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Division 11

NATIONAL DEFENSE RESEARCH COMMITTEE

of the

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

OSRD No. 4205

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REPORT

Upon

Contract No. OEMsr-1057

Stanford University

by

Professor J. W. McBain

<u>Short Title</u> "Fundamental Study of the Structure and Characteristics of Soap-Thickened Fuels".

<u>Scope</u> Study of the structure and phase relations of thickend fuels in order to provide a more fundamental basis for understanding their properties.

<u>Specific Assignments September 1943</u>

1. Continued fundamental investigation of pure aluminum soaps of single and mixed acids.
2. Investigation of the effect of moisture on the gelling properties of the pure aluminum soaps.
3. A thorough investigation of the effect of moisture on Napalm and its gelling properties.
4. The form in which moisture is held by Napalm.

<u>General Field</u> Gels, jellies and the theory of their structure.

<u>Personnel</u> Dr. Karol J. Mysels, full time since May 15, 1943.
Mr. Gerould H. Smith, part time since May 15, 1943.
Mr. C. G. McGee, part time July 1943 to April 1944.
Dr. E. B. Working, part time since September 1943.
Mr. George Shreve, part time since January 1944.
Mr. H. Pomeroy, full time since May 1944.
Dr. L. B. Rogers, part time since May 1944.

<u>Supervisor</u> Professor James W. McBain.

STANFORD UNIVERSITY
DEPARTMENT OF CHEMISTRY
Stanford University, California

File No. 11-455
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Problems CWS-10, 21

Report to Division 11 of the National Defense Research Committee on "FUNDAMENTAL STUDIES ON ALUMINUM SOAPS"

covering period May 1943-June 1944

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SUMMARY

1. The problem assigned was to study aluminum soaps; to identify the phases utilized; and to find how water is held by Napalm and its function in their hydrocarbon gel systems.

2. Beginning with carefully prepared aluminum soaps of pure fatty acids, the most important were found to be the di-soaps such as $Al(OH)L_2$, $Al(OH)Str_2$, $Al(OH)Cl_2$, and aluminum dinaphthenates. The pure aluminum dilaurate $Al(OH)L_2$ in many respects typifies the behavior of Napalm.

3. Pure aluminum dilaurate was carefully characterized by various physical chemical methods including the criteria demanded by the phase rule, and its structure was examined by means of X-rays. It exhibits a monoclinic crystalline structure similar to that of the gamma sodium soaps and the corresponding fatty acids.

4. From the point of view of the behavior with hydrocarbons, the degree of crystallinity is most important. When the pure dilaurate is well crystallized it is inert towards paraffins and even cyclohexane at ordinary temperature; whereas when the same pure dilaurate is more amorphous or glassy it readily swells and forms a true jelly. The jelly form is that which is useful in thickened fuels. Both crystallized and amorphous forms of pure dilaurate produce clear elastic jellies but the temperature required is much higher for the crystallized form.

5. Monosoaps such as $Al(OH)_2X$ are likewise formed during precipitation of Napalm. Aluminum monolaurate is converted to alumina by 95% ethyl alcohol but is obtained by a preparation in anhydrous methyl alcohol with subsequent extraction with acetone. Moisture present during any extractions tends to cause hydrolysis and produce monosoap or alumina. The monosoaps are comparatively inert toward hydrocarbons.

6. The composition of aluminum soaps and Napalms precipitated in the usual way lies between mono and disoaps. The higher the temperature of precipitation the more nearly is the product disoap. The excess acid is not free but is loosely bound or sorbed. Exhaustive extraction with the driest possibl acetone is required to remove it. Heat treatment of the precipitate, particularly in the mother liquor causes further reaction between fatty acid and monosoap to form more disoap.

7. Much information has been obtained as to the relation between all these aluminum soaps and water by use of the McBain-Bakr sorption balance. Sorption isotherms have also been obtained with volatile hydrocarbon.

8. Whereas pure aluminum dilaurate is readily and rapidly rendered anhydrous and its sorption and desorption of 1 or 2% of water is rapidly reversible; Napalm behaves quite differently, and also differs at 50°C from 25°C. At 25°C it loses about 2% of water on drying, at first rapidly, then slowly over 24 hours. At 50°C it loses twice as much, yet at both temperatures sorption and desorption are finally nearly reversible. Napalms of different manufacture vary by about 1% in their moisture uptake under identical conditions.

9. Napalms contain appreciable amounts of inorganic impurities capable of sorbing or combining with water.

10. The Karl Fisher method of determining moisture is too drastic as it extracts moisture from hydroxyl groups by condensing them.

11. Aluminum soaps placed in contact with hydrocarbons form a gel, a sol, or a jelly. Gels consist of opalescent noncoherent lumps of swollen undissolved soap; if excess of liquid is present it remains as such, almost free from soap. A sol is a clear and freely flowing liquid colloidal solution. The jelly is a definite truly stable clear, rigid, coherent, and elastic form existing under intermediate conditions; it may be reversibly produced from either sol or gel. There is no sharp line of demarkation between jelly and sol but a big difference in degree of rheological properties.

Many observations with various hydrocarbons involving these three forms are recorded.

12. Osmotic examination shows that a solution of aluminum dilaurate in benzene is a sol. The particle weight varies from several thousand to several million depending solely upon concentration and temperature. Hence aluminum soaps in hydrocarbons are association colloids.

13. The viscosity of the hydrocarbon gels and jellies i caused by loose linkages and aggregations of these colloidal particles. The structure of the jelly is therefore like those of the well investigated aqueous jellies of all sorts; namely, a brush heap or streptocollol arrangement of ramifying aggregates of colloidal particles enmeshing and partly immobilizing

sol or solvent. The particles themselves contain both solvent and soap and are not identical with the original soap put in.

14. Many observations of viscosity and thixotropy are recorded.

15. Peptizers act upon the linkages between the colloidal particles. It is shown by comparison of these dinitrobenzenes that their action bears no relation to dipole moment.

16. Since there is close parallelism between hydrocarbon systems of sodium soaps, silver soaps and aluminum soaps, their general properties cannot be due to any peculiarity of aluminum.

17. Data are given for the system, sodium stearate-cyclohexane.

18. During the course of the investigation various suggestions have been made. It has been shown that a very small percentage of metallic sodium can be dispersed through an incendiary jelly or Napalm in gasoline, making it ignite spontaneously on contact with water. It was demonstrated that a number of these remain stable and unaffected by the sodium over long periods. The use of gelatine capsules to enclose the sodium completely prevented any contact while retaining much of the spontaneous inflammability of the fuel and also of its residual ash.

19. Other suggestions are listed at the end of this report

This report covers work to June 1944; subsequent work is contained in monthly reports.

J. W. McBain

INTRODUCTION

When the Stanford group joined the Napalm research program on thickened fuels, the type of thickener was already decided upon and Napalm was in production. The important control factors for its production were known as well as the essential rheological requirements.

Our problem was to explore the nature of aluminum soaps and their mixtures with hydrocarbons and contribute a definite scientific basis for an understanding of the manufacture, testing, and application of Napalm as well as for the development of substitutes. As a sideline, suggestions for practical improvements were explored.

Few methodical investigations of pure aluminum soaps, or of their mixtures with hydrocarbons, have been published. Even the empirical knowledge was very limited although the metallic soaps find many applications in the grease and paint industries. The phases present in greases and thickened hydrocarbons had not been identified. Hydrocarbon systems containing calcium soaps had special properties which could not be attributed to those containing aluminum soaps. The chemistry of the aluminum soaps was obscure and the existence of aluminum soaps of definite composition was still uncertain.

A sound beginning was made by obtaining proof of the existenc of several aluminum soaps as definite chemical individuals. These include mono-soaps $Al(OH)_2L$, di-soaps $Al(OH)L_2$, and acid di-soaps $Al(OH)L_2.HL$, where L stands for the laurate radical and the three soaps are similar to the corresponding stearates. The pure dilaurate in many respects resembled Napalm. Hence it is suited for a thorough study, both as regards preparation and properties, including influence of physical state on gelling behavior with solvents, and its relation to moisture.

The report then properly begins with a comprehensive study of the aluminum soaps, followed by their relations to moisture and then the hydrocarbon systems.

I

THE ALUMINUM SOAPS

Knowledge of the chemistry of aluminum soaps seems to be a necessary foundation to the understanding of aluminum soap-thickened hydrocarbons.

Thickened fuels of the Napalm type contain appreciable quantities of the many hydrocarbons of gasoline, the many non-hydrocarbon "polar compounds" present therein, "free" fatty acids, inorganic salts and water from the Napalm together with thickening ingredients which are a mixture of aluminum soaps of unknown constitution...

The possible formulae for aluminum soaps are complex. We have definite evidence for three definite chemical compounds:

(a) The di-soaps $Al(OH)X_2$ where X stands for a fatty radical such as laurate, myristate, palmitate, stearate, oleate or naphthenate. Aluminum dilaurate is the best single representative of the general behavior of Napalm.

(b) The mono-soaps $Al(OH)_2X$.

(c) The acid di-soap $Al(OH)X_2.HX$.

We have no evidence for the existence of the simple normal aluminum soaps $Al\,X_3$.

There may possibly be other soaps. Likewise there may be basic compounds derived from aluminum hydroxide or mixed with it and fatty acid in colloidal form. Eigenberger (1) failed to prepare aluminum tristearate, distearate or monostearate but he

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(1) E. Eigenberger and A. Eigenberger Bittner, Koll. Zeit 1940, 91, 287 -294; E. Eigenberger, Fette and Seifen 1942, 49, 505-508.

favors a pseudo monostearate consisting of colloidal $Al(OH)_3$ peptized by sorbed fatty acid which enables it to simulate a monostearate and to swell and form jellies in organic solvents and also to form syneretic gels which split off water on heating. The base of his pseudo stearate is assumed to be a condensed or polyaluminum hydroxide containing 4 - 8 atoms of aluminum. He also assumes a true "basic"salt "$Al\ Str_2O\ (Al\ O\ Str)_6\ Al\ Str_2 \cdot aqua$" of molecular weight, when anhydrous , 3302, and of constant ash value 12.3%. Other condensation products have also been suggested. Of course a formula may be fitted to any empirical composition and the study would be almost hopeless if mixtures could not be separated.

In approaching the problem, we recall that the handbooks of inorganic chemistry of the 19th century recorded as compounds, thousands of formulae representing compositions empirically observed. Most of these formulae have been weeded out by applying the criteria of physical chemistry for compounds to them, using in particular the phase rule, and more recently X-rays. X-rays serve the purpose of determining crystallinity for the numerous cases in which crystalline form is not directly visible.

The phase rule presents a number of rigorous requirements for crystalline compounds of which the most general is that a chemical compound must act as a single component over some range of experimental conditions. Miller and Kenrick (2) in 1903 pointed

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(2) W. L. Miller and F. B. Kendrick, J. Phys. Chem. I: 260 - 268 (1903).

out a searching test which may be applied by using successive small quantities of solvent in contact with the solid, measuring at each point the concentration of the small amount of liquid and the composition of the solid. For example, for three components, if the composition of the solid is constant while that of the liquid varies, the number of solid phases is one: if that of the liquid remains constant while the solid varies then there are two solid phases present, if both vary, then there is present a single solid phase of variable composition as a solid solution or a sorption compound. For example, in the present study, if a small amount of acetone is exposed to a solid, free fatty acid is present if, and only if, the acetone yields a solution of the same concentration as if it had been exposed to and saturated with free fatty acid. Otherwise the fatty acid present in the solid must either be sorbed or combined, as may be determined by successive measurements.

X-ray examination serves as a useful adjunct to the phase rule criterion. If the latter shows that only a single compound is present, the X-rays give a characteristic fingerprint of it by which it may be traced thereafter.

Even a powder diagram shows by concentric rings the presence of crystallized material, with a pattern which may be compared with other known crystals such as fatty acids or sodium soaps. Differences of the rings gives an indication of particle size. Halos show amorphous or liquid matter. With soap, the long spacings are readily distinguished from shorter side spacings. From the long spacings the monoclinic angle of inclination β and the head to head, tail to tail arrangement can be deduced.

The X-ray method is not sensitive. The presence of 10% of a substance seldom gives a definite pattern. The presence of 10% of an impurity seldom affects the pattern of another substance.

A. The Precipitation of Aluminum Soaps and Factors Influencing the Results.

This section presents first, a general discussion of our method of preparation; and second, a study of the factors involved.

The influence of manufacturing conditions upon the properties of Napalm is a separate problem being studied by the Harshaw Company, and our work does not duplicate those experiments. Napalm is prepared by adding an excess of aluminum salt solution to a soap solution in the presence of additional alkali in either solution. This seems to be the most suitable for producing good Napalm but it does not lend itself to ready interpretation. The pH of the mother liquor changes from over 9 to less than 5, and the first portions of the aluminum solution are precipitated in a highly alkaline medium. It is probable that at least some aluminum hydroxide is then formed, and, due to the well known lack of reversibility in the formation of this compound, some alumina or basic aluminum salt remains in the final soap. We were later able to isolate such inorganic compounds as a turbidity factor in Napalm gels by sedimentation from peptized solutions. (Chap.III Finally, the composition of the mother liquor varies from a soap to an alum solution in the course of the precipitation.

This led to the adoption for our work of the reverse method, i. e. addition of a soap solution to an aluminum salt solution. To avoid, as much as possible, changes in the mother liquor of the precipitate, we use a large excess of the aluminum salt solution so that the precipitate is always surrounded from beginning to end by aluminum chloride solution. We add a neutral soap, both because it is the easiest to prepare and store and because the pH of the mother liquor may be least affected.

We use hydrated aluminum chloride rather than the sulfate, because of the known lesser tendency of the chloride ion to enter complexes, and thus the greater ease with which it can be washed out when compared with the sulfate ion. The nitrate ion might be preferable to the chloride, as it possesses the above qualities to a greater extent but there is no good simple test to ascertain its presence in small amounts, so that the washing operation would be more difficult to control. Furthermore, its oxidizing tendencies would render the soap less stable thermally if traces were present. We are using potassium soaps rather than sodium soaps because of their greater solubility.

Under these conditions, a precipitate is formed which contains all the fatty acid (since the mother liquor has a low pH) either in the form of soap or soaps or loosely bound and free acid, while the mother liquor contains the chlorides of aluminum and potassium.

In general, precipitation is carried out in a blendor by adding a 2% solution of neutral potassium soap of the fatty acid (prepared in large batches and stored as a dry powder) to an equal volume of 1.5% solution of Baker's C.P. hydrated aluminum chloride $AlCl_3 \cdot 6H_2O$. The precipitate is then separated by filtration and washed with distilled water until free of chloride. It is then dried over P_2O_5 and the soaps separated from loosely bound acid by extraction with dry acetone (see p. 21 and 22). Samples were ashed at 1000°C, giving results reproducible to 0.04%.

Minor details of technique play an appreciable role in these preparations.

Factors determining the final composition of the soap, particularly in case of the stearate, are as follows:

(a) The temperature of precipitation has a pronounced effect both upon the physical characteristics of the product and upon the chemical composition of the extracted soap.

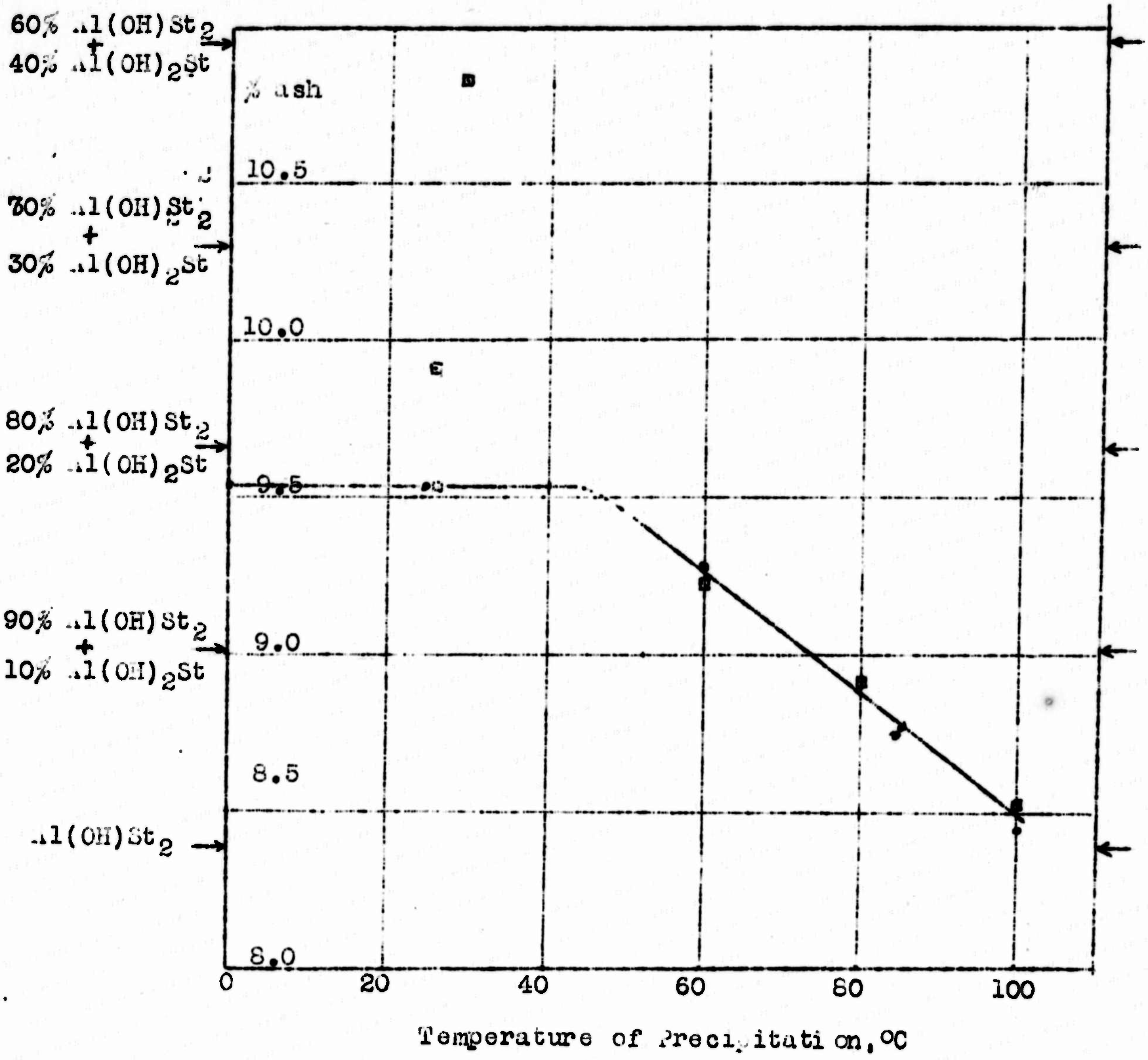
In the case of the stearate, the soaps precipitated at temperatures from 0° up to ca. 50-60°C usually formed soft and slow filtering sludges. They were thoroughly wetted by the aqueous medium and formed a stable dispersion of foam on agitation in the blender. In this condition, vacuum filtration by means of either coarse sintered glass funnels or filter paper supported by a Buchner funnel was often found to take as much as 1 1/2 to 2 hours for the filtration of 500 ml. of the aqueous mixture containing only five grams of soap. However, samples prepared at a temperature of 70°C or above coagulated and floated to the top of a clear aqueous medium. Filtration was very rapid (a matter of seconds) and the resulting filter cake was powdery and readily manipulated.

The dried soap from the batches prepared at temperatures below 50-60°C were flaky, compact, white products; while the high temperature of precipitations resulted in light, powdery and very finely divided soaps.

The higher the temperature of precipitation of aluminum stearate, the more nearly does the composition of the extracted soap approach that of aluminum distearate $Al(OH)Str_2$. Figure 1 shows the composition of extracted soap formed at various

Figure V

Variation of Ash Content of Extracted Aluminum Stearate with the Temperature of Precipitation.



temperatures from 0 to 100°C. From 0 to about 45°C the ash value is constant at 9.55% and may be compared with values of 8.38% for pure distearate and 14.86% for monostearate which have been calculated based on the acid number of the particular sample of fatty acid used. According to this, the soap is a mixture of 18% monostearate and 82% distearate.

As the temperature of precipitation is raised from 50° to 100° the composition of the extracted soap linearly changes toward that of the distearate, apparently reaching it just above 100°C.

In case of laurate the results are less definite but the low temperature soft sludge formation has not been encountered. At higher temperatures a taffy-like mass is obtained which hardens upon cooling and may be washed, dried, powdered, and extracted. The composition of the extracted soap is very close to the dilaurate at all temperatures from room to 100°C.

(b) <u>Heating the precipitate in the mother liquor</u> causes a definite reduction in the amount of free acid and a change from mono- to distearate. This demonstrates that fatty acid reacts with monostearate to transform it into distearate - a reversal of the well known reaction of hydrolysis. The duration of heating seems to be of secondary importance and the process is not readily reversible on cooling. In the following experiments soap was precipitated at 25°C and then heated in its mother liquor with continuous stirring at 80°C.

