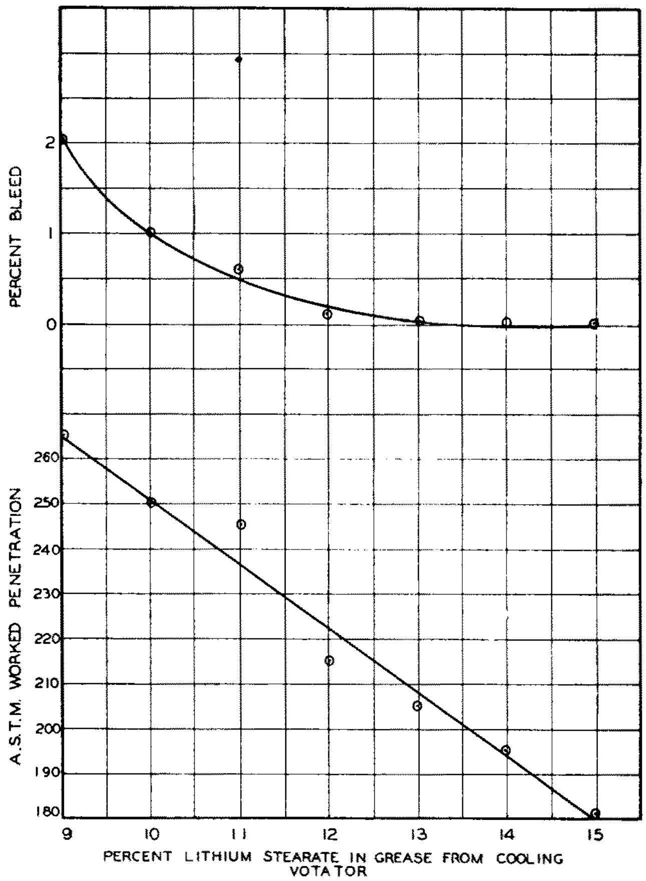

FIG. 4. Effect of soap content on properties of cooling votator lithium grease.

Gelling Stage. As shown in Table III grease taken from the cooling Votator had an appreciable difference in unworked and worked penetration. In order to bring these values closer together and produce a worked consistency grease a gelling stage was introduced to allow the grease to set. Once the grease gel had completely set simultaneous working and cooling could again be applied without detrimental results. No agitation occurred in the gelling section.

The type of oil used and the inlet temperature to the gelling stage were two variables which affected the gelling time. Gelling times of 10 to 20 minutes were found satisfactory for most products. Table IV shows that grease leaving the working Votator was of a worked consistency, i.e., further working only changed the grease slightly. The 60 stroke difference is the difference in penetration unworked and worked 60 strokes, likewise 500 stroke difference is the difference when unworked and worked 500 strokes in the ASTM worker.

TABLE IV

Comparison of Lithium Grease Taken from Cooling Votator and Working Votator

Source	Per cent Bleed	Penetration Differences	
		60 Stroke Difference	500 Stroke Difference
Cooling Votator	0.2	44	97
Working Votator	1.2	18	32

Gelling and working sections had the advantage that the grease gel thus reached a structure such that further working had only a slight effect. The increased bleed was still well within the range of a satisfactory and stable product. Grease with this amount of leakage had a high sheen which would add to its sales appeal.

Lithium Grease Characteristics. Grease leaving the heating unit was sticky, clear and about the consistency of thin syrup. The material leaving the cooling Votator was slightly rubbery with some stickiness and in this state resisted deformation somewhat. The gel may be foggy or clear depending on the oil used. Material leaving the gelling section had lost all its rubbery properties, was not sticky and was easily deformed. The gel exhibited shear planes and was generally cloudy in appearance. The grease leaving the working Votator was buttery in consistency and texture.

Effect of Oils Used. Oils from three different sources were tried: A Pennsylvania base, a Mid-Continent base and a Coastal base stock. It was found that a pure Pennsylvania stock differed from either the Mid-Continent or Coastal stock in the amount of soap necessary to give the same worked penetration. Since these oils had different refinery treatments, it is not known whether one source of oil is superior to another source of oil on the basis of yield.