Procedure	Ash
Standard 25°C	9.55%
Kept at 80°C for 2' filtered immediately	8.76%
" " " " 10' " "	8.60%
" " " " 2' " after rapid cooling	8.51%
" " " " 2' " " slow "	8.70%

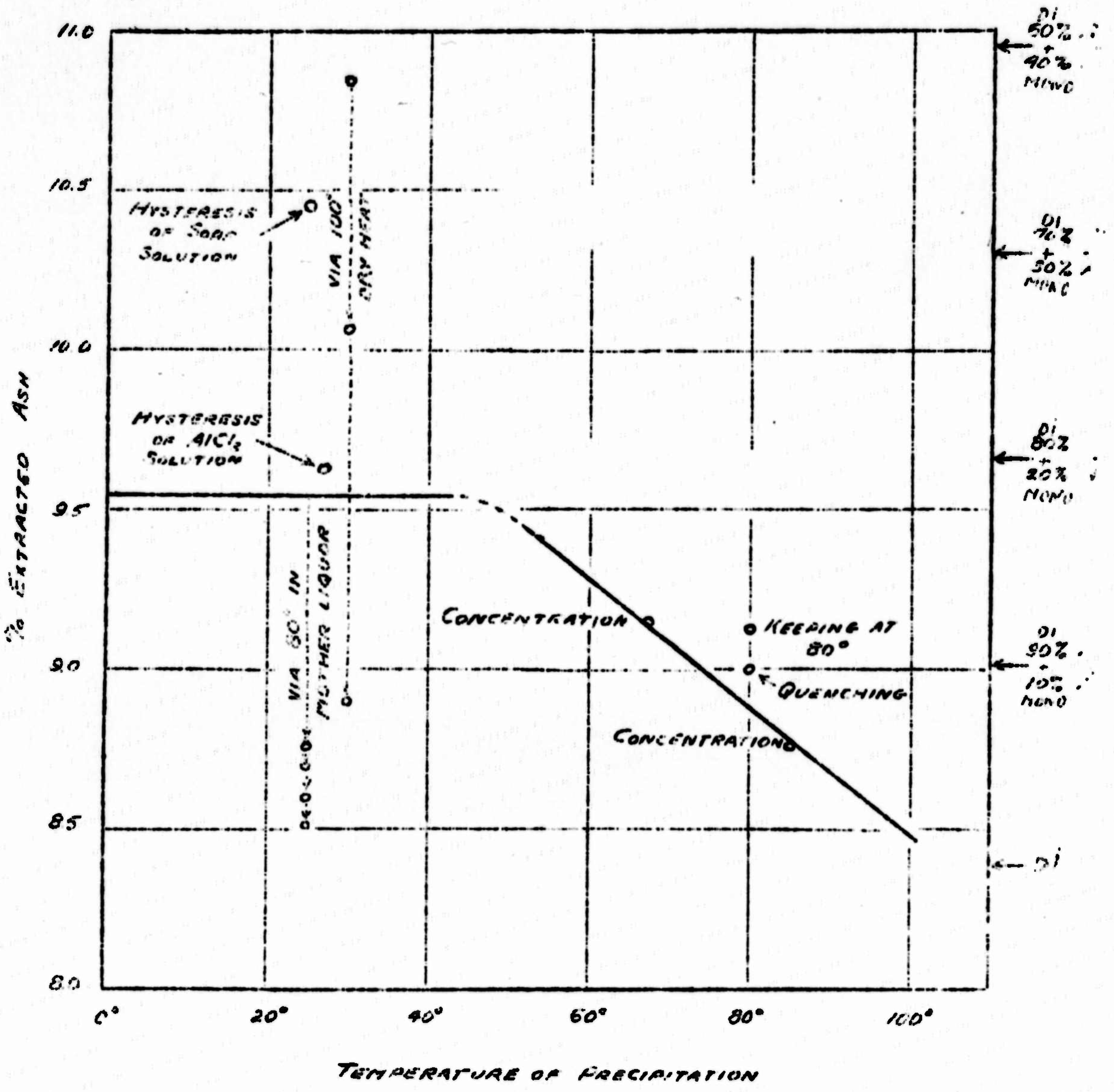
These results are shown in Figure 2.

(c) Heating the dry precipitate. Portions of unextracted soap, (washed free of chloride and then dried) a sample of which after extraction had an ash of 10.83%, were heated to 100°C in a test tube open to the air, then dried and extracted. The extracted ashes were 8.9% and 9.47% indicating again the reaction between stearic acid and monostearate. (Fig. 2).

(d) The effect of concentration of reactants. Variation of concentration of the soap and aluminum chloride solution before mixing, while maintaining the ratio of the amounts of the two ingredients unchanged, (by adjusting the volumes) has little effect on the composition of the extracted soap. For example, a sample prepared at 85°C using a 14.3% solution of potassium stearate, instead of the standard 2% solution, but retaining the standard 1.5% aluminum chloride solution gave an extracted aluminum soap with an ash of 8.76%. Another, prepared at 58°C, using a 9.38% aluminum chloride solution and a 4.44% potassium stearate solution gave an ash of the extracted soap of 9.24%. (Fig. 2).

Figure 2

Variation of Ash Content of Extracted Aluminum Stearate with Factors other than Temperature of Precipitation.



(e) The effect of ageing (solidifying) the potassium stearate solution at 25°. A freshly prepared potassium stearate solution (heated till clear at about 70°C, then cooled rapidly) is quite liquid and produces an extracted precipitate with 9.55% ash. However, if it is allowed to stand for 48 hours before use, the extracted ash value may be as high as 10.45% or possibly higher. (Fig. 2).

(f) Possible thermal hysteresis of aluminum chloride solution. It was thought that aluminum chloride solution may show a thermal hysteresis similar to that exhibited by its close relative chromium chloride. A solution of aluminum chloride was prepared, heated to 80°C and after 1 minute at this temperature quenched by immersion in ice water. The ash of the extracted aluminum soap prepared at 25°C from this solution was 9.64% showing that there was no appreciable effect. (Fig. 2).

As a check, the conductivity of a 1.5% solution of aluminum chloride was measured before and after heating to 100°C with rapid quenching. The difference was 1 part in 5000, i. e. negligible.

B. The Extraction of Fatty Acids by Solvents.

Extraction with 95% ethyl alcohol yields aluminum products approaching the composition of alumina. Preparations made in 95% ethyl alcohol yield alumina substantially free from fatty acids.

Methyl alcohol, on the other hand, whether anhydrous or containing 5% of added water, fails to degrade aluminum dilaurate beyond the composition of monolaurate, yielding 17.5% ash which would correspond to a mixture of three parts of mono- to one of dilaurate. Preparations made in anhydrous methanol, after extraction with acetone, gave samples corresponding to the monolaurate.

Moisture present during extraction with acetone hydrolyzes the soap to give mono-soap or even alumina. Hence before extraction *both* soap *and* acetone must be carefully dried.

We use for extraction acetone dried over Drierite (anhydrous calcium sulphate).

The problem of drying acetone. The problem of drying the acetone must be faced as a compromise at best, since it has been shown by Timmermans and Gillo(3) that acetone twice distilled at reduced pressure over phosphorus pentoxide still has .0002% of water by infra red spectroscopic analysis and a large loss of solvent occurs. The best results given by Weissberger and Proshauer (4) for drying acetone were obtained by use of K_2CO_3

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(3) J. Timmermans and L. Gillo, Roczniki Chemii 18, 812, (1938) (in French).

(4) A. Weissberger and E. Proshauer, Organic Solvents, Oxford Press (1935).

(only) which left .18% of water. The use of phosphorus pentoxide as well as use of potassium hydroxide pellets and of metallic sodium results in condensation products.

We have used Drierite, anhydrous calcium sulfate, since it is readily obtainable, easy and safe to handle. Only anhydrous $Mg(ClO_4)_2$ Dehydrite, which is potentially explosive, and those excluded because of tar formation are more efficient drying agents. However since the drying agent merely competes for any water present with the solvent being dried, an equilibrium distribution of water is established. The consumption of the water in the extracting acetone by hydrolysis of the soap may disturb this equilibrium distribution and cause the acetone to absorb moisture from the drying agent. Thus the drying agent would have become the reservoir and source of water.

The importance of traces of moisture in acetone may be illustrated by the following data and calculations which all assume pure aluminum distearate with an ash of 8.38% as a reference point:

(1) Complete hydrolysis of the soap to the hydroxide could be achieved by .06 grams water/gram soap.

(2) Hydrolysis to a soap with an ash value $>$9% could be accounted for by .003 grams of water/gram soap.

(3) Using 1000 ml. of acetone to treat 1 gram of soap only 6×10^{-5} gram water/ml. of solvent would be necessary for complete hydrolysis of the soap. This would be equivalent to .007% by weight of water in the acetone.

(4) The soap used is dried over phosphorus pentoxide to a

constant weight. The accuracy of the balance is at best .05-.1 mg. and a variation of this degree would represent .001-.002% water by weight in the soap which is not significant.

The degradation of the soap, represented by the portion of the curves having a constant slope, could be due to a concentration of 4×10^{-7} grams of water/ml. of acetone, or 5×10^{-7}% water by weight in the solvent, which is a dryness never attained.

Consideration of the traces of water required for the observed hydrolysis of the soap compared to the much larger concentration which exists after drying with any drying agent, tends to the belief that hydrolysis of the soap does not proceed so far that all the water present in the acetone is consumed. Whether this is due to the attainment of an equilibrium or insufficient time of contact is an open question.

Acetone appears to be the best solvent for extracting free or loosely combined fatty acid from our soaps because it does not dissolve or decompose the latter; the extracts show no ash. Its main drawback is that it cannot be obtained absolutely dry, so that a residual hydrolysis must be taken into account when, as in our experiments, enormous volumes of acetone are used to extract small samples of soap.

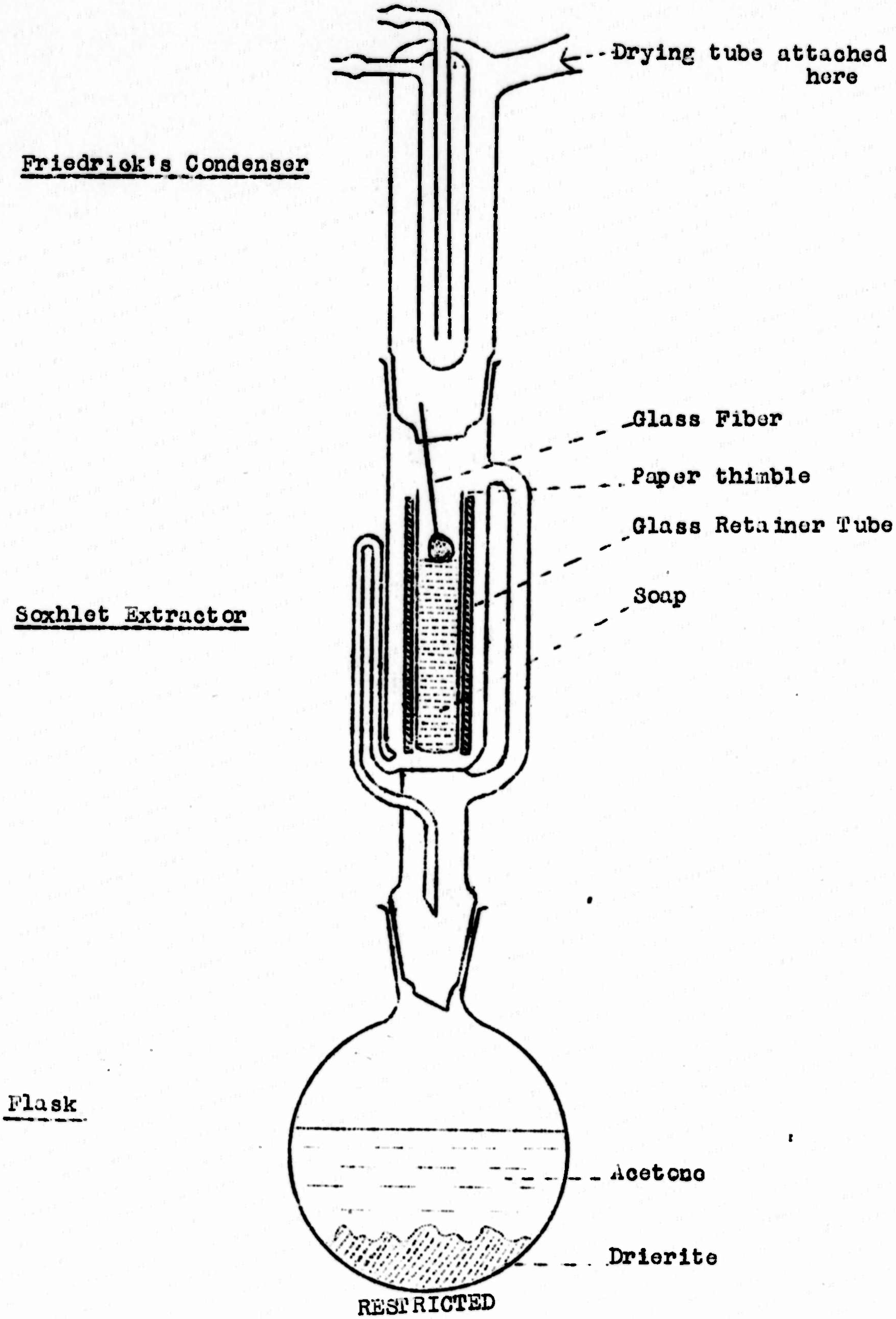
It has been already noted (Broughton and Byfield, O.S.R.D. Report 2036 and C.W.S. Columbia Napalm Summary No. 2) that extraction of aluminum soaps with dried acetone in a Soxhlet type extractor yields fatty acids at a decreasing rate as extraction proceeds. It has been suggested that at first free (or loosely bound) acids are extracted and thereafter those freed by hydrolysis by any moisture present.

We have modified the classical Soxhlet extractor to obtain better control of the variables.

The volume of solvent passing through the samples has been controlled by the arrangement shown in Figure 3 as adapted to an ordinary Soxhlet apparatus, having a Friedrick's condenser and standard taper ground glass joints, used for extraction "at the boiling point of acetone". Samples of powdered soap are weighed into a filter paper thimble, which is enclosed in a glass tube open at both ends. This tube, containing the thimble of soap, is cut long enough to stand above the level of the solvent in the Soxhlet, thus preventing the solvent outside of the tube from contacting the soap. All of the solvent is passed through the soap by conducting the reflux from the condenser down a glass fiber onto the surface of the soap. The solvent then passes through the whole soap column, flows out the bottom of the tube, and rises up around the outside until the level is high enough to siphon from the Soxhlet extractor. Thus, all the solvent passes through the soap once and only once at a rate controlled by the use of a calibrated variable heating cone. Channelling is largely avoided by using the Soxhlet extractor. A constant reflux rate has been used on all samples as part of the standard procedure of soap preparation.

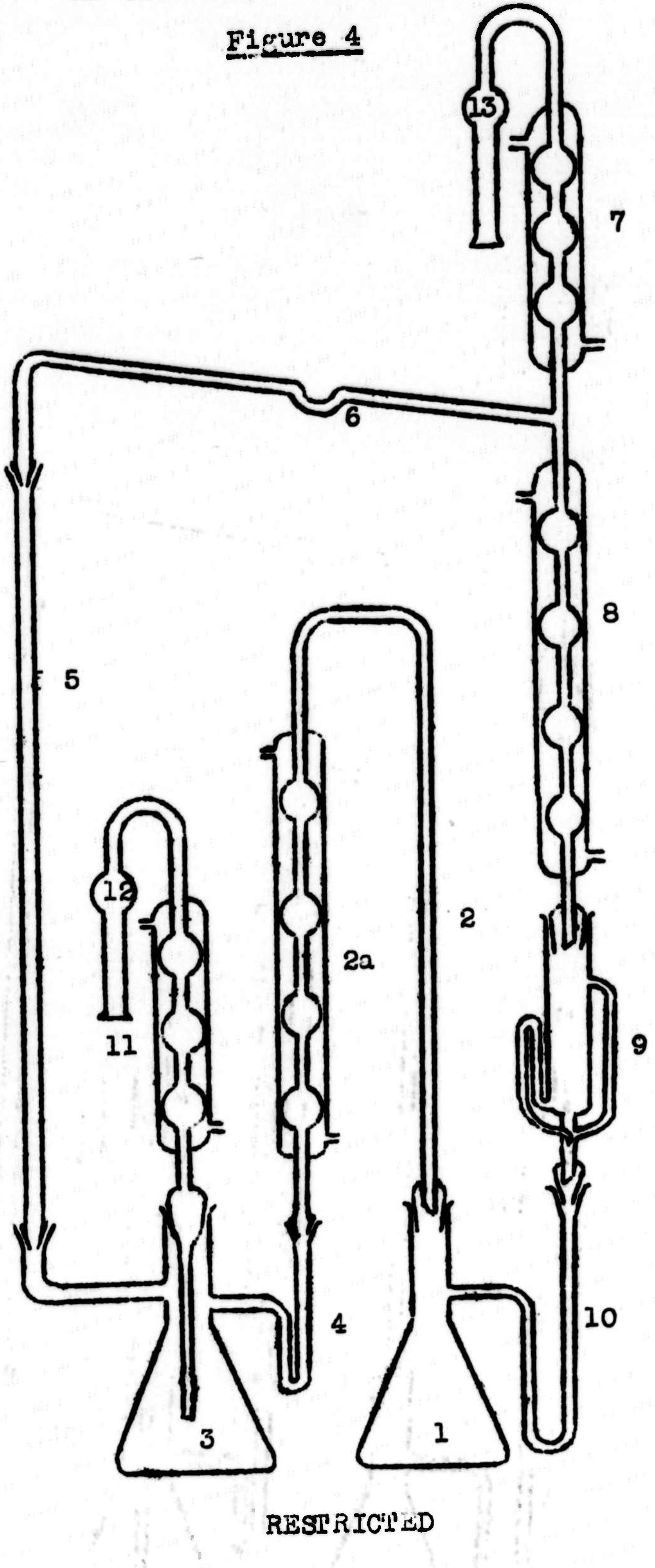
A more complete modification shown schematically in Figure 4 allows continuous drying and neutralization of the solvent, control of the extraction temperature, recovery of uncontaminated extract and continuous unsupervised performance.

Figure 3


Drying tube attached here
Friedrick's Condenser
Glass Fiber
Paper thimble
Glass Retainer Tube
Soap
Soxhlet Extractor
Flask
Acetone
Drierite

MODIFIED SOXHLET EXTRACTION APPARATUS FOR OPERATION AT CONTOLLED TEMPERATURES

Figure 4



Principles: The solvent goes through two successive distillations, the first being to separate it from the extract, and then after condensation it is redistilled to separate it from the drying agent before it is employed in extraction. It is condensed and cooled prior to contact with the substance to be extracted. The rate of heating during the first distillation is kept definitely slower than during the second one. A reflux condenser keeps the level of liquid during the second distillation from falling below a given point. The direction of flow of vapor is controlled by 3 goose-neck liquid traps.

Description: The solvent is separated from the extract by vaporization in flask 1. The vapor proceeds through tube 2 into condenser 2a and the liquid enters flask 3 through trap 4. Contact with drying and dehydrating agents is effected in flask 4 and the solvent is vaporized therefrom through tube 5 and trap 6 into condenser 7, where it is condensed and flows into condenser 8 where it is cooled to the desired temperature (e.g. 0°C) before entering conventional Soxhlet extractor 9. This extractor may be surrounded by a container (not shown) for thermostating at the desired temperature. Once the extractor 9 is filled to the proper level the solvent and extract are syphoned through trap 10 into flask 1.

Flask 2 is heated at a faster rate than flask 1. This prevents the level of liquid in flask 1 from getting too low. The level of liquid in flask 2 is kept constant by means of reflux condenser 11 co-acting with trap 6. When this level falls below the lower tip of condenser 11 the back pressure of trap 6 forces the vapor into condenser 11. When the level is above the lower tip of condenser 11 only a very small portion of the vapor formed is refluxed and most of it flows past trap 6 into condenser 7.

Guard tubes 12 and 13 prevent entry of atmospheric humidity into the system.

Specifications: The apparatus used at present has the following dimensions:

Flask 1 and 2 are 250 cc. Erlenmeyers. Height, overall 118 cm.; to trap 6, 92 cm. Head of traps: trap 6, 1 cm.; trap 4, 6 cm.; trap 10, 9 cm. Horizontal distances between centers of flasks 1 and 2, 12 cm.; tube 5 and condenser 8, 12 cm.; tube 2 and condenser 2a, 6.5 cm. O.D. of tubes and traps 11-15 mm. The side arms of flask 2 are at right angles. Four and 10 are filled with glass beads. A suggested improvement is to reduce the O.D. of traps 4 and 10 to 5-7 mm. to reduce back suction.

Modification: When the recovery of extract is not necessary and only control of temperature is desired, flask 1 is connected by means of a glass tube, not shown, directly to the horizontal tube 6, thus bypassing flask 3 and its condensers.

With the aid of these extractors, we were able to obtain the curves shown in Figures 5 and 6 for the variation of ash of aluminum stearate when extracted at about the boiling point of acetone and aluminum laurate when extracted at 3 temperatures respectively as a function of the volume of solvent.

Figure 5 is particularly interesting. It shows rapid leaching of material from the soap by the first liter of solvent.

The curves then level off to a constant slope which indicates an increase of less than 0.1% for the ash values per liter of solvent.

As a working hypothesis we too assume that free acid and acid loosely bound (i.e. as acid soap) is extracted first, leaving a residue of soap or soaps containing only acid combined or held by ionic bonds; and that the constant slope section of the curve represents degradation of this soap due to a small but continuous hydrolysis by traces of moisture.

This hypothesis is supported by the knowledge that wet acetone does result in hydrolysis as has been demonstrated, for example by C.W.S. Columbia, and has been confirmed by extracting a sample of the soap used in obtaining the upper curve in Figure 5 with two liters per gram of soap, employing 67% acetone - 33% water as solvent. The ash value for the extracted soap was 19.6% (i.e. way out of bounds of the figure.)

During all our standard Soxhlet extractions the acetone is being dried continuously by the presence of "Drierite" in the reboiler flask although it has been dried previously by the same drying agent for several days. The value of this precaution, however, has been shown to be real and significant inasmuch as refluxing the previously dried acetone during extraction from fresh "Drierite" decreases the slope and therefore the degradation rate. The triangle above the curves in Figure 5 shows the result obtained by using acetone which had been dried for two weeks over "Drierite", without drying agent present during extraction.

Variation of Ash Content of Aluminum Stearate During Exhaustive Extraction with Dried Acetone.

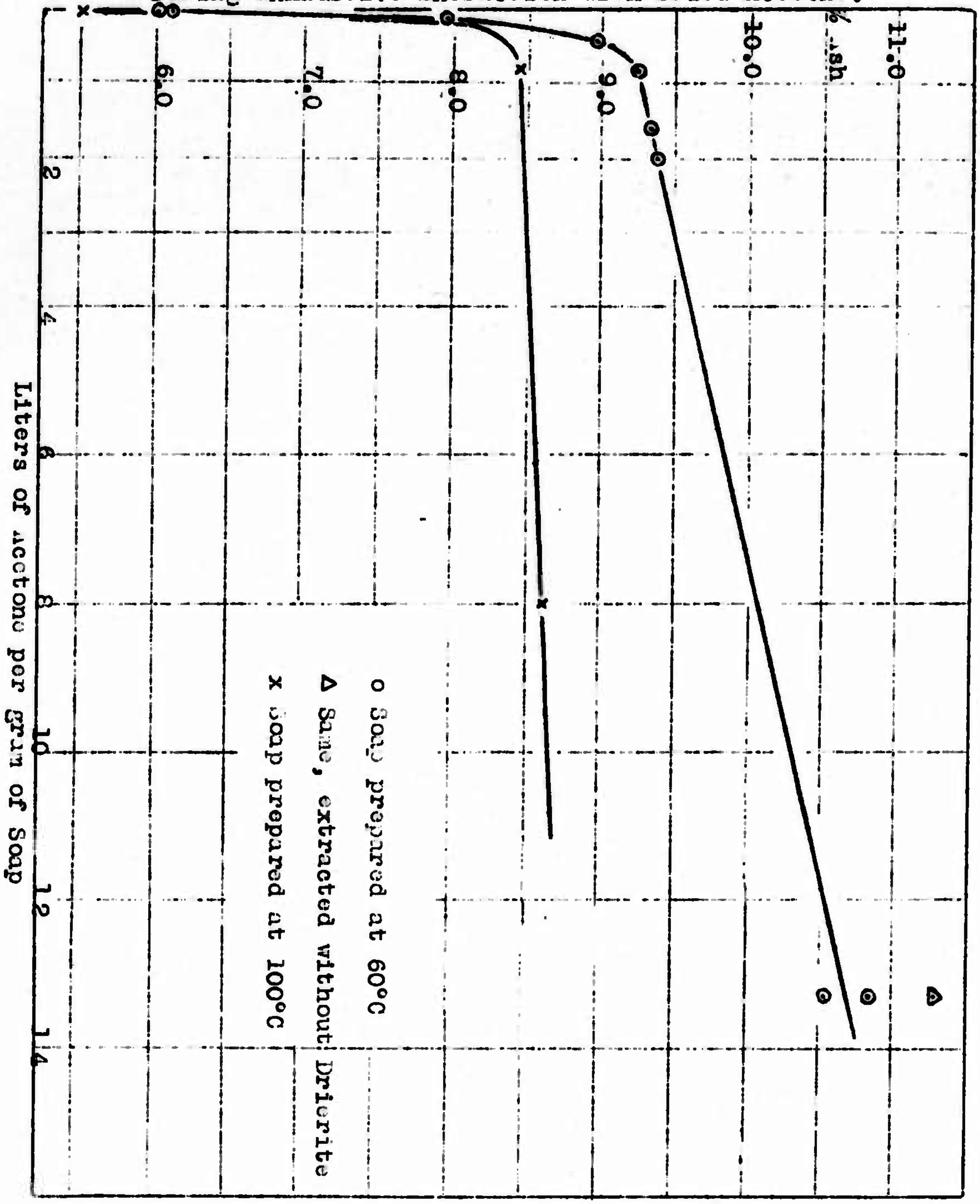
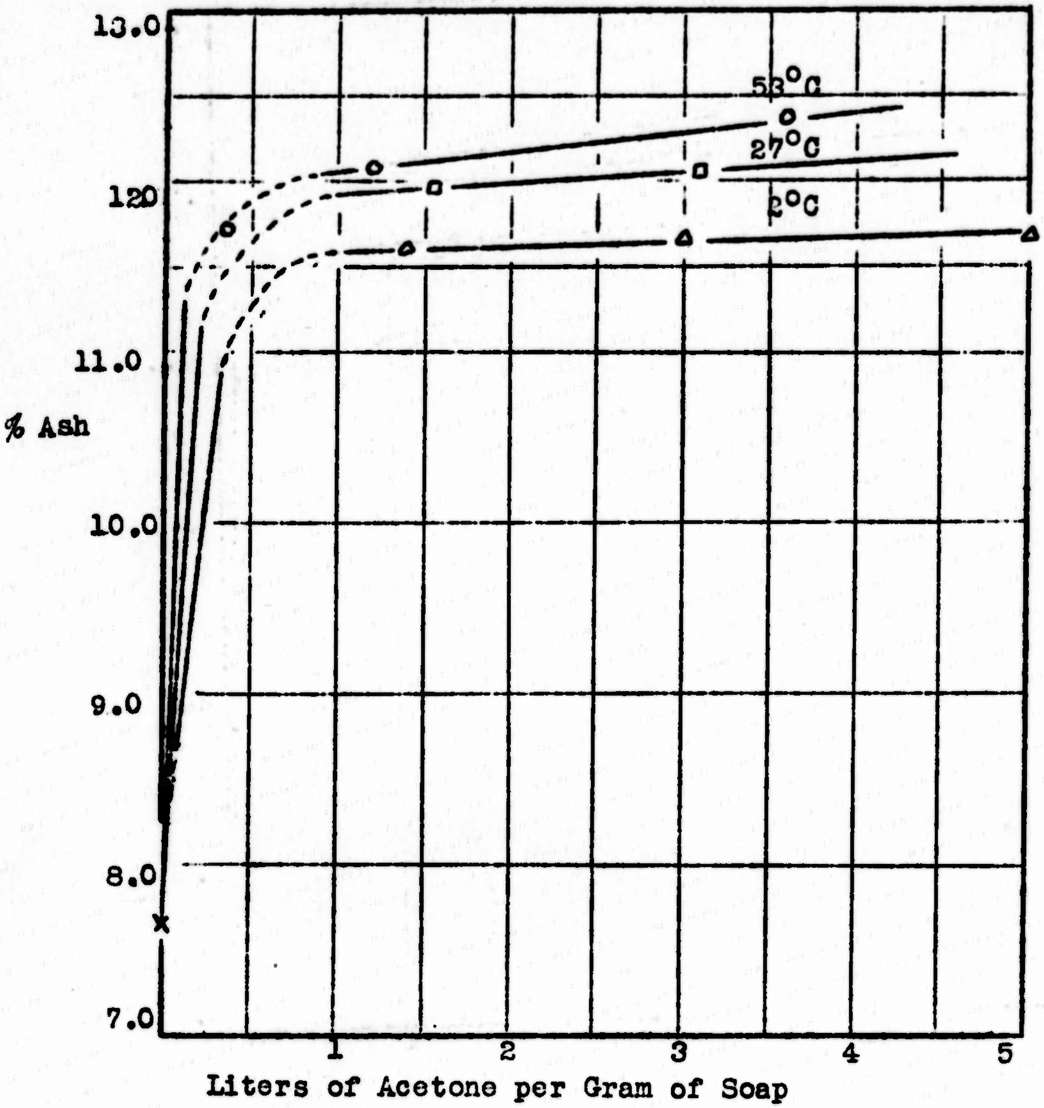


Figure 5

Figure 6
Variation of Ash Content of Aluminum Laurate
During Exhaustive Extraction with dried Acetone
at Three Temperatures of Extraction.



The temperature of extraction affects the rate of hydrolysis by the unavoidable traces of moisture, the hydrolysis being more pronounced at higher temperatures as shown, for example, by Figure 6 for aluminum dilaurate, which is practically unaffected at 0°C, more at room temperature, and rapidly at the boiling point of acetone. At the same time this graph shows that the extraction of loosely held acid is accelerated by higher temperatures so that a soap free from such acid may be obtained in shorter time of extraction.

Inspection of the curves of Figures 5 and 6 shows that the problem of freeing the soap of loosely bound acid without hydrolyzing it at all is not yet completely solved. We obtained, however, values for ash within 0.07% for the stearate, 0.04% for the laurate and 0.1% for the cyclohexane carboxylate. Extrapolation of the flat portion of the lower curve of volume of extractions versus composition (Figure 5) to zero extractant shows that if no degradation occurred, the stearate would have an ash within 0.00 - 0.02% of the theoretical (8.38%).

We have also developed a simple titrimetric method for determining free and loosely bound lauric acid in aluminum dilaurate giving results accurate probably to 0.1 - 0.2% and reproducible to about 0.05%.

The method is similar to that developed by the C.W.S. Columbia group but applicable to small samples, 0.2 - 0.3 grams of the soap being required. If only one fatty acid is present it gives results in weight % of free acid; if several fatty acids are present it gives only equivalent % of free fatty acid.

The soap is weighed into a 25 cc. volumetric flask, dried by evacuation for 30 minutes. The flask is then filled to the mark with acetone which has been stored over "Drierite" and anhydrous K_2CO_3. The flask is stoppered and shaken frequently at room temperature (22-25°C). The ratio of solvent to soap is sufficiently large to dissolve all loosely bound lauric acid at this temperature. (The maximum concentration of acid being ca. 1 per 100 cc., which is about 2% of saturation.)

After 15 minutes the clear solution is siphoned off under pressure through a cotton plug. The first 1 - 2 cc. are discarded and the following 10 cc. collected in a 10 cc. volumetric flask. This method separates completely the soap from the solution with a minimum of evaporation.

The 10 cc. collected are transferred to a beaker, the flask rinsed with 10 cc. of alcohol and 25 cc. of water, 3 or 4 drops of phenolphthalein are added, and the mixture titrated with 0.04 N KOH.

A blank is always run on the solvents and indicator, and subtracted from the result. The result is then computed assuming that the soap was in contact with 25 cc. of solution.

Presence of water is of course an important source of error in this method. In a test 0.29 gm. of water (comparable in weight to the soap) sufficed to increase the free acid content from 0.7% to 2.0%. When the extraction was conducted at 0°C, 0.15 gm. of water raised the free acid content of the same soap to only 0.9%.

If the amount of soap is varied the result is not affected significantly. In a test 0.17, 0.48, 0.88 g . of soap gave 0.7(4), 0.7(5), 0.6(8)% respectively. Too low concentrations reduce of course the precision of the method.

If the same method of extraction is applied several times to the same sample of soap the free acid content drops immediately to about 0.1-0.2% and levels off. The significance of this apparent amount of residual free acid is not clear. It could be due to hydrolysis by traces of moisture, but we obtained some indications that it may be due to oxidation of acetone by oxygen sorbed by the soap since a test, blowing CO_2-free oxygen through the acetone during extraction, increased the apparent free acid content from 0.3 to 0.5%; while storing the soap in a CO_2 atmosphere over night reduced it to 0.15%. This amount is sufficiently small however to be taken as the limiting factor on the accuracy of the method.

C. The Individual Aluminum Soaps.

The two most important properties of aluminum soaps, their behavior towards water and towards hydrocarbons, are treated in later chapters of this report. Here are collected the observations of the various other properties of the several soaps and their preparation. We deal in turn with aluminum dilaurate which has been studied in most detail, followed by aluminum distearate; acid aluminum dilaurate and acid aluminum distearate; aluminum monolaurate (and monostearate); and aluminum di-cyclohexane carboxylate.

Aluminum dilaurate, $Al(OH)L_2$.

(a) Preparation

Aluminum dilaurate was best prepared by adding an 8% neutral aqueous solution of potassium laurate (from Eastman Kodak lauric acid and aqueous potassium hydroxide, using carbonate-free water and potassium hydroxide) slowly to a large excess of a 2% aqueous solution of hydrated aluminum chloride ($AlCl_3.6H_2O$) (Baker's analyzed).

The precipitation was carried out at 25°C using strong mechanical agitation. The precipitate was washed with cold boiled-out distilled water until free from chloride. It was then dried over P_2O_5 in vacuum. The dried product contained about 30% of loosely bound fatty acid which was extracted rapidly, in 5-10 minutes, in a fritted glass Büchner funnel with dried, neutral, cold acetone using 80 ml. of solvent per gram of soap in 5-10 equal portions.

The ash value is 11.56 - 11.62% Al_2O_3, theory 11.49. The loosely held acid amounts to about 1% as determined by the method p. 25 ff.

Alternative Soxhlet extraction at 0°C (see p. 25) with 3000 - 5000 ml/g. has been used. Both yielded good results.

The soap obtained is a fine white powder which is caked by pressure. It is slightly hygroscopic taking up 0.4 to 1% moisture from the air. For analysis, it may be completely dried by evacuation or storage over P_2O_5 at room temperature. It shows no distinctive features under the microscope and even under the electron microscope only irregular agglomerates are found, too thick to be translucent to electrons. The X-ray pattern is similar to that of Napalm and shows a series of relatively sharp lines and a halo.

Upon heating in sealed evacuated tubes the powder sintered to a white opaque mass at 150 to 170°C and became transparent rather sharply at a temperature between 190 and 193°C; this is taken as the melting point because the resulting mass is homogeneous and isotropic although of exceedingly high viscosity. It withstands heating for short periods to 300° C and flows slowly at this temperature. Prolonged heating at 300°C in a sealed tube or even at much lower temperatures with drastic temperature gradients results in degradation, one of the products appearing to be dilauryl ketone. This might indicate that the uniformly heated soap remains in equilibrium with its volatile decomposition products.

When cooled from the molten state the original appearance of the soap is not restored; instead a hard brittle mass is formed whose properties depend on how it is cooled.

On cooling slowly and keeping the soap for between 15 minutes and an hour between 160 and 170°C, the mass becomes strongly birefringent and markedly opalescent. This is the "crystallized" form. Upon heating again it melts sharply over a range of 1° C between 193 and 196°, the exact range of temperature depending on the sample of soap and on the way it was crystallized. The sharp melting point is indicative of a definite compound and not a mixture. Upon cooling it yields a white brittle solid.

(b) Different physical forms of aluminum dilaurate, $Al(OH)L_2$. The dilaurate exists in several polymorphic forms which differ in their appearance, swelling in solvents, and details of X-ray diffraction; yet may have the same melting point and likewise are, to some extent at least, reversibly transformable into each other. The X-ray diffraction pattern of the "crystallized" form (Fig. 14) shows lines in the same position as the original form but much sharper, and the diffuse ring of the latter is resolved into several sharp lines. This shows that the arrangement of molecules was much more orderly after crystallization, presumably being in the form of larger crystals, and explains the difference of about 3°C between the melting points of the "original" and "crystallized" form.

As will be discussed in more detail in Chapter III, the crystallized form is inert towards cyclohexane at temperatures at which the original form swells enormously and forms an opalescent noncoherent "gel" and a very dilute sol. At higher temperatures both crystallized and original form produce a clear elastic jelly. These various systems may be frozen and the solvent sublimed off, leaving different physical forms "recovered from gel", "from jelly" and "from sol".

The form recovered "from gel" is quite similar in its properties to the "original" one. That "from jelly" swells without limit at room temperature in cyclohexane, forming a clear jelly; and its X-ray diffraction pattern is much more diffuse, though the position of the lines is still the same, and it contains only traces of free acid as determined by the method described on p. 22. The one recovered "from sol" is an extremely fluffy white powder which dissolved rapidly in cyclohexane and gives barely discernable lines in X-ray diffraction.

If the molten soap is quenched rapidly it yields a solid transparent "glassy" form whose X-ray diffraction is somewhat more diffused than that of the original and whose behavior in cyclohexane is irregular, part dissolving and part swelling, thus showing physical inhomogeneity due to uneven heat treatment during quenching.

Table I summarizes the properties and preparation of these various forms.

All these forms upon heating and proper cooling give the "crystallized" form having the same melting point and sharp X-ray diffraction lines, proving that they are different physical forms of the same compound, differing probably by the size and perfection of their crystal structure.

The "glassy" and the "original" forms are shown by their behavior in cyclohexane to be physically inhomogeneous. Indeed, the glassy form is visibly inhomogeneous. The original form contains about 8% of forms very soluble at 21°C and about 23% soluble at 25°C, while the remainder is quite insoluble at these

TABLE I

Properties and transformations of Aluminum dilaurate (Ash value 11.55%).

Name	1 Original	2 Crystalline	3 Glassy	4 Recovered from gel	5 Recovered from jelly	6 Recovered from sol
Appearance	White caking powder	Bluish-white slightly translucent brittle solid	Slightly brownish transparent brittle glass	Translucent or transparent brittle glass	Transparent brittle solid	Extremely fluffy white powder
1 g. of solid in cyclohexane swells at room temperature to	25-50cc	less than 2 cc.	Large but very indefinite	8-15 cc.	Unlimited	-
X-ray crystallinity Figure 14	Micro-crystalline	Very sharp	Definite	Micro-crystalline	Very faint	Extremely faint
Preparation	Extraction with acetone of acid aluminum dilaurate	Melting of 1 or 5 and probably of any other form in sealed tube, cooling to 160-170°C until crystallized and slow cooling.	Melting of 1 or probably any other form in sealed tube, and quenching by immersing in hot water.	Adding 5-7 parts by weight of cyclohexane to 1, letting stand overnight and drying in vacuo.	Adding 5-7 parts by weight of cyclohexane to 1, heating to 60-85°C until clear, cooling and drying in vacuo.	Adding 100-150 parts by weight of cyclohexane to 1, letting stand at room temperature with occasional shaking, centrifuging to clear the supernatant liquid, decanting and evaporating the decantate in vacuum.

temperatures; but all of these forms can be converted into the same sharply maelting crystallized form. Hence they differ only in physical properties.

The existence of the definite compound $Al(OH)L_2$ is further confirmed by the fact that when it distributes itself between gel and sol in cyclohexane the products recovered from both show no appreciable difference in melting point. This is discussed in Chapter III.

(c) Aluminum dilaurate in benzene solution.

Aluminum soaps are not high polymers. In solution, the high polymers such as cellulose derivatives, rubber, etc., are assumed to have a high molecular weight independent of temperature and concentration and derived by extrapolating the actual measurements to infinite dilution. At finite concentrations their osmotic pressure is low and increases faster than the concentration.

Aluminum dilaurate in benzene on the other hand has a rather low osmotic pressure which decreases much more slowly than the concentration. Aluminum dilaurate (and Napalms) must be recognized as association colloids. There is a great change of apparent molecular weight (change in degree of association) throughout the measured range corresponding to $(Al(OH)L_2)_{500}$ in 1.0% and $(Al(OH)L_2)_6$ in 0.001% solution. While extrapolation to infinite dilution is difficult under these circumstances, it is certain that the actual molecular weight of aluminum dilaurate is not higher than $(Al(OH)L_2)_5$, and its true molecular weight may well be $Al(OH)L_2$.

X-ray examination of Napalm, aluminum dilaurate, and aluminum distearate. The X-ray diffraction diagrams were kindly made by Dr. Sydney Ross without support of O.S.R.D. funds. Their general significance was indicated in the introduction.

Napalms give X-ray powder diagrams consisting of fairly sharp rings as shown in Figure 7. They closely resemble those of aluminum dilaurate, likewise given for comparison in Figure 7. Figures 8 and 9 give microphotometer tracings for the X-ray patterns of ten Napalms as received by us. Figures 10, 11, 12 and 13 give typical microphotometer tracings of Napalms, dilaurate, lauric acid and sodium laurate. Figure 14 shows the X-ray patterns of the dilaurate in its different physical forms ranging from the highly crystallized substance to the almost amorphous form recovered from jelly as already described in Table I on page 32.

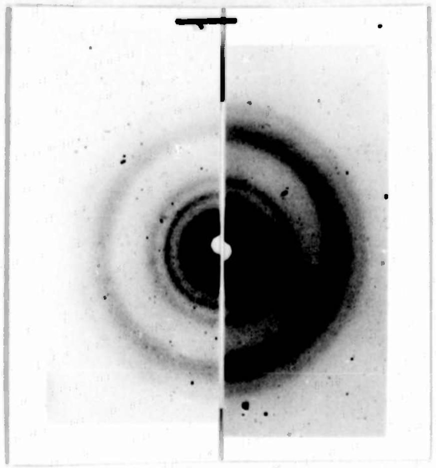
Microphotometer tracings of X-ray diffraction patterns of aluminum distearate in its original form and in the crystallized form are shown in Figure 15. Both are highly crystalline.

Figure 16 is a diagram of X-ray diffraction patterns of the known forms of aluminum and its hydrates. Comparison of the lines for aluminum dilaurate and aluminum monolaurate show that these are distinct chemical species, and not mere adsorbates or peptisates of aluminum by fatty acid. The alumina pattern is absent from their X-ray diagram.

The Napalms shown in the last two tracings of Figure 13 were obtained by drying systems containing 6 to 7% of Napalm in toluene and isooctane, respectively. In toluene it formed a very stiff elastic jelly, transparent but containing, at first, numerous slightly

PHOTOGRAPHIC REPRODUCTION X-RAY DIFFRACTION PATTERNS OF A NAPALM AND ALUMINUM DILAURATE

Figure 7



Aluminum dilaurate
$Al(OH)L_2$

Napalm Nuodex Batch
No. 13571

Figure 8

Microphotometer Tracing of X-ray Diffraction Patterns of Ten Representative Napalms.