The heating and cooling stages were operated under approximately the same conditions. The time necessary to gel the Pennsylvania Stock differed from either the Mid-Continent or Coastal Oil. The Coastal oil, however, needed special treatment in the working Votator. It seemed to be more sensitive to working than either the Pennsylvania or Mid-Continent oils. This Coastal stock differed appreciably from the other two in its physical characteristics and in addition a different lithium stearate was used with it, so

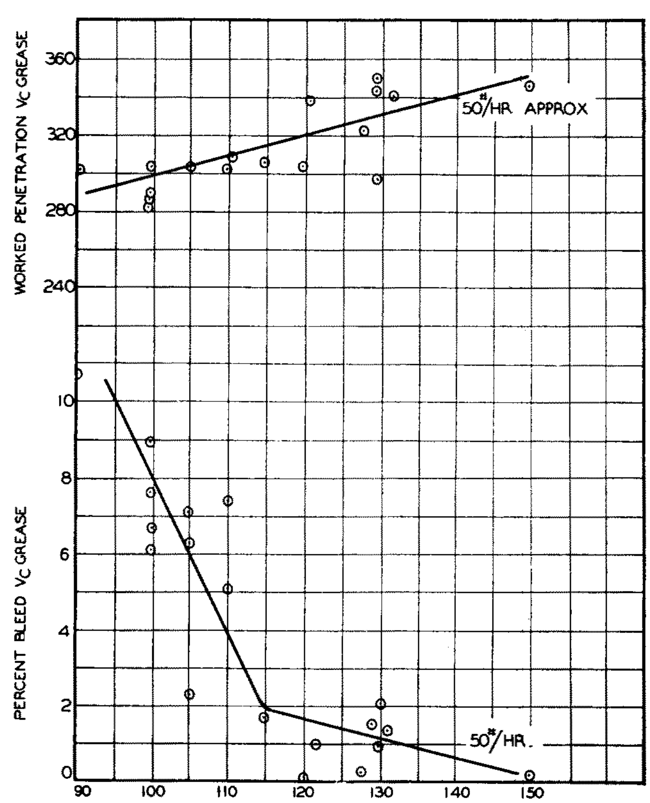

FIG. 5. Effect of outlet temperature on properties of cooling votator aluminum grease.

that direct comparisons of the greases were not too conclusive.

Aluminum Grease Manufacture

ALUMINUM grease is manufactured from a much wider variety of oils than is lithium grease at present due to the fact that the lithium greases are new to the lubricating field. These oils come not only from different fields but also vary widely in refinery treatment and viscosity. A large volume of the aluminum grease is manufactured from an oil of about 100 SSU at 210° F., and this section deals with the process of manufacturing continuously aluminum grease from this type of oil.

Process and Operation. The same general processing procedures were used as with lithium greases. A slurry of, say, Coastal-Mid-Continent blended oil and aluminum stearate was made, using a "Lightnin'" mixer. This slurry was passed through the deaerating equipment to remove any air that had been picked up in mixing the slurry. It was then pumped directly through a heating Votator jacketed for steam or equivalent, such that the temperature of the slurry would reach about 300 to 325° F.

The hot grease was then immediately cooled to approximately 120° F., and passed at this temperature into the gelling section where sufficient time was allowed for the gel to set after which the set gel was then further cooled and worked simultaneously in the working Votator.

Cooling Stage. Figure 5 shows the effect of the cooling Votator's outlet temperature on the grease properties, bleed and penetration. The curves show that the lower the outlet temperature, the firmer the grease gel as measured by penetration. The grease, however, exhibited marked syneresis below 110° F. In order to obtain the highest possible grease yield, the lowest outlet temperature was selected consistent with acceptable bleed values.

Figure 6 shows the effect of through-put rates on the properties of the grease. The lower rates produced a softer grease. The higher rates produced a harder grease but the bleed was increased in these cases. Visible bleed was noticed in the high rate at 100° F., so no accurate penetration value could be obtained on this sample. Table V gives additional data concerning this problem.