Sample to plate distance 5 cm.

magnification 2x.

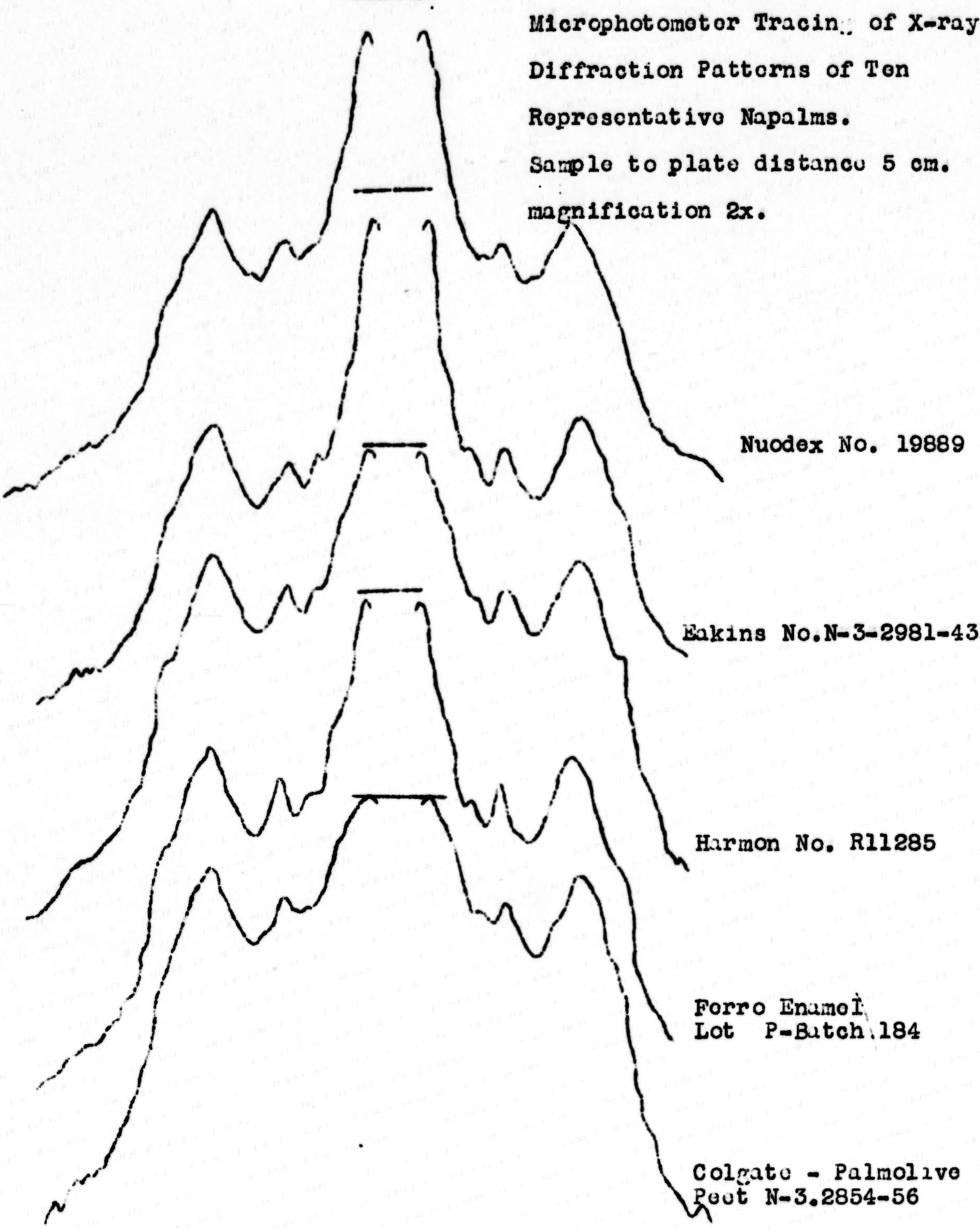
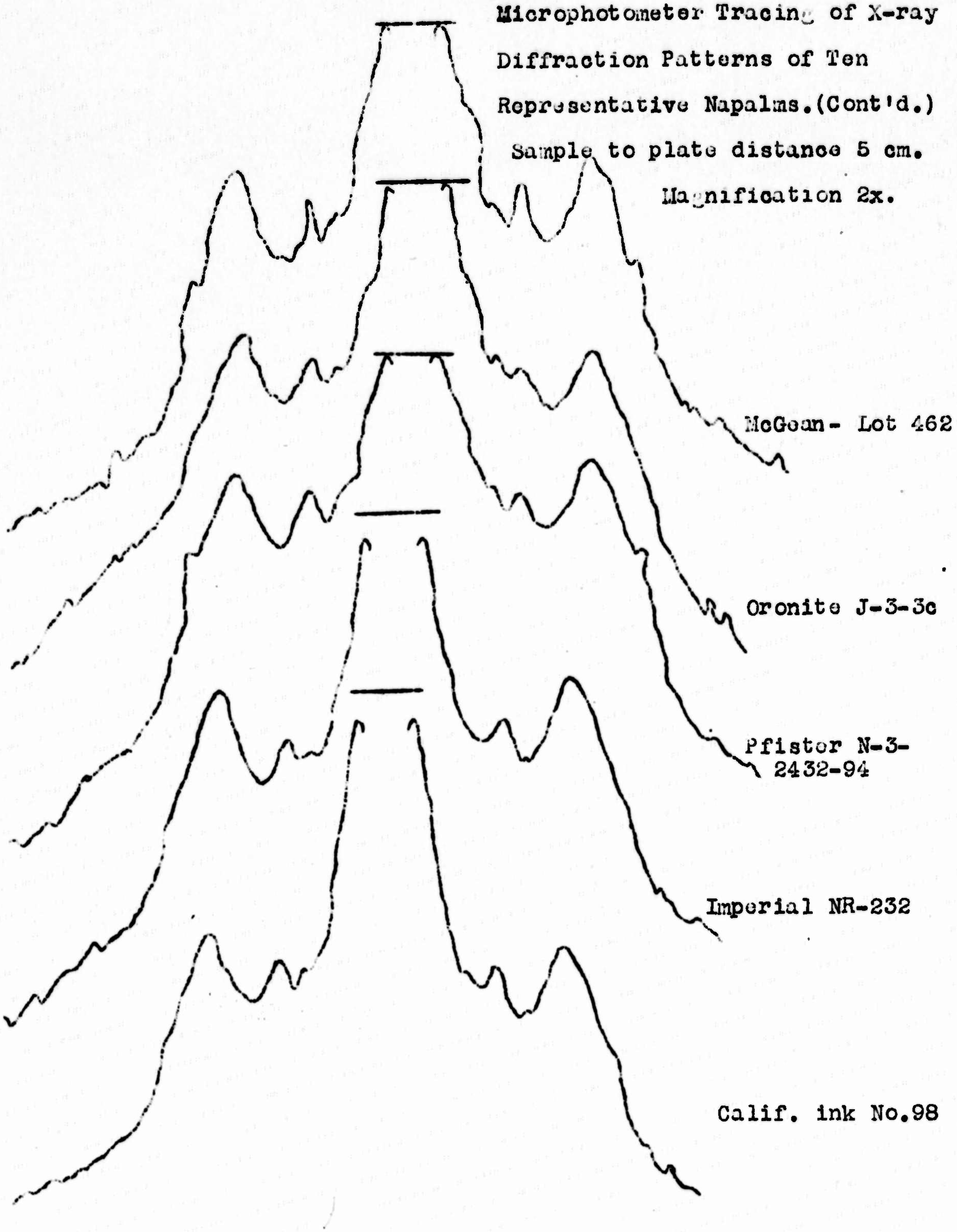


Figure 9

Microphotometer Tracing of X-ray Diffraction Patterns of Ten Representative Napalms.(Cont'd.)

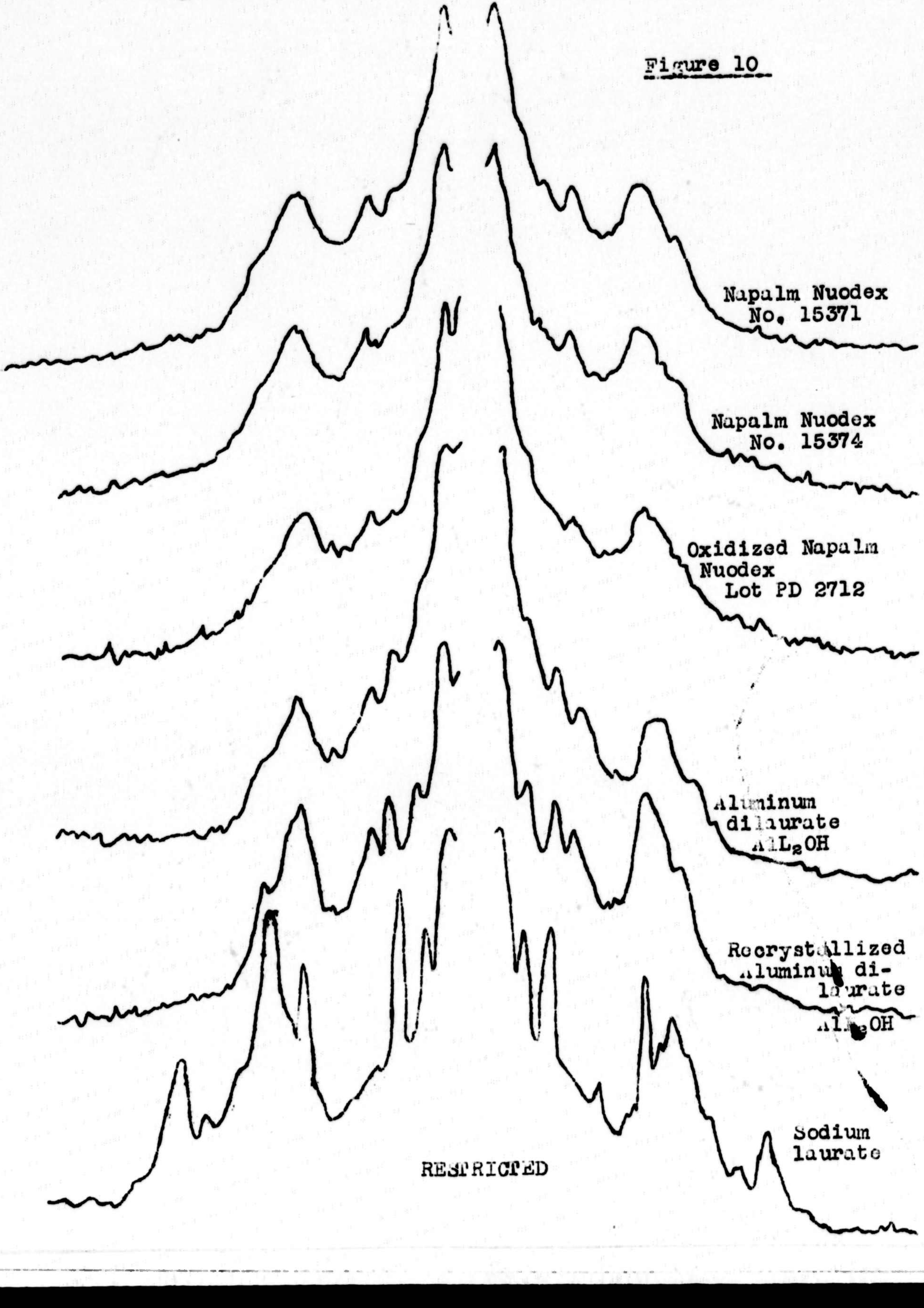
Sample to plate distance 5 cm.

Magnification 2x.



REPRODUCTION OF MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS
Magnification 2x. Sample to plate distance 50 mm.

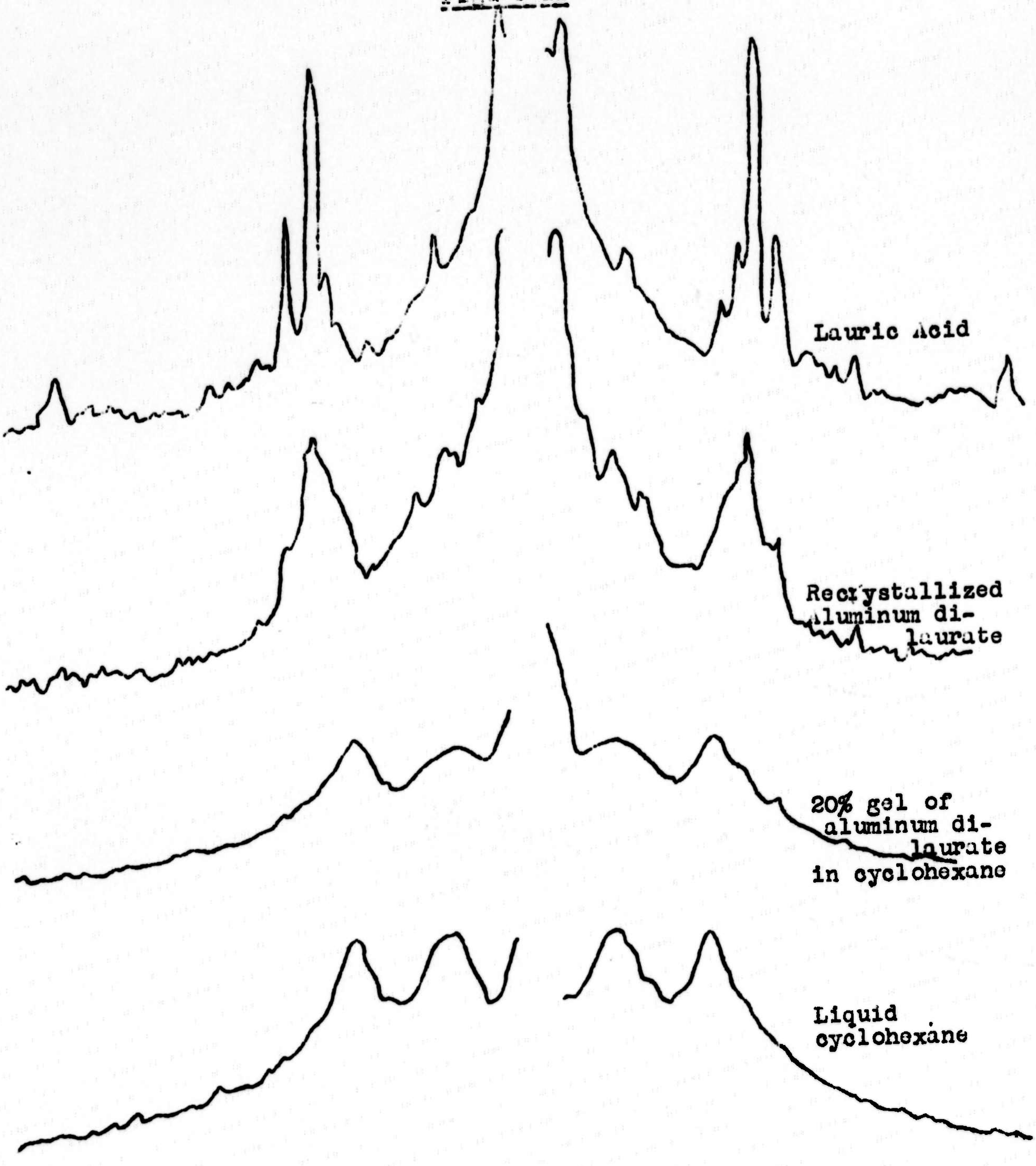
Figure 10



REPRODUCTION OF MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS

Magnification 8x. Sample to plate distance 50 mm.

Figure 11



COMPARISON OF PAIRS OF MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS

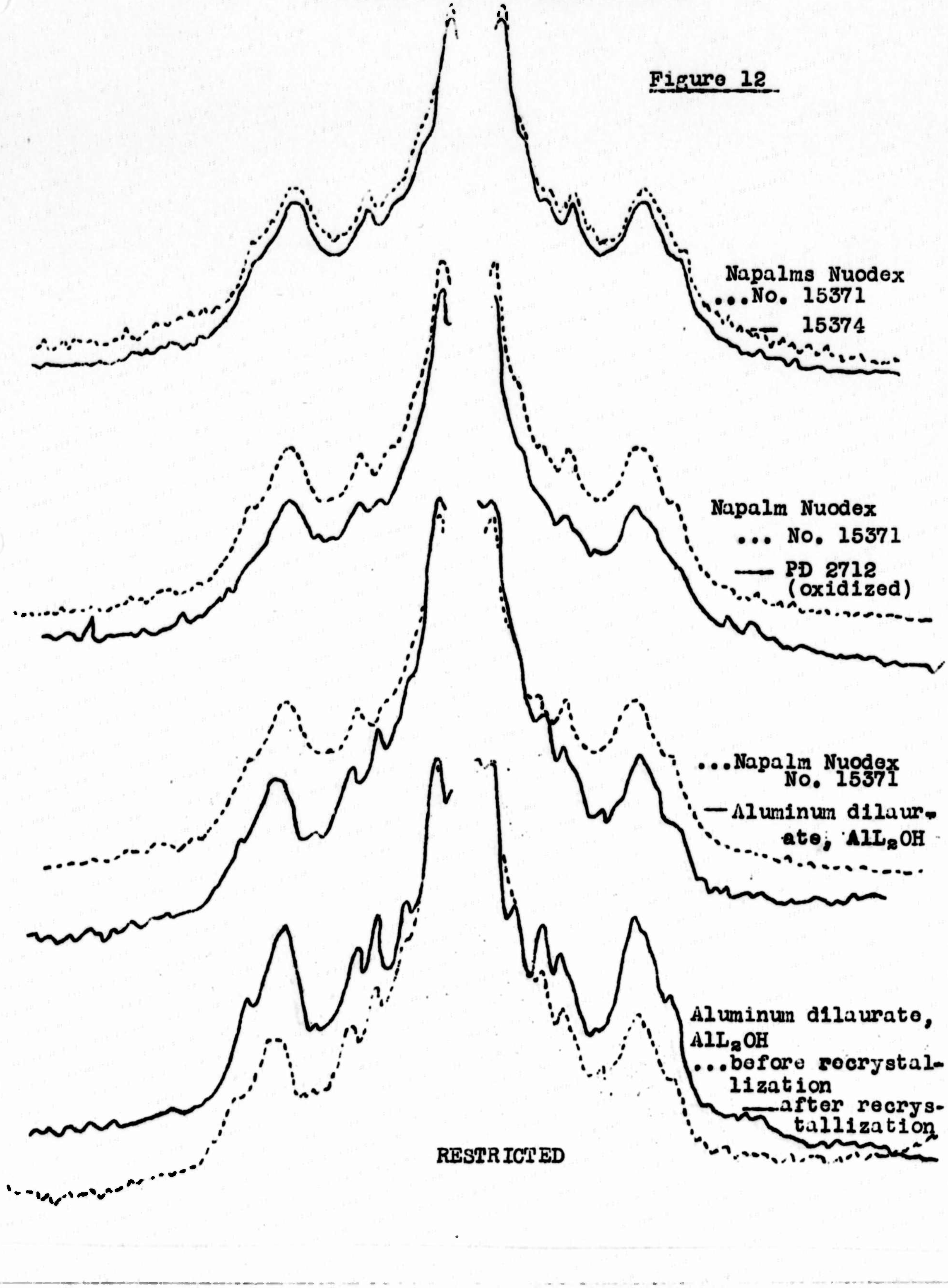
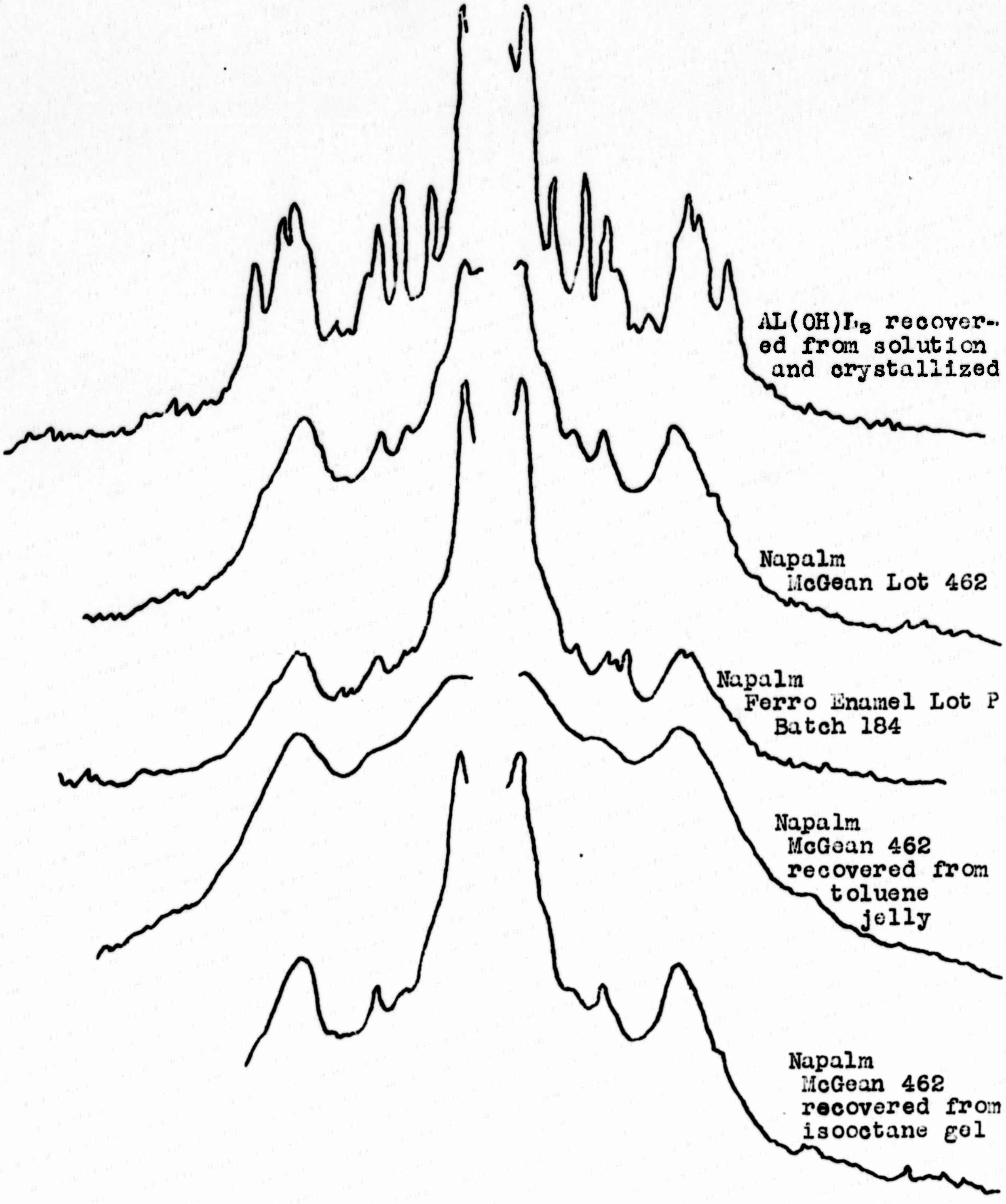


Figure 12

MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS

Sample to plate distance 5 cm. Magnification 2x



MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS OF VARIOUS FORMS OF ALUMINUM DILAURATE

Magnification 2x.
Sample to plate distance 50 mm.

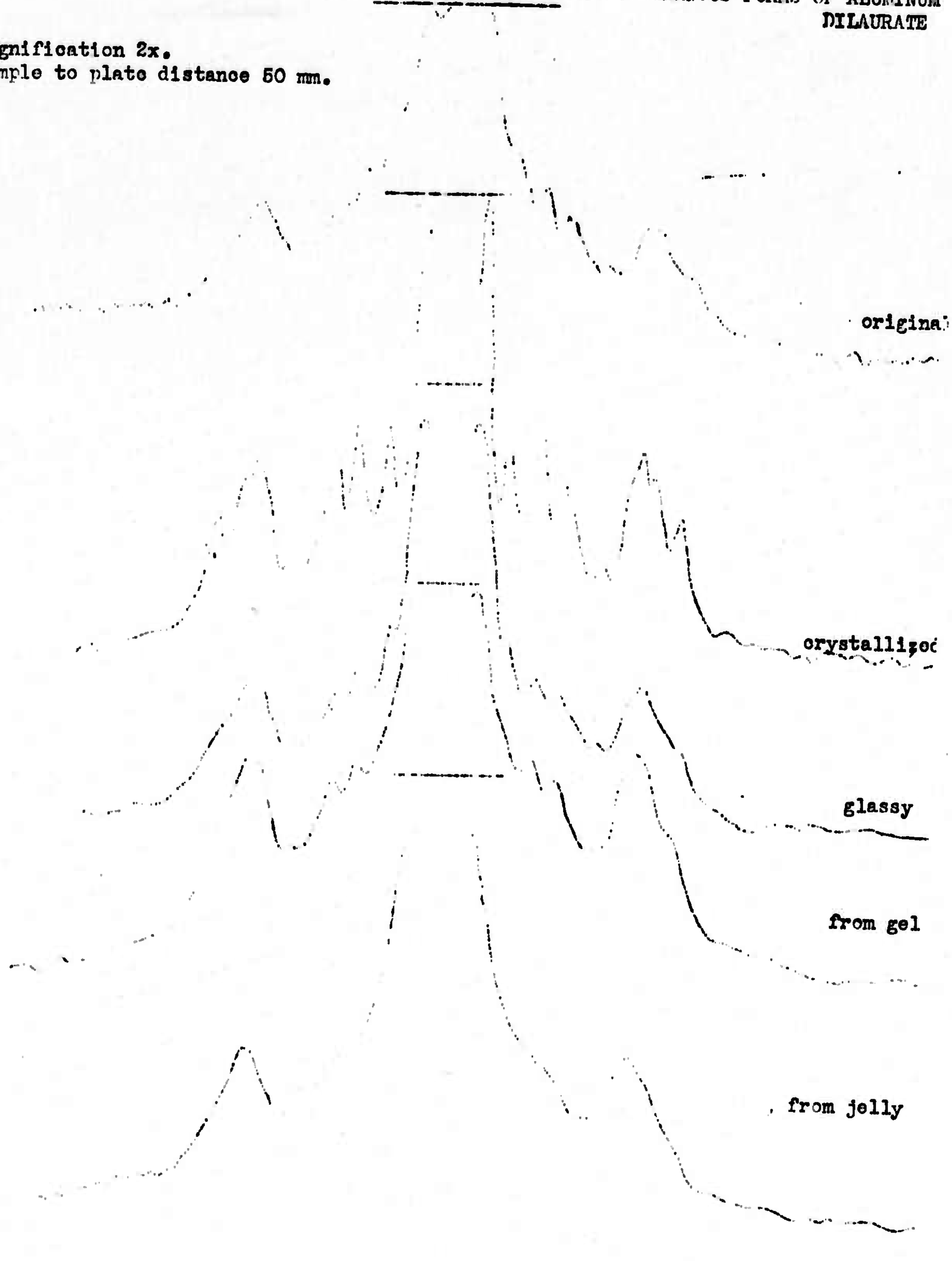


Figure 14

MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS OF ALUMINUM DISTEARATE. PLATE DISTANCE 5 CM. MAGNIFICATION 2X.

Figure 15

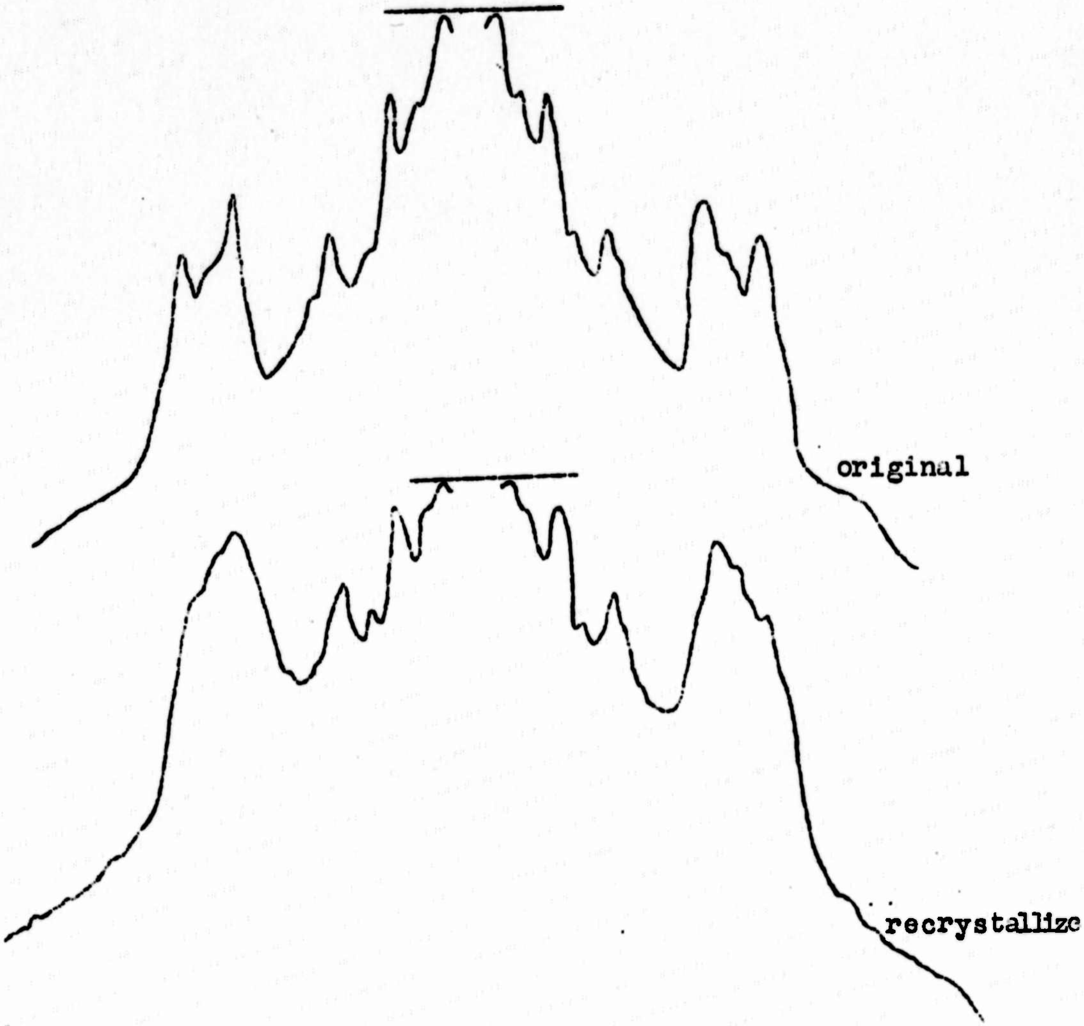


Fig. 16

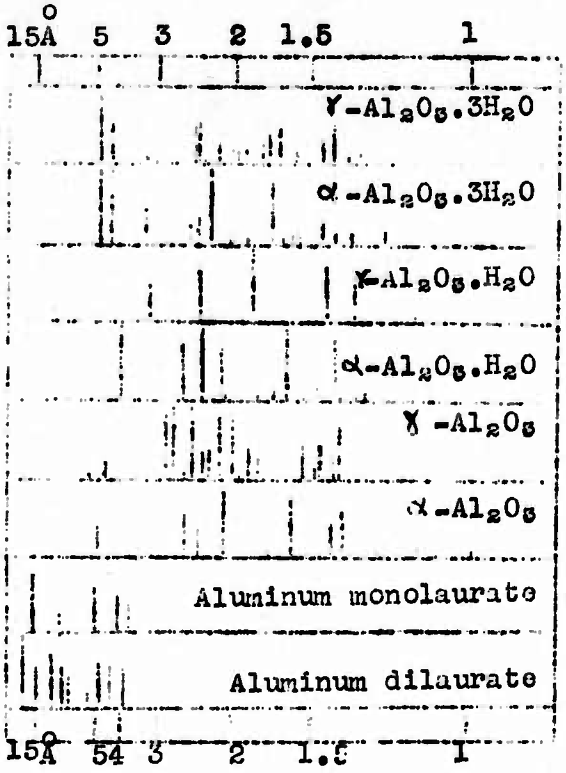


Diagram of x-ray diffraction patterns of aluminas and their hydrates (according to Weiser, 1935) and of aluminum monolaurate and dilaurate.

opalescent flocs; this dried to a transparent waxlike film, yielding a very different X-ray diagram.

In anhydrous isooctane the grains of Napalm were swollen to transparent lumps of gel with thin liquid left over even after two weeks at room temperature. This X-ray pattern is definitely crystalline.

Figure 17 records X-ray results from the McGean Napalm showing clearly the retention of crystallinity in soap recovered from a gel and its absence in soap recovered from a jelly. The individual specimens were as follows:

(1) Napalm McGean Lot 462 untreated. The pattern shows rather sharp lines.

(2) Same soap placed in 11.5 weight parts of isooctane for three days forming a two phase system of a small amount of thin clear liquid and swollen murky lumps of soap, then dried by evacuation below room temperature. Figure 17 shows distinct lines, confirming the presence of the gel phase.

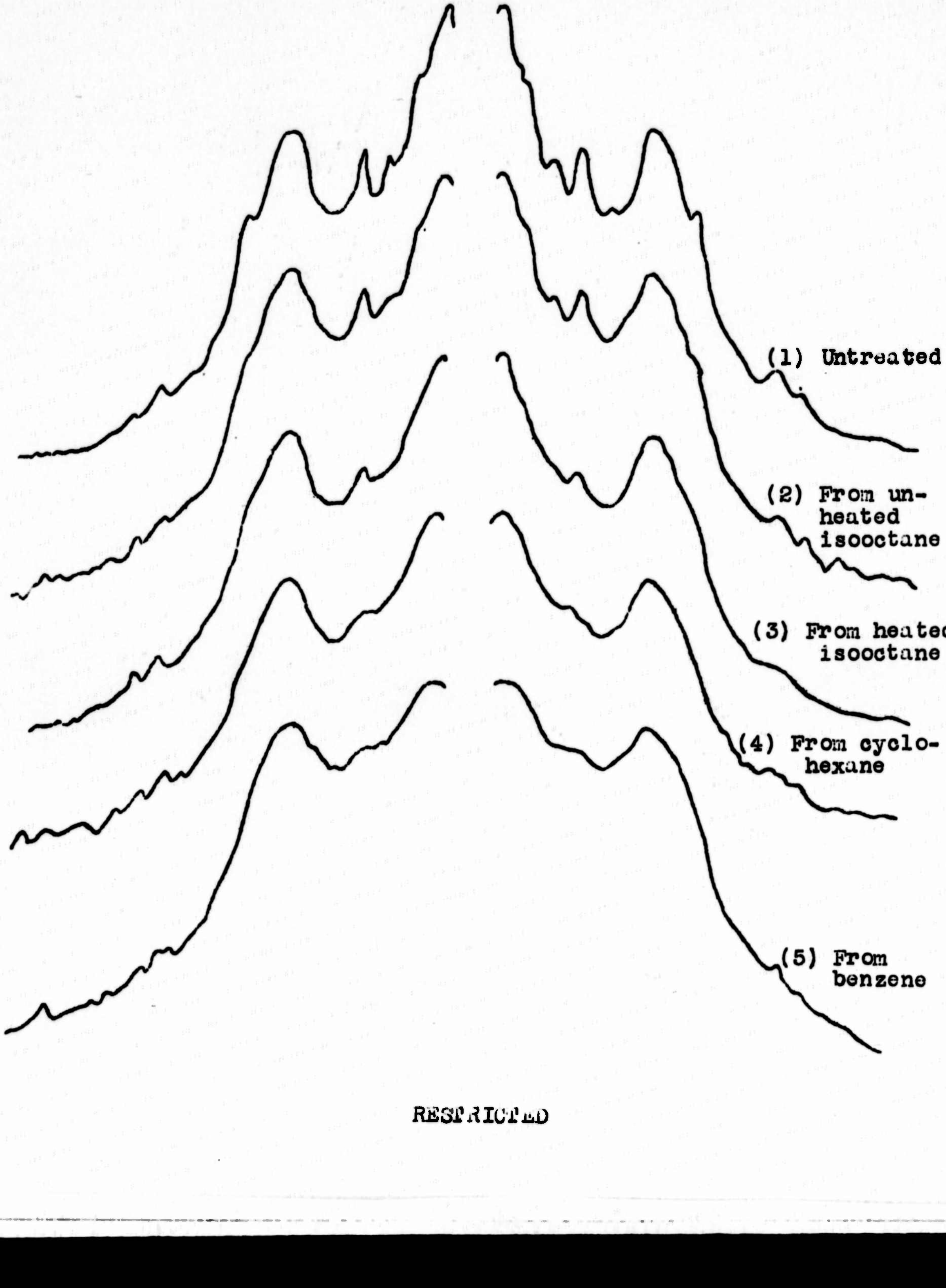
(3) Same as 2, but heated on the steam bath for one hour, forming a coherent mass of somewhat lower turbidity than 2. It shows only halos and proves that the gel phase has given way to the jelly.

(4) Some Napalm placed in 11.5 parts of cyclohexane at room temperature formed a turbid mass. Frozen and dried by evacuation. It shows a pattern of jelly not gel.

(5) Same process as (4) but with benzene. An almost clear transparent mass was formed, and it shows again a pattern of jelly similar to that obtained from the turbid samples 3 and 4.

PHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS OF NAPALM MCGEAN 462 UNTREATED AND RECOVERED FROM HYDROCARBONS

Figure 17



Crystal structure of aluminum dilaurate. The crystal structure of sodium soap, fatty acids and a number of other related homologous series is well established. Comparison of their patterns with those obtained for aluminum dilaurate and aluminum distearate affords a partial interpretation of the structure of the latter. In all these series the long spacings are so clearly separated from the short or side spacings that they are unmistakeable. Indeed they are so long that they require that the fatty acid chains must be placed end to end in pairs to produce the distance between the (001) planes, c sin β. Aluminum dilaurate and aluminum distearate have such similar X-ray patterns that they must have the same polymorphic forms. The microphotometer tracings for these two soaps are reproduced for comparison in Figure 18. Two different sets of lines may be noted. Those near the center correspond to successive orders of the long spacing and those grouped together between 6Å and 3Å correspond to short or side spacings between chains.

The short spacings are identical for the two soaps showing that they are independent of the length of the hydrocarbon chain and that both soaps have the same polymorphic form.

The normal configuration of paraffin chain crystals is full extension, with each chain straight except for the zigzag necessitated by the tetrahedral angle of the carbon bonds. Close packing of the chain is favored by certain angles between the direction of the chain and that of the plane of the terminal groups. In practice, angles of approximately 90°, 70°, 62°, 54° and 48° have been encountered (cf. Schoon, Z. Phys. Chem. 39, 404. (1938) and Brill and Meyer, Z. Kryst. 67, 570 (1928).).

Microphotometer Tracings of X-ray Diffraction Patterns

Distance - sample to plate .. 5 cm
Magnification .... 2 x
Bragg spacings in Angstrom units.

Figure 18

Aluminum Dilaurate

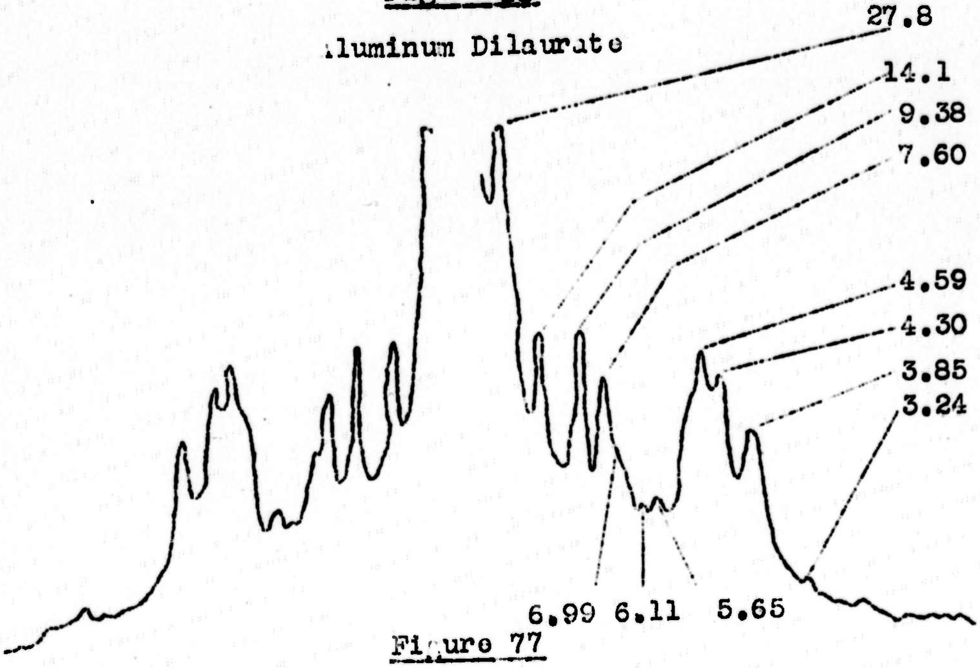
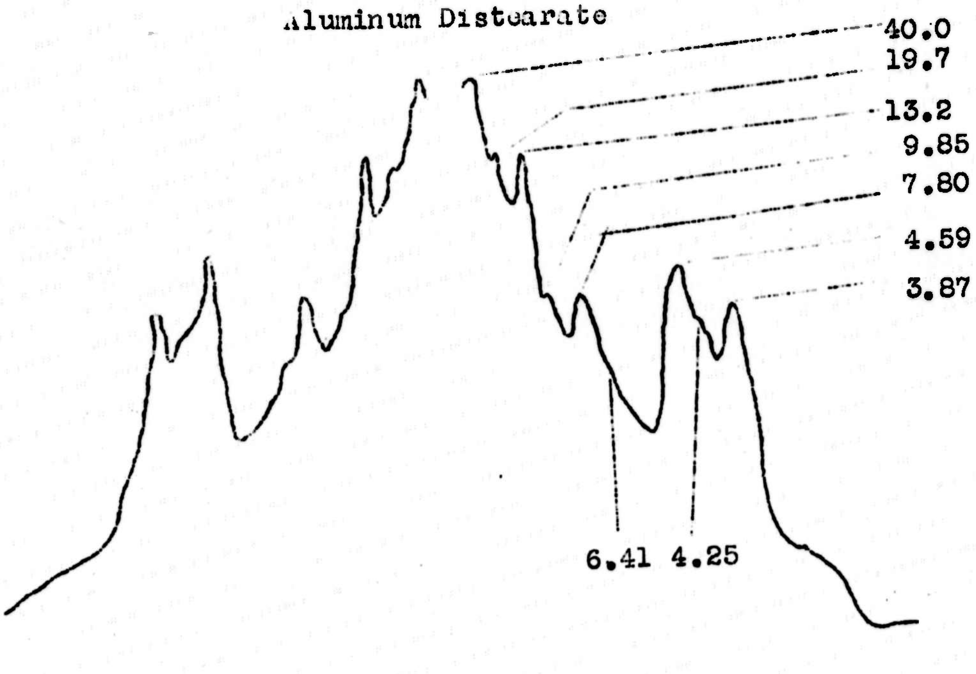


Figure 77

Aluminum Distearate



All the lines corresponding to long spacings are due to successive orders of diffraction (00l) by the one long spacing of 28.1 Å in case of the dilaurate and 39.4 Å in case of the distearate. Their difference is 11.3 Å = $\Delta c \sin \beta$. Since the distance between alternate carbon atoms in a hydrocarbon chain is 2.54 Å the corresponding value for Δc for double molecules is 6 x 2.54 Å= 15.24 Å. The ratio of these values is $\sin \beta = 0.741$. Hence β, the monoclinic angle for both soaps, is 48°. The same value of $\beta = 48^\circ$ was experimentally obtained by Brill and Meyer for lauric acid.