TABLE V
Effect of Through-Put Rates on Properties of Aluminum Grease Leaving Cooling Votator

Lbs./Hr.	Outlet Temp. °F.	Per cent Bleed	Worked Penetration
70	106	2.7	285
115	106	3.0	268
120	106	4.4	256

The effect of through-put rates or retention times was found to be more pronounced with the aluminum greases than with the lithium grease. Aluminum greases in general were also found to be more sensitive to all changes in operation. The grease leaving the cooling stage was not of a worked consistency. The unworked and worked penetrations varied about 70 to 100 units depending on operating conditions.

Gelling and Working Stages. It was found that with the particular formula employed using an inlet temperature of 115-120° F., to the gelling section,

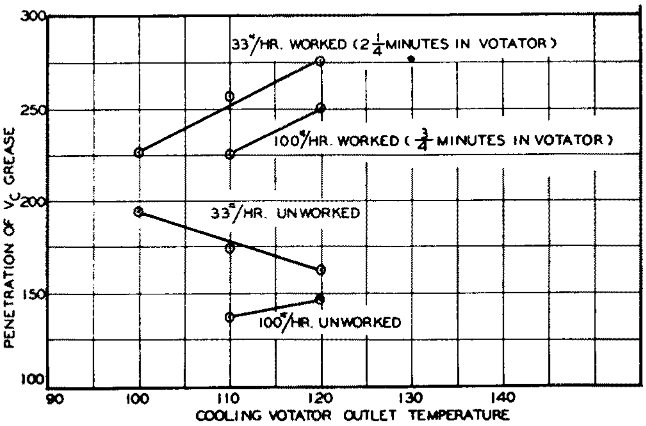

Fig. 6. Effect of through-put rate on properties of cooling votator aluminum grease.

the gel would set in about 20 minutes. Once the gel had completely set, simultaneous agitation and cooling could again be applied without detrimental results. Due to the high transparency of aluminum grease slight differences in appearance could be easily detected. The working Votator had, therefore, to produce a uniform appearance in addition to cooling, working the grease and producing a buttery texture.

The worked consistency of the final grease was shown by the difference in unworked and worked penetration. This difference was less than 40 units. Figure 7 shows not only this difference but shows also its consistency with through-put rates. The effect of through-put rates on the grease characteristics was also shown to carry through from the

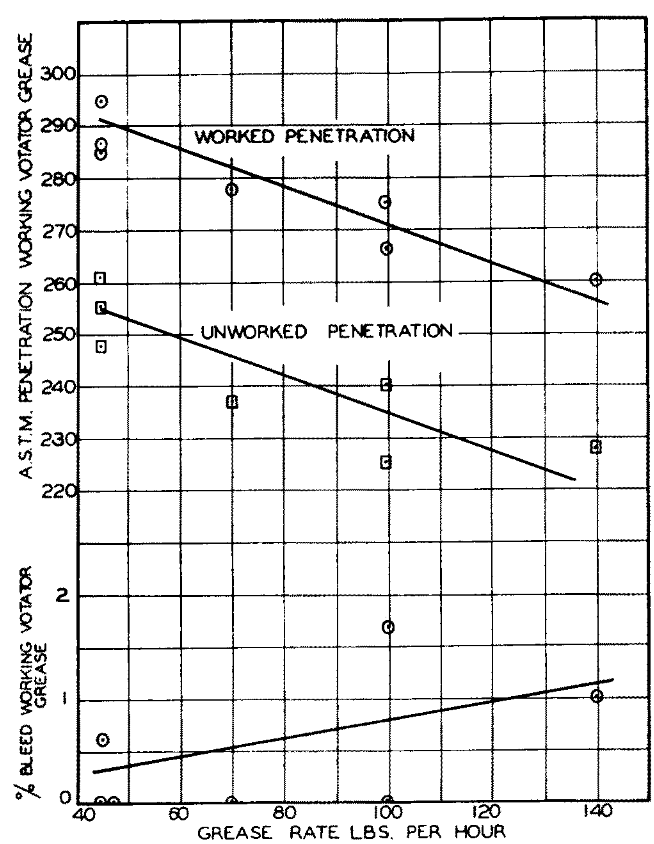

FIG. 7. Effect of through-put rate on properties of working votator finished aluminum grease.

cooling stage in that higher through-put rates produced a harder final product. Thus an increased yield was obtained since the syneresis of the grease was still very small and well below that permitted in commercial products.