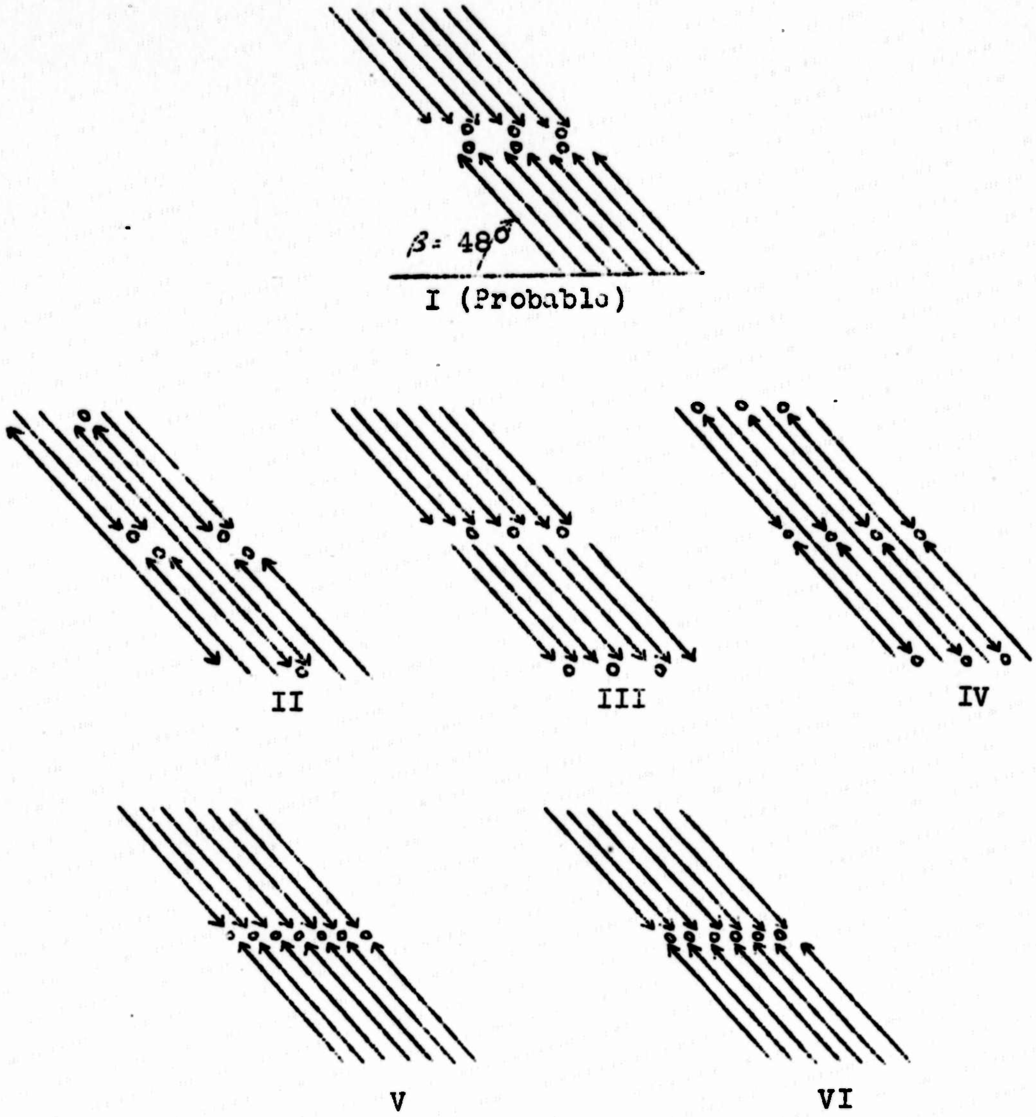
If the length of aluminum soaps with its two chains side by side were taken as equal to that of the corresponding sodium soaps, 18.3 Å for laurate and 25.4 Å for stearate, the value of the monoclinic angle β would be 50°. This is in good agreement with the 48° derived above, especially since the aluminum atom is somewhat smaller than the sodium atom, and may be taken as proof that, as in the sodium soaps, the aluminum atoms are arranged in a double row, head to head with the double tails also side by side and end to end, as in Figure 19.

Aluminum distearate $Al(OH)Str_2$.

Potassium stearate was first prepared by adding 1.5 normal methyl alcoholic KOH to a slight excess of a 10% solution of Eastman Kodak pure stearic acid in acetone, with thorough stirring at about 40°C. The precipitate was washed repeatedly with neutral acetone until the wash liquid was practically neutral, then dried to constant weight over P_2O_5.

Figure 19

Diagrams Representing Probable (I) and Some Excluded Alternate Arrangements (II - VI) for the Fatty Acid Chains of Aluminum Di-soaps.



A 2% solution by weight of this neutral potassium soap in boiled-out distilled water was added to an equal volume of 1.5% solution by weight of Bakers' C.P. hydrated aluminum chloride, $AlCl_3.6H_2O$, in boiled-out distilled water, maintaining vigorous stirring by a blendor. Both solutions were heated to 100°C and the blendor can was made of metal and was wound with nichrome wire to allow operation at this temperature. The soap as precipitated was washed free of chloride ion with distilled water and subsequently dried to constant weight over P_2O_5.

The dried precipitates were extracted with dry, boiling acetone in the modified Soxhlet apparatus (page 18) with 1200 cc. per gram of soap and dried first in air, then over P_2O_5. Aluminum distearate resembles the dilaurate. Its melting point may be observed readily in transmitted polarized light, and, with some care, also in ordinary light.

The original white powder sinters somewhat below 100°C and melts to a colorless, isotropic, extremely viscous liquid at 173-4°C. The liquid may be crystallized by cooling to about 110°C (for seeding) then warming to about 165°C (for rapid growth of the crystals). It is then strongly birefringent and slightly opalescer

Once crystallized, the soap melts over a range of about 1 1/2°C between 175-177°C. If the melting process is stopped before completion , i. e. while there are still birefringent portion to act as nuclei, recrystallization proceeds rapidly at 165-170°C. If melting is allowed to proceed to completion, seeding at 110 - 120°C again becomes necessary.

Upon cooling below about 100°C the appearance of the soap changes markedly, due to rapidly increasing opalescence and turbidity, which make it almost opaque at room temperature. This change of appearance is gradual over a range of 20 - 30° and is almost reversible. We believe at present that it is due not to a phase change but to the formation of minute cracks in the rigid soap upon thermal contraction. The presence of large macroscopic cracks which disappear upon heating to about 110°C and the brittle and grainy feel of the cooled soap when crushed led to this belief.

The relatively narrow temperature range of melting of this soap indicates that it is a definite chemical species (aluminum distearate) capable of acting as a simple component in the sense of the phase rule, and that it is not a mixture.

This melting point of aluminum distearate, 175 - 177°C, may be compared to that of the dilaurate which we found to be 193 - 196°C; that is, 20 degrees higher.

Aluminum acid dilaurate $Al(OH)L_2.HL$ and aluminum acid distearate $Al(OH)\ Str_2.\ H\ Str.$

In our report of November 15, 1943 we postulated the presence of acid aluminum dilaurate $Al(OH)L_2.HL$ instead of a trilaurate AlL_3 or a simple mixture of dilaurate with free lauric acid $Al(OH)L_2+HL$. This hypothesis was based mainly on the effective rate of extraction of lauric acid from this soap using dried acetone.

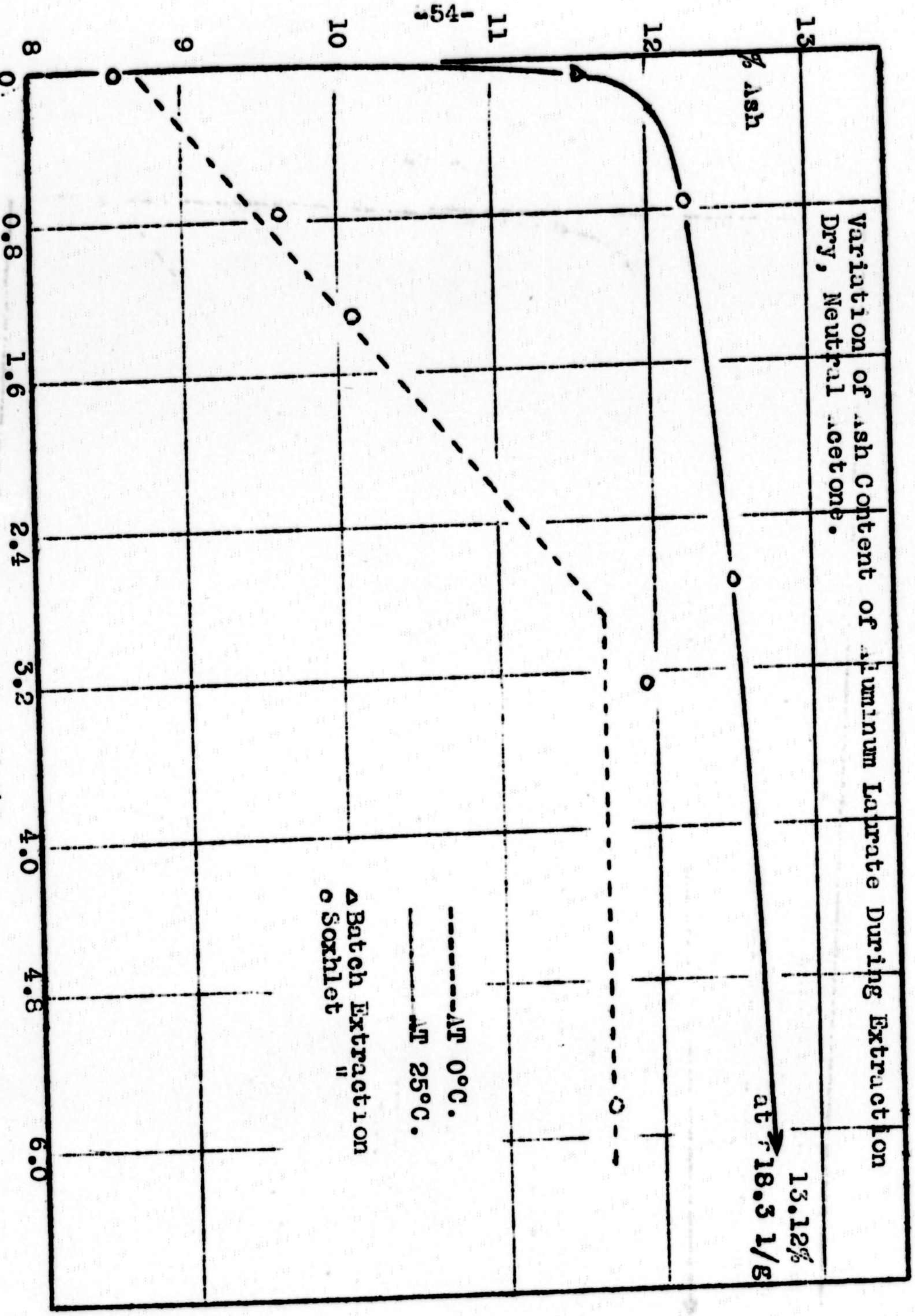
Extraction was very rapid at room temperature and very slow at 0°C. The former showed that the lauric acid was not combined as AlL_3 because hydrolysis was most unlikely to occur under these conditions. The latter showed that the acid was not "free" but definitely "bound" or "loosely held".

McBain and McClatchie, Jour. Amer. Chem. Soc. 54, 3266, (1932) found it impossible to prepare aluminum tripalmetate AlP_3 even under the most anhydrous conditions. The acid dilaurate results from precipitation of excess aluminum trichloride with potassium laurate at room temperature, washing with water only and drying. We have not prepared it pure and it melted over the range 110 - 120°C.

When extracted at room temperature with dry acetone, this product loses rapidly approximately one molecular weight of lauric acid, yielding aluminum dilaurate. (Upon longer extraction the amount of lauric acid extracted increases further, reaching 33% after 18000 cc. per gram).

Extraction at 0°C with dry acetone in the modified Soxhlet apparatus described on p. 20 shows, however, a quite different picture. The extraction of lauric acid proceeds but slowly and at a steady rate of .01 g. HL per 100 cc. of acetone until the composition of $Al(OH)L_2$ is reached and then practically ceases. Figures 20 and 21 show this striking difference. Figure 20 shows the variation of ash content of the extracted product as a function of the volume of extracting acetone per gram of soap. Figure 21 shows the same experiments in terms of extracted acid as obtained by titrating the extracts.

The solubility of lauric acid in dry acetone is quite large (we have found it to be 8% at -3°C) and the rapid extraction at room temperature indicates that diffusion is no obstacle. Therefore at 0°C the lauric acid is not present as a simple admixture; in other words, the acid, while extractable, is not free at 0°C.



Variation of Ash Content of Aluminum Laurate During Extraction Dry, Neutral Acetone.

Figure 20

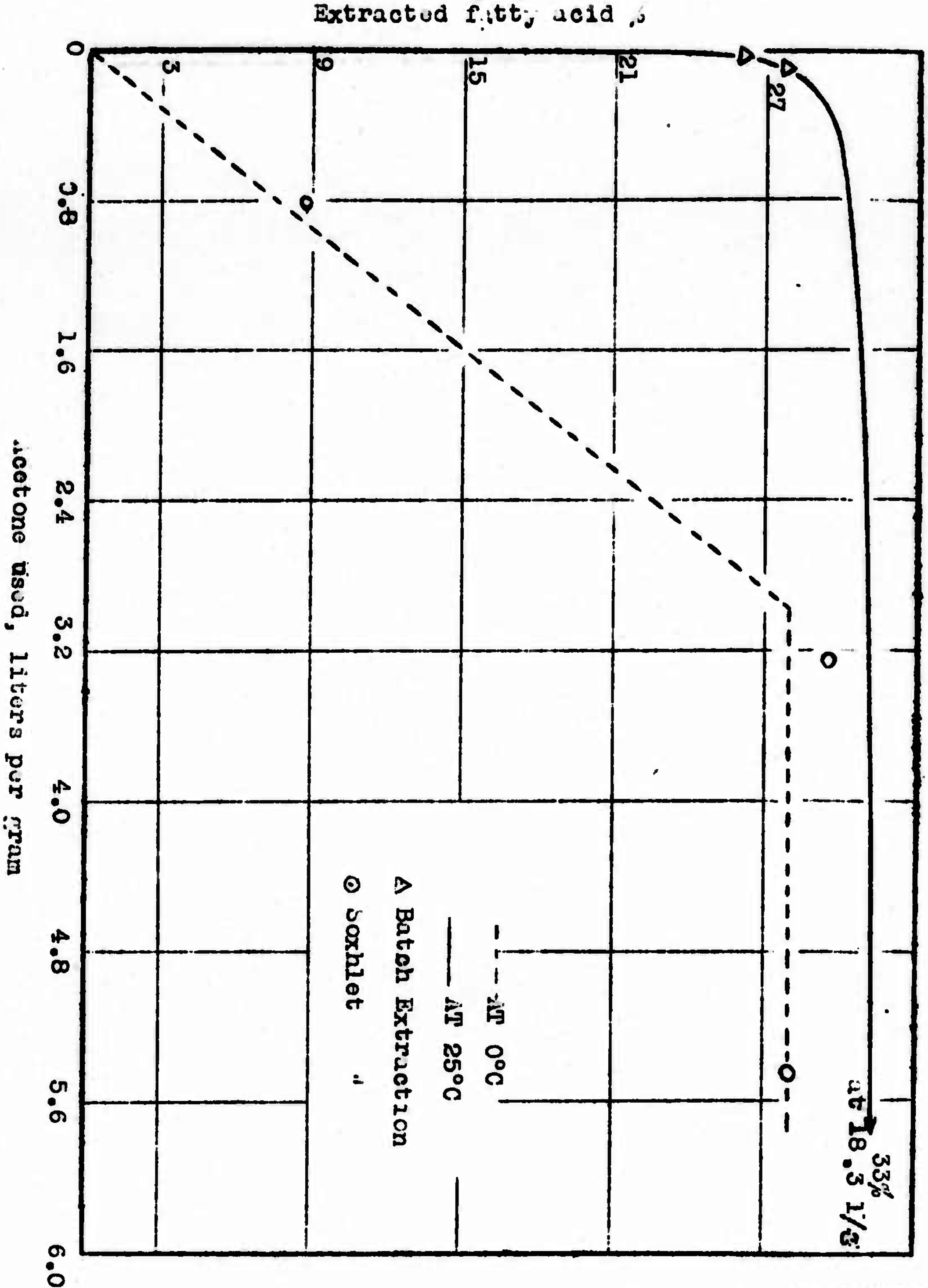


Figure 21
Extraction of fatty acid from Aluminum laurate using dried acetone.

Within experimental error the extraction at 0°C proceeds at the steady rate quoted above. Therefore the lauric acid is not held in the form of solid solution which would give a constantly decreasing rate. Hence we infer the formula $Al(OH)L_2.HL$. The X-ray diffraction pattern of the acid soap is shown in Figure 22. It differs both from lauric acid and aluminum dilaurate.

It is extremely unlikely that aluminum trilaurate, AlL_3, would rapidly yield dilaurate with dry acetone at room temperature, in the absence of compounds such as water or alcohol. (A reaction with formation of lauric anhydride and aluminum dilaurate anhydride could however be conceived.) This is further confirmed by a slow but prolonged loss of weight, extending to at least 9% by this soap over P_2O_5, and somewhat faster loss over CaO in vacuo.

The main weakness of this argument with the acid dilaurate was that it drew thermodynamic conclusions from a kinetic experiment. Since then efforts have been made to determine by equilibrium measurements the solubility of lauric acid in the acid soap, but no conclusive results could be obtained owing to experimental difficulties and the very high solubility of lauric acid.

It was then decided to study the stearate in order to encounter more favorable conditions owing to the much lower solubility of stearic acid in acetone.

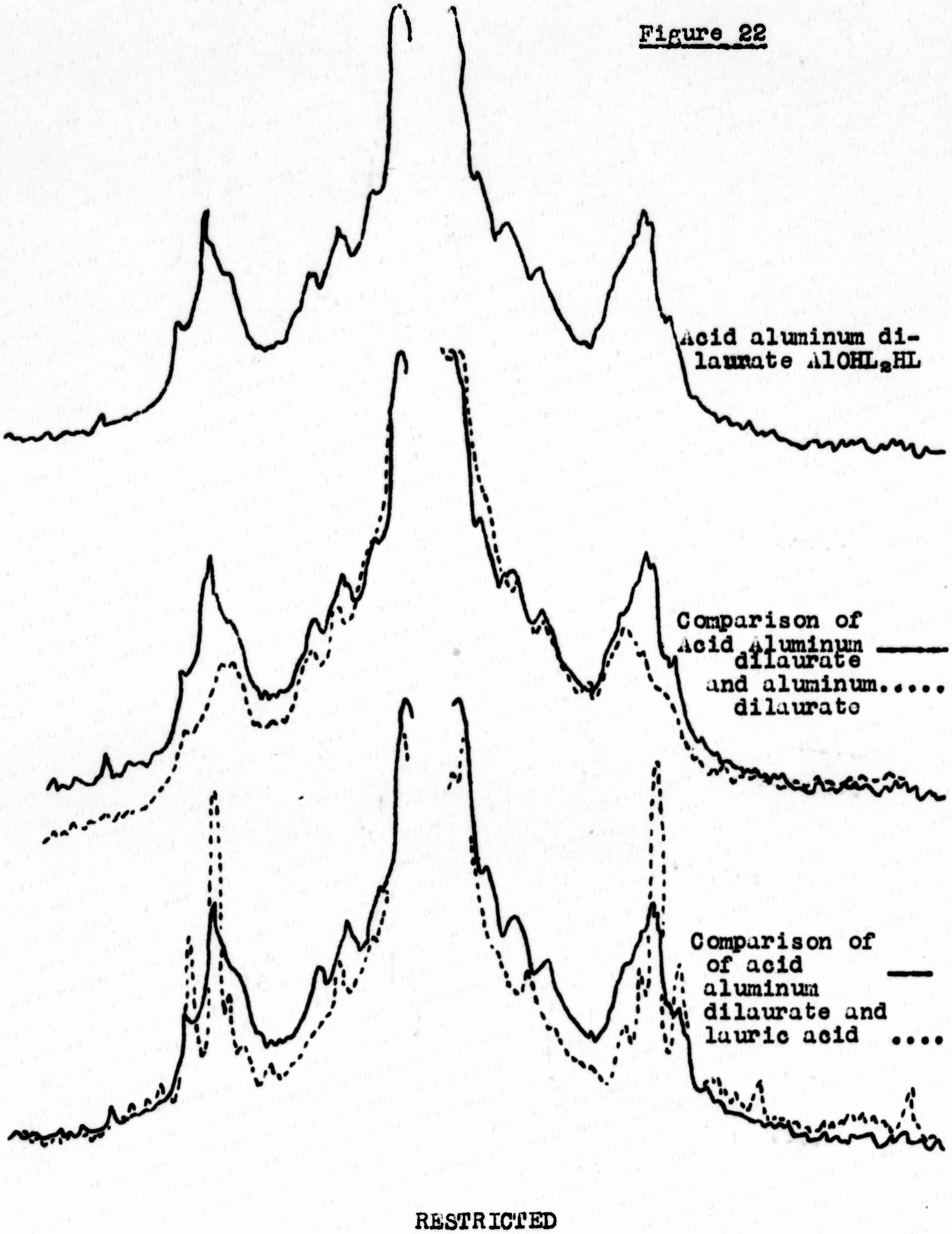
The sample studied was "aluminum stearate" as obtained by precipitation of an excess of 3.70% aluminum chloride solution with a 3.85% potassium stearate solution at 60°C, washing the precipitate until free from chloride, and drying. It had an ash of 5.50%.

After Soxhlet extraction with 1200 cc. of boiling acetone per

MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS

Magnification 2x. Sample to plate distance 50 mm.

Figure 22



gram of soap the ash was increased to 9.55%. Extrapolation back to zero acetone volume (to correct for residual hydrolysis during this extraction) gave an ash of 9.45%. In other words, 41.2% of the original product is extractable with boiling acetone.

The solubility of stearic acid in acetone at 21.5°C is about 9.0 grams per liter. It is clear that if a small volume of acetone is exposed to a product containing stearic acid in the free condition, this will dissolve until the concentration of the acetone solution corresponds to an extraction of 9 grams per liter. Proof that stearic acid is not free is obtained in the following series of experiments in which acetone is shown to extract only a small fraction of this amount per liter.

> Varied amounts of dried soap were placed in stoppered mixing cylinders with 25 cc. of dried acetone each and shaken slowly for 18 hours at 21.5°C in an air thermostat. Ten cc. of acetone was then withdrawn through a cotton plug and the concentration of acid in it determined by titration as described on pages 5 and 6 of our March report. The total amount of acid dissolved was calculated therefrom and expressed in terms of percent ash content of the undissolved residue.

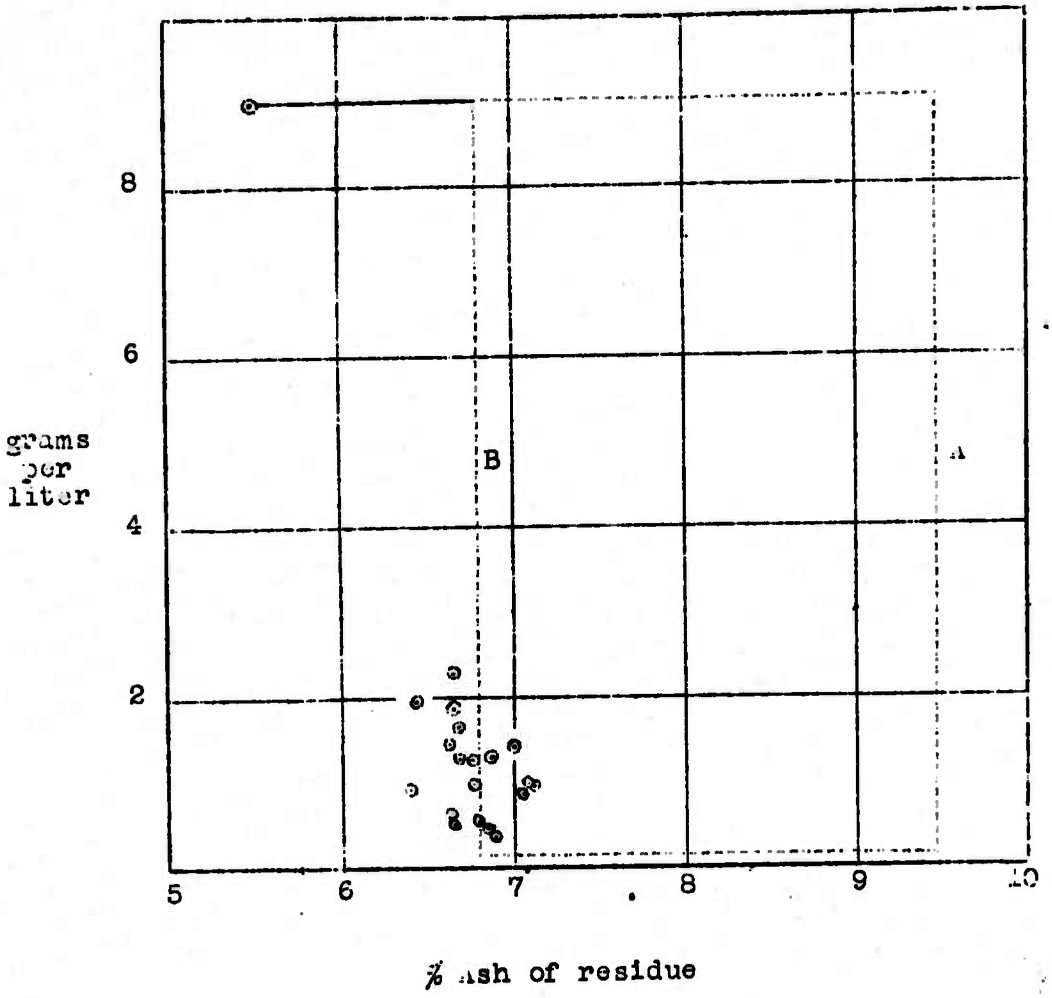
Figure 23 shows the results. It is a plot of concentrations of stearic acid in the acetone as a function of the composition of undissolved soap.

It proves that a large proportion of the acid extracted with boiling acetone is almost insoluble in acetone at low temperatures, and that it is definitely bound. If the acid extractable with

Figure 23

Solubility, in Acetone at 21.5°C, of Stearic Acid from a Sample of "Aluminum Stearate" as a Function of the Percent Ash of the Extracted Residue.

A Expected solubility if the acid was free.
B Expected solubility if an acid soap was present.



boiling acetone were all free the expected solubility curve would be as indicated by the dotted line A. This is obviously excluded by the experimental data.

From a soap having an ash content above about 6.9% the acid dissolves to less than 0.3 grams per liter.

The existence of this bound acid, which is nevertheless readily extractable with boiling acetone, points to the existence of an acid soap.

On the other hand, some of the acid is much freer, and from a soap of ash content below about 6.5% dissolves to the extent of at least 2.3 grams per liter. This result suggests that the "bound" acid is bound in equimolecular proportion by the distearate, as would correspond to the formula $Al(OH)St_2.HSt$.

We have shown previously the existence of aluminum mono- and di-soaps. The soap obtained by extraction with boiling acetone may be expected to be a mixture of these two types only, and from its ash content the composition 13.5% $Al(OH)_2St$ + 86.5% $Al(OH)St_2$ is deduced.

If one molecule of stearic acid is bound to one of distearate and the remainder of the stearic acid contained in the original soap (of 5.5% ash) is free, the expected solubility curve would be as indicated by the dotted line B of the figure. It may be seen that the experimental points are in agreement with this hypothesis.

The compositions indicated by this interpretation are tabulated in the following Table II.

Table 11

Composition of Aluminum Stearate precipitate, made at 60°C before and after extractions with acetone.

	Mols	Parts by wt.	%
Original soap.			
Free stearic acid HSt	0.848	240.0	19.2
Acid distearate $Al(OH)St_2.HSt$	1.00	891.1	71.3
Distearate $Al(OH)St_2$	0	0	0
Monostearate $Al(OH)_2St$	0.350	120.0	9.6
Total	2.198	1251.0	100.0
Ash Al_2O_3	0.675	68.8	5.50
Soap freed from free acid.			
Free stearic acid HSt	0	0	0
Acid distearate $Al(OH)St_2.HSt$	1.00	891.1	88.2
Distearate $Al(OH)St_2$	0	0	0
Monostearate $Al(OH)_2St$	0.350	120.0	11.8
Total	1.350	1011.1	100.00
Ash Al_2O_3	0.675	68.8	6.81
Soap freed from free and loosely held acid.			
Free stearic acid HSt	0	0	0
Acid distearate $Al(OH)St_2.HSt$	0	0	0
Distearate $Al(OH)St_2$	1	608.0	83.5
Monostearate $Al(OH)_2St$	0.350	120.0	16.5
Total	1.350	728.0	100.0
Ash Al_2O_3	0.675	68.8	9.45

Aluminum monolaruate $Al(OH)_2L$.

Preparation of this soap involved many experimental difficulties due to the frequent formation of unfilterable gummy precipitates, extremely small particle size and difficulties of extraction. The following method was finally used:

An excess of methyl alcoholic ammonia was rapidly added to a boiling solution containing 3.3% of lauric acid and an equimolecular amount of $Al(NO_3)_3$. Slow addition of ammonia resulted always in a gummy precipitate. The soap was washed thoroughly with boiling methyl alcohol containing a small amount of lauric acid, to eliminate ammonium nitrate, then with acetone to eliminate free or loosely bound fatty acids. The resulting product, after drying over concentrated H_2SO_4, in vacuo, had an ash content of 20.0% (theoretical for $Al(OH)_2L$ = 19.6% for $Al_2(OH)_2OL_2$ = 20.3%). Other samples of monolaurate had ash contents varying between 19 and 21%.

It seems that the formulas $Al(OH)_2L$ or $Al_2(OH)_2OL_2$ are preferable to AlOL because the latter could be formed from the dilaurate Al OH L_2 without hydrolysis. We know, however, that the presence of traces of moisture promotes this reaction greatly so that hydrolysis must be involved.

The monolaurate too is a fine white powder. It decomposed without melting when heated in a sealed tube at about 260°C, was insoluble in acetone, alcohol, cyclohexane, toluene and Nujol, but swelled readily and dissolved to a clear solution in some mixed solvents such as ether-lauric acid, alcohol-benzene, phenol-benzene and morpholine-benzene.

The original product gave a very diffuse X-ray diffraction pattern consisting of two very diffuse rings (Fig. 24). This was due probably to the extremely small size of ultimate particles. The particle size could be increased, however, and a correspondingly sharper diffraction pattern was obtained (Fig. 22) by storing the product for several weeks under methyl alcohol at 90°C. Figures 16 and 24 show that the X-ray pattern of samples of aluminum laurate whose composition approaches $Al(OH)_2L$ is distinct from both that of the dilaurate and from all known forms of alumina.

Aluminum dicyclohexane carboxylate $Al(OH)\ (C_6H_{11}COO)_2$.

Twenty-five cc. of a 6% solution of potassium cyclohexane carboxylate (prepared from CO_2 free KOH and Eastman Kodak acid) was added under very strong agitation to 400 cc. of a 6% solution of $AlCl_3.6H_2O$ (reagent) at room temperature. The white precipitate was washed with cold boiled-out distilled water till free from chloride.

Cyclohexane carboxylic acid differs from fatty acid by being somewhat soluble in water, as are some lower napthenic acids. Washing of the precipitate with water to remove soluble salts removes therefore also a large part of the free or loosely bound acid.

The water washed precipitate was dried over P_2O_5 and had an ash of 15.1%, corresponding to about 2.4 $(C_6H_{11}COO)$ per 1 $Al(OH)_3$. It was washed twice with 100 cc. of dry acetone per 5 g. of soap, allowing 1 hr. of contact for each washing. The product, dried over P_2O_5, had an ash content of 16.95%, compared with 17.09%

calculated for $AlOH(C_6H_{11}COO)_2$. This extracted soap was a fine white powder having a very faint odor as opposed to the strong and extremely unpleasant odor of the free acid or unextracted soap. At room temperature it was insoluble and apparently inert in water, acetone, ethyl alcohol, and ethyl ether. It showed a slight tendency to swelling and gel formation in n-amyl alcohol, di-isobutylene, cyclohexane, specification gasoline and dioxane. It swelled to a limited extent, giving a gel, not jelly, in carbon tetrachloride and a jelly plus excess liquid in toluene.

This soap has a remarkable thermal stability, and showed no decomposition at about 450°C.

The X-ray diffraction pattern of the product was included in Figure 24.

MICROPHOTOMETER TRACINGS OF X-RAY DIFFRACTION PATTERNS

Magnification 2x
Sample to plate distance 50 mm.

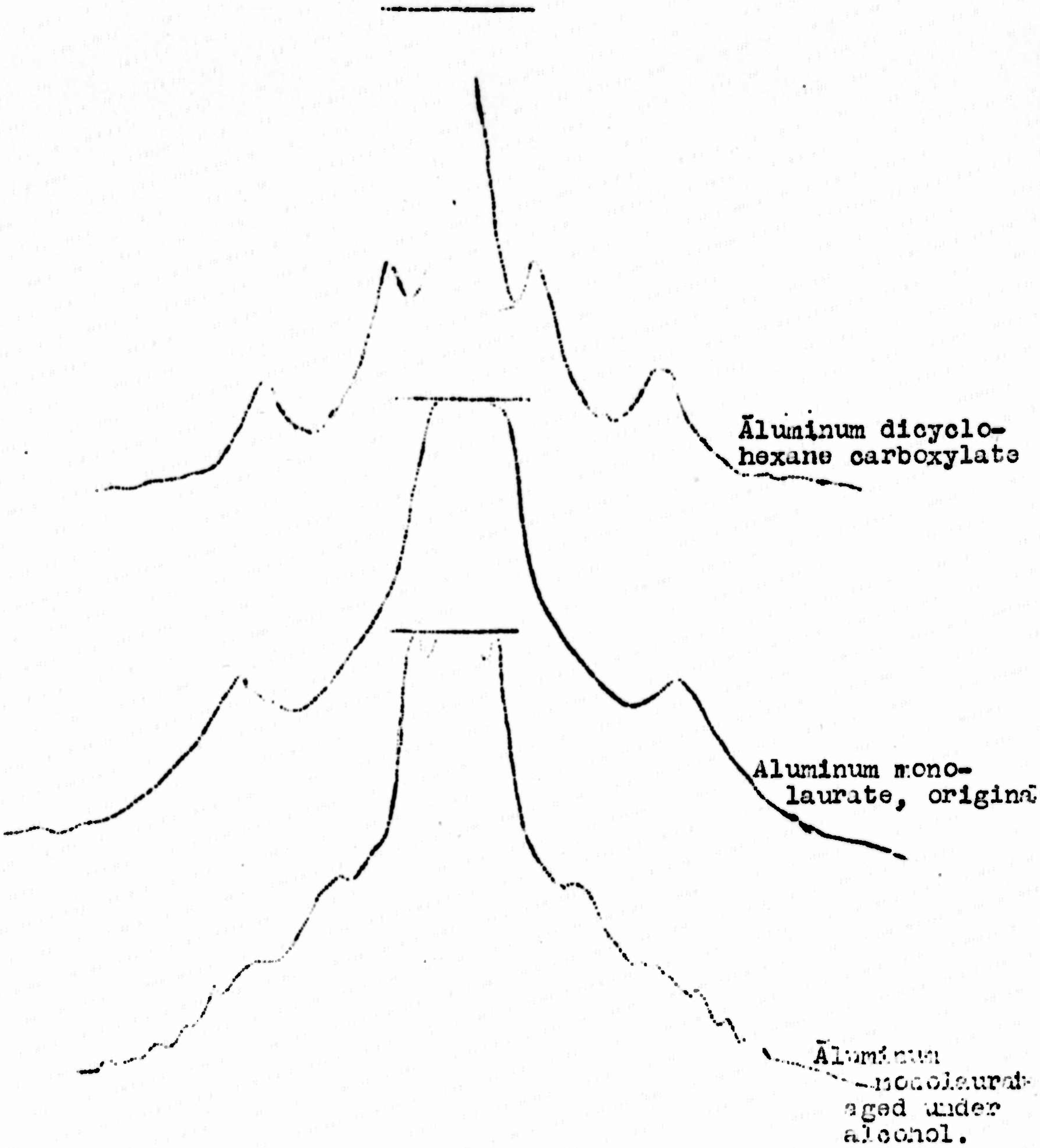


Figure 24

CHAPTER II

ALUMINUM SOAPS AND WATER

Water is always present in Napalm and may have a decisive influence upon the quality of its gels. The problem of its determination in the soap, of its pick-up by the soap and its influence upon the gel has been therefore studied by almost all who have worked on the subject, and the results have been repeatedly reviewed in detail and are available for example in O.S.R.D. reports 2036 and 2036a, "The Manufacture, Properties, and Testing of Napalm Soaps by A. C. Broughton and A. Byfield Nov. 17, 1943 and March 7, 1944.

Our main contribution to this problem has been based upon the use of the McBain-Bakr Sorption balance (Jour. Amer. Chem. Soc. 48, 690, 1926). Using it, it is possible to expose Napalms and pure aluminum soaps of any desired pre-history and at any specified temperature or a series of temperatures to water vapor of various degrees of saturation, i. e., relative humidity (actual pressure of water vapor divided by the vapor pressure of pure water at the temperature of the soap); and these measurements may be repeated as often as desired and over any period of time without unsealing the sorption tube.

Such a study determines how readily or otherwise water is given off by soap; whether the dehydration is reversible in whole or in part, thus distinguishing between various forms of free sorbed or bound water; it determines the rates as well as the equilibrium of evolution and sorption of water.

Such study also leads to a decision as to the correct point of departure or reference point corresponding to "dry" soap.

The sorption balance consists of a large vertical sealed glass tube. In its upper end is placed a calibrated fused silica spring whose lower end supports a small platinum bucket containing the soap. The weight of the contents, soap and sorbed cyclohexane is determined by the elongation of the spring which is measured very accurately by a traveling microscope.

The lower end of the sealed tube contains the liquid whose sorption is studied. The tube is thoroughly evacuated before sealing so that it contains only the soap and the liquid.

The temperature of the two ends of the sealed tube is controlled independently. The temperature of the upper end determines the temperature at which sorption takes place. The pressure at which the vapor of the liquid is present in the tube is determined by the temperature of the lower end containing the liquid. Thus by maintaining the temperature of the upper end constant and varying that of the lower end the amount sorbed by the soap at a given temperature at varying pressures of the vapor is determined

A. The Existence and Preparation of Dry Aluminum Soap.

A dry soap, or a soap of definitely defined moisture content must be obtained before its constitution and the ways in which it can hold water may be settled. Then its possession also eliminates numberless difficulties in the study of its non-aqueous systems.

(a) Anhydrous aluminum dilaurate $AlOH.L_2$. There is a great difference between Napalm and aluminum dilaurate.

Napalm loses weight slowly when dried intensively until an ill-defined equilibrium is reached depending upon the temperature of the soap and the relative humidity.

Aluminum dilaurate under these conditions reaches rapidly (a matter of minutes in vacuo) a weight which is not very sensitive to low relative humidities (i.e. below 5%) and is independent of temperature of the soap in the range of 25-60°C and probably higher as shown by equilibrium measurements with the sorption balance (p. 72) and by drying at room temperature in vacuum desiccators over P_2O_5 and CaO.

The dehydrating conditions under which the weight remained unchanged were very drastic: vacuum over P_2O_5 at room temperature in a desiccator and relative humidity of $6x10^{-4}\%$ at 50°C for 85 hours in the sorption balance (soap at +50°C exposed to water at -78°C) so that the presence of a hydrate stable under these conditions is extremely unlikely. (Note, added subsequently:- Analysis of the dry soap for laurate radical precludes the presence of more than 0.25 H_2O.).

Oven drying at 100°C of aluminum dilaurate leads to a rapid although small loss of weight (within less than a day), followed by a constant weight up to 3 days and then a rapid drop of the order of 3% per day. This constant weight corresponds to the same dry soap $AlOH.L_2$; while the ensuing rapid drop is accompanied by obvious decomposition with sintering and then darkening of the soap. Similar decomposition occurs in the sorption balance at 100°C; products of decomposition such as lauryl ketone or hydrocarbon then appear upon the walls of the sealed glass tube.

Thus anhydrous aluminum dilaurate $AlOH.L_2$ may be prepared by any of these methods, provided that decomposition is avoided. We have prepared most of our samples by evacuation with a "Hyvac" pump for 1/2 - 3 hours at room temperature.

Due to the extreme avidity of the soap for hydrocarbon vapor, greasing of stopcocks and joints must be avoided or done with products of very low vapor pressure such as "Apiezon".

Napalm behaves quite differently, and its true anhydrous condition is ill-defined. For the sorption measurements, it is therefore necessary to choose an arbitrary zero point. The Napalms as received were obviously too variable. Hence an equilibrium under specified conditions had to be chosen. In order to avoid negative numbers as far as possible we selected the most drastic dehydrating conditions encountered in our experiments i.e. soap at 50°C exposed to water at dry ice-cellosolve (-78°C), yielding a relative humidity of 6×10^{-4}%. We think that degradation decomposition of the soap under these conditions is negligible although a tiny oily film was observed in the cold part of the tube.

This treatment of the soap is probably more drastic than vacuum oven drying at 10 mm. Hg so that our % moisture values appear larger by 1 1/2 - 3% than those reported on the basis of oven drying. However, differences between any two equilibrium values for two relative humidities are of the same order as those obtained when vacuum oven drying is employed.

B. The Sorption of Water Vapor by Aluminum Soaps.

In our first determinations of the sorption isotherms of water by aluminum soaps, the temperature of 50°C was chosen for experimental convenience. Experiments at 25°C were then put in hand. The behavior of Napalms is not the same at 50°C as at 25°C.

(a) Pure aluminum dilaurate $AlOH\ L_2$. The isotherm obtained at 50°C for this soap is shown in figure 25. It was obtained by placing the soap as prepared in the bucket, while the lower end of the tube containing water was in a mixture of dry ice and cellosolve. The tube was then evacuated rapidly, during which time the soap lost 0.63% of weight, and the tube was then sealed. This loss of weight was completed within two or three minutes. The weight of the soap remained unchanged from then on when kept at room temperature over water at dry ice temperature (vapor pressure 0.0006 mm. Hg) for 5 days.