Aluminum Grease Characteristics. The grease leaving the heating unit was sticky, clear and about the consistency of syrup. If undissolved soap was present, it could be seen and felt as small lumps on a spatula. Material leaving the cooling Votator was a very rubbery gel, with some stickiness and was very clear. The gel resisted deformation and could be stretched an appreciable amount and still regain its original shape. It was also characterized as "gutty". The material leaving the gelling section had lost all its rubbery properties, was not sticky, was easily deformed and the mass as a whole was not clear. The grease leaving the working Votator was buttery in consistency and texture and was clear and bright in appearance.

Effect of Oils Used. Oils from three different sources were tried. A Pennsylvania base, Mid-Continent base and Coastal base stock. It was found that a pure Pennsylvania stock required an outlet temperature from the cooling Votator of about 200° F., the Mid-Continent and Coastal stock a range of 110 to 130°F. They all gelled in about 20 minutes and had about the same final properties. These temperatures were found to be also influenced by the refinery treatment of the oil. These oils did not have the same treatment so that the above comparison is indicative only.

Effect of Soaps Used. It was found that there was an appreciable difference in the soaps on the market for making aluminum grease and in particular they affected not only the quality of the grease, but also appreciably affected the time of gelling. This is shown in the following table:

TABLE VI

Effect of Soap Type on Properties of Aluminum Grease

Soap		Cooling Votator Outlet °F.	Gel Time Minutes	Worked Penetration	Unworked-Worked Difference
Type	%				
A	8	110	30	325	50
B	8	130	30	290	39
A	9	120	15	300	42
B	9	120	11	264	38
C	9	120	17*	320	78*

* Took three hours for gel to set so that unworked-worked penetration was less than 40 points.

Summary

1. Lithium and aluminum greases can be made continuously by using heating, cooling, gelling and working stages in series. Votators can be used successfully for heating, cooling and working. The entire process from slurry to finished grease takes about 20 minutes, most of which time is in the gelling section.

2. The source and refinery treatment of the oil and the type of soap affect the process appreciably.

Report of the Referee Board, 1943-44

IN addition to the reappointment of 23 referee chemists whose names have already been published in *Oil and Soap,* four new applications were approved as follows:

> Mr. R. H. Acock received a certificate on cottonseed, oil cake and meal, and on cottonseed oil.
>
> Messrs. D. A. Bradham, G. C. Henry, Jr., and G. H. Nelson received certificates on cottonseed and on oil cake and meal.

The usual check samples of cottonseed, of soybean oil, and of cottonseed oil were distributed. The required analyses on the soybean oil samples were changed so as to include determination of refining loss and color, as prescribed in the amended grading methods of the National Soybean Processors Association. The present confused situation on grading soybean oil must be watched closely in planning further collaborative tests on this product.

Complaints on late delivery or non-delivery of check samples increased, and the number of late or missing reports suggests that as many as 4 or 5% of all the oil samples may have failed to arrive on time. Allowance for this must be made in scheduling samples next season.

The handling of applications for Referee Certificates alone involves about as much work as the average committee cares to undertake. A large additional burden is involved in handling the check samples needed by the Referee Board in the discharge of its duties. The committee has sought a correspondingly large amount of outside help on these samples and again makes grateful acknowledgment to the following:

> to Dr. Frank G. Dollear and the Southern Regional Laboratory, for tabulation of reports on cottonseed oil.
>
> to Dr. R. T. Milner and the Northern Regional Laboratory, for tabulation of reports on soybean oil.
>
> to R. T. Doughtie, Jr., and the Agricultural Marketing Service, for tabulation of reports on cottonseed.
>
> to T. C. Law and his Atlanta Laboratory, for preparation and shipment of the check seed samples.

MUCH thought has been given to the future of the check samples of oil and of cottonseed. These particular samples have been sponsored by the Referee Board because no other committee was responsible for them. The referee chemists regularly constitute a minority of the collaborators. The best interests of the Society as well as the selfish interests of the Referee Board could probably be better served if responsibility for all the check samples were placed in other committees. All the collaborative tests seem important enough to justify, if necessary, a special committee to handle each set of samples, like the Smalley Foundation committee. It is recommended that the Society proceed to create new committees for