Thus a constant dry weight of the soap was obtained. This same weight was restored after the isotherm at 50°C had been run during 23 days; and it persisted at 60°C (with water still at dry ice temperature) for 2 days. At 87°C, however, it lost 0.7% in 2 hours. Finally, at 100°C rapid decomposition took place, the sample losing 14.2% by weight in 4 days.

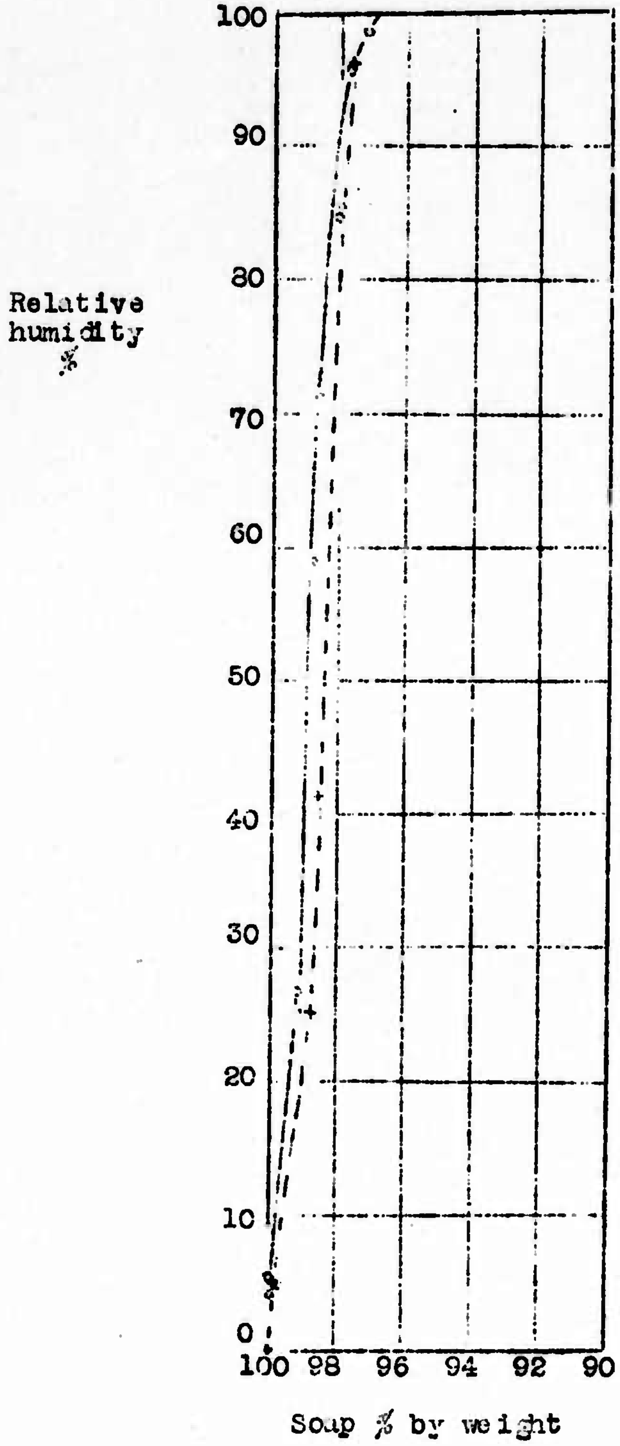


Figure 25

Sorption of Water by Aluminum Dilaurate at 50°C.

The 50°C isotherm shown in figure 25 was determined by raising the temperature of the lower end of the tube containing water in successive steps until it reached the same temperature as the soap, giving 100% relative humidity; then it was again lowered stepwise to the temperature of dry ice, -78°C.

At each step the conditions were maintained constant until the weight of the soap did not further change; 24 hours were always ample, probably much more than ample.

Aluminum dilaurate takes up practically no water in an atmosphere up to 5 or 10% relative humidity but between 25 and 95% relative humidity it takes up to between 1 and 2% of water. Hence for intermediate relative humidities the isotherm is almost vertical, the composition varying but little.

(b) Napalms. In contradistinction to pure dilaurate, Napalm does not reach a constant weight independent of temperature as shown by an exploratory experiment on dehydration and rehydration of a sample of Napalm (Imperial NR232) under special conditions. The sample was introduced into a McBain-Bakr sorption balance, the tube evacuated rapidly, and sealed off without adding any liquid. Thus the only moisture available to the soap was that contained in the Napalm itself at the moment of sealing. Then the maximum water vapor pressure, and the temperature of the soap were regulated independently. The following table gives the sequence of operations, together with the relative humidity when known, and the weight of soap at each stage in percentage of the initial weight of soap as received and used.

This shows that at room temperature Napalm lost but 1.9% of weight under extremely severe dehydrating conditions (relative

Table III

Procedure	Temp. of soap	Temp. of bottom	Wt. of soap	Relative Humidity %	H_2O vapor pressure mm. Hg
Soap placed in bucket	Room	Room	"100"	---	---
After 2 minutes of evacuation. Tube then sealed permanently.	"	"	99.47	<5%	<1
One hour later	"	"	99.47	---	---
Two minutes after plunging into dry ice	"	-78°C	99.31	0.002%	0.00[illegible]
3 1/2 hours later	"		98.10	"	"
Bottom brought back to room temperature and left overnight	"	Room	99.28	---	---
2 hours after raising temperature of soap to 50°C	50°C	"	99.07	<25%	<20%
Soap cooled slowly and left overnight at room temperature	Room	"	99.38	---	---
Bottom cooled to 0° for 24 hours	"	0°C	98.82	20%	4.58
Same for five more hours	"	"	98.69	"	"
Soap heated to 50°C for 2 hours	50°C	"	98.04	5	"
Same for 17 more hrs.	48°C	"	96.76	"	"
Same for 3 more hours	"	"	96.61	"	"
Soap and bottom at room temperature for 2 1/2 days	Room	Room	99.41	---	---

humidity about 0.002% for 3 1/2 hours), while at 50°C it lost 1.9% in two hours, and as much as 3.4% in one day, under very much milder dehydrating conditions (5% relative humidity). Furthermore, the losses were both reversible, the soap reabsorbing all when the initial conditions are restored.

In further contradistinction to aluminum dilaurate, Napalms are very sensitive to low pressures of water vapor, their weight changing rapidly at relative humidities below about 5% as may be seen for example from isotherms of two Napalms at 50°C shown in figures 26 and 27.

To obtain these isotherms the samples were used as received. The tube was evacuated with water in the lower end at 0°C giving 4.6 mm. pressure, the soap being maintained at room temperature. Then the temperature of the soap was raised to 50°C and the sorption run started by gradually raising the temperature of the water. After saturation pressure was reached a desorption run followed, the temperature of the water being gradually lowered to that of dry ice (-78°C). The weight of Napalm under these final conditions was taken as that of dry soap.

(c) Direct results from the sorption isotherm.

i Aluminum dilaurate in contradistinction to Napalm may be prepared readily in a well defined dry condition completel invariable over a wide range of temperatures, and practically invariable over a narrow but appreciable range of low relative humidities. It sorbs only 1 or 2% of water between 25% and 95% relative humidity. It requires only a few minutes to establish equilibrium on drastic desorption.

ii The amount of water sorbed by Napalm is still fairly small in absolute numbers, reaching less than 10% at

Figure 26

Sorption of Water by Napalm Imperial NR 232 at 50°C.

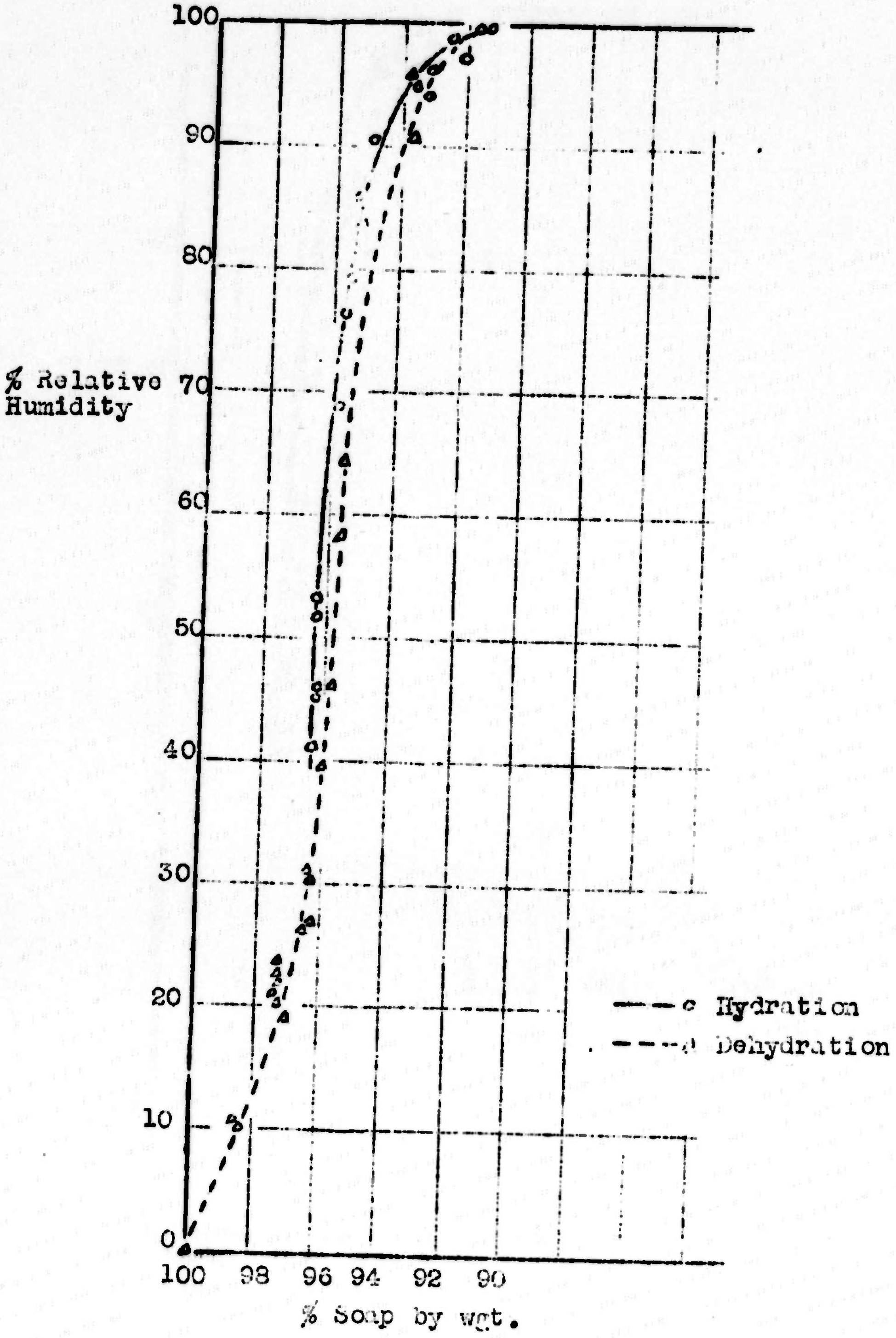
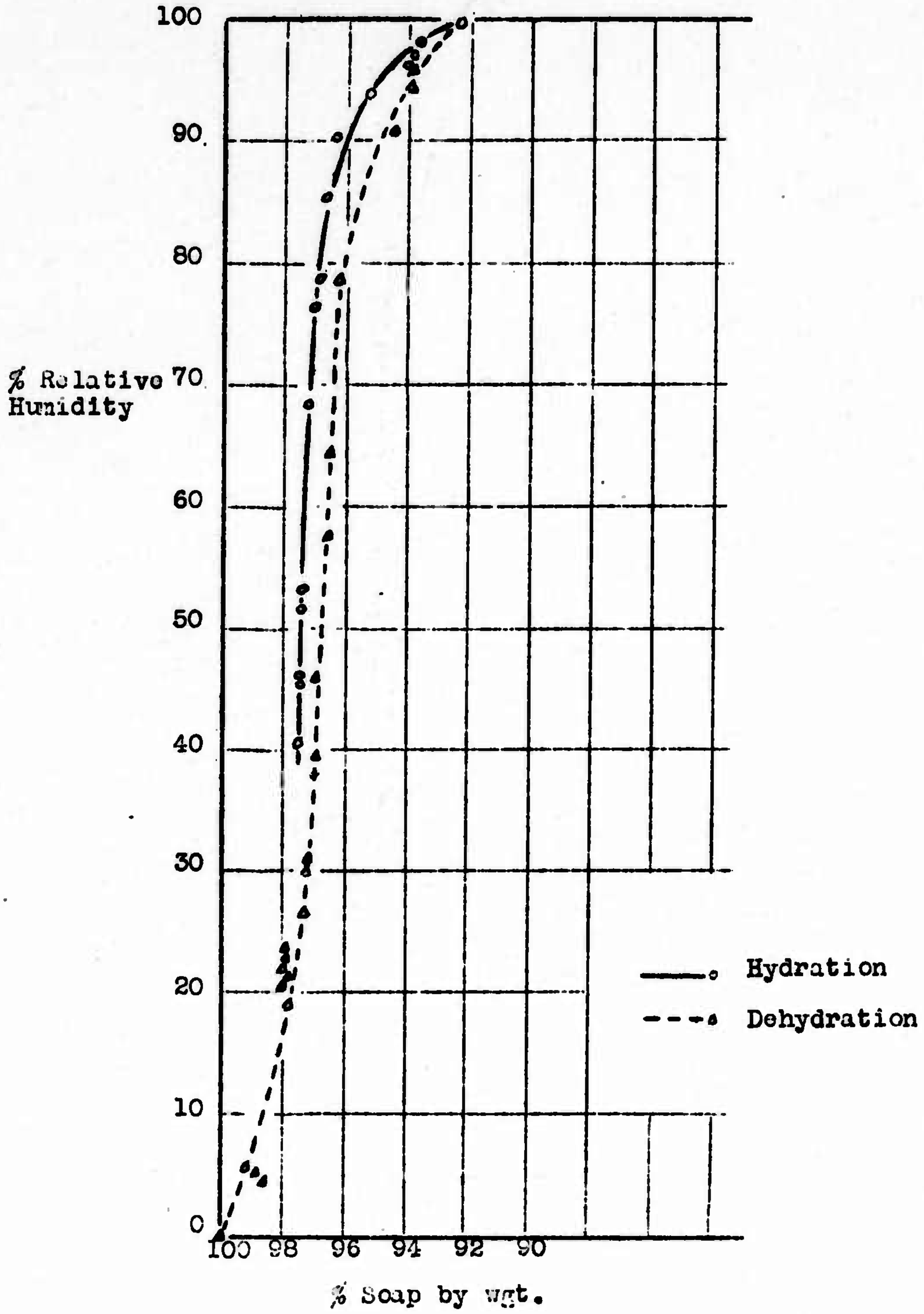


Figure 27

Sorption of Water by Napalm Imperial NR 232 at 50°C.



saturation. This is however very large when considered from the point of view of the effect on gel strength where 1% is deleterious.

iii The isotherms are almost vertical (constant composition) between 30% and 70% relative humidity. This confirms that little advantage is gained by reducing the humidity of the atmosphere in which Napalm is handled within the range of 30 to 70%. It is only a drastic reduction to 20% or less that is effective. However, if the handling is quick any reduction of pressure is helpful in hindering uptake of water. Humidities above 70% are very dangerous if maintained for an appreciable time.

iv The fact that Napalms of different manufacture vary by about 1% in their capacity for taking up water is confirmed.

v Napalms sorb more water than pure aluminum dilaurate. This finding however rests upon the zero point chosen for the latter. The different Napalms definitely differ in their moisture uptake. The change in amount of water taken up with changing humidity is also different for different Napalms, as is shown by lack of parallelism of the respective isotherms.

vi There are no horizontal flats in the curves, or inflection points which would indicate formation of definite compounds or hydrates or different phases of Napalm under these conditions.

(c) Hysteresis.

i Isothermal hysteresis. The isotherms show that there is some hysteresis, the desorption run showing always a slightly greater moisture content at a given relative humidity. The difference is small but significant in the middle of the range, but is more marked at high relative humidities. The dilaurate shows much less of this effect than the Napalms.

Such behavior is often met with, especially among porous or powdered solids. It indicates that when the driving force is small i.e. when the soap is near equilibrium, small passive resistances within the system have a detectable effect preventing the establishment of true reversible equilibrium. No definitive explanation of such hysteresis has yet been agreed upon by various authorities.

ii Thermal hysteresis. Due to a mishap the temperature of the Napalm was raised to 77°C in the middle of the 50°C run while the water vapor pressure was maintained at 42.4 mm. As soon as possible, the soaps were brought back to the original temperature of 50°C.

The amount of water sorbed at 50°C at a relative humidity of 45.8% was markedly greater before the accidental elevation of temperature than afterwards. The following Table IV gives the amount of water sorbed at equilibrium before and after the heating. It confirms that previously heated Napalm has less affinity for water.

A sample of aluminum dilaurate which was subjected simultaneously to the same treatment showed of course no appreciable change in the affinity for water.

Table IV

Per cent of water sorbed by four different Napalms at 50°C, before and after accidental heating to 77°C, the pressure of the water vapor being 42.1 mm. Hg throughout.

Napalms	Before	After
Imperial Lot NR232	2.6%	1.9%
Harmon No. R 11285	1.6%	0.6%
Ferro Enamel Lot P, Batch 184	1.5%	0.9%
Pfister Chemical Co., No. N-3-2 432-94	3.8%	3.3%

C. Forms in which Water is Held by Aluminum Soaps.

Water might be held by aluminum soaps in the following forms:

(a) Free water possessing substantially the vapor pressure of water itself e.g. water occluded and condensed in larger capillaries.

(b) Bound water present in the form of water molecules, but having appreciably reduced vapor pressure, held either by surface forces; e.g. sorbed on the surface or condensed on the finest capillaries, or as part of the crystal structure e.g. as a true hydrate.

(c) Potential water which may be formed under the experimental conditions out of H and OH groups present; e.g. by reaction between hydroxyls of alumina and fatty acids or by reaction of two hydroxyls to form oxygen.

(a) Effect of impurities. Moisture might be held in any of these forms by either the soap or soaps or by the inorganic impurities now known to be present.

The moisture held by the inorganic impurities cannot be neglected *a priori*. According to the analysis of Harshaw of Napalms from ten manufacturers the contents of sodium sulfate (as anhydrous Na_2SO_4) varies between 0.18 and 0.74%; and the content of $Al_2(SO_4)_3$ have 0.33 to 2.95%. This latter content is *calculated* from the excess of sulfate over sodium. We have found that water insoluble basic salts or alumina are present (p.93-4) so that Harshaw's figures for inorganic impurities are certainly conservative.

Sodium sulfate as well as aluminum sulfate and alumina are all capable of forming hydrates with many molecules of water, and as shown by Table V may under certain conditions fix about 100% of their own weight of water. The hydration of pulverulant basic salts is not well known but presumably is similar, in addition to effects of sorbed water.

Table V

Water content of hydrates of the seven mineral impurities in Napalm

Anhydrous form	Hydrated form	% increase in weight
$Al_2(SO_4)_3$	Alunogenite $Al_2(SO_4)_3$ $18H_2O$	94.8%
Al_2O_3	Gibbsite $Al_2O_3 \cdot 3H_2O$	55.0%
Na_2SO_4	Glauber's salt $Na_2SO_4 \cdot 10H_2O$	126.5%

Thus the amount of water held by the impurities of Napalm may be of the order of from one to three percent of the weight of the Napalm, which is of the same order of magnitude as the moisture usually determined. This introduces an important complication which is absent in the case of pure soaps. The question whether the impurities actually do act in this way in Napalm remains to be answered.

(b) Free water. This is probably eliminated in the drying process during manufacture and no free water should be restored unless the soap is exposed to water or a saturated atmosphere. Thus it is of minor practical and theoretical interest.

(c) Bound water. The sorption isotherm of aluminum dilaurate shows that aluminum soap can take up small amounts of moisture having appreciable but reduced vapor pressure. The rapidity with which this water is given off under drastic dehydrating conditions shows that this moisture remains in the form of water molecules.

Sodium and calcium soaps are known to form hydrates, but the smoothness of the sorption isotherm of aluminum dilaurate indicates that aluminum soaps do not form them. Therefore the moisture bound by these soaps may be considered as sorbed.

(d) Potential water. The two obvious sources of potential water are:

Reaction between fatty acid and hydroxyl groups such as:

i Alumina $Al(OH)_3 + HR \longrightarrow Al(OH)_2R + H_2O$

ii Monosoaps $Al(OH)_2R + HR \longrightarrow Al(OH)R_2 + H_2O$.

iii Discoaps $Al(OH)R_2 + HR \longrightarrow AlR_3 + H_2O$

Reaction between two hydroxyls forming an oxygen

iv Within a molecule

$$Al(OH)_2R \longrightarrow AlOR + H_2O$$

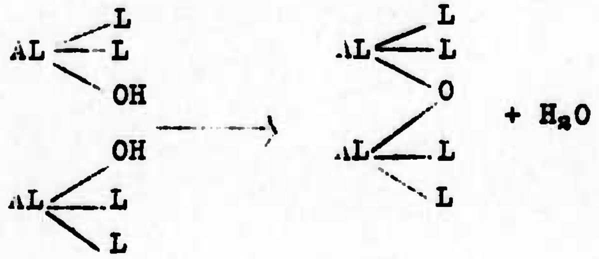
v Between two molecules e.g.

$$2Al(OH)R_2 \longrightarrow Al_2OR_4 + H_2O$$

Reaction between hydroxyls. Preparation of soaps free from uncombined fatty acids provides a tool for distinguishing between these two sources of potential water.

Pure aluminum dilaurate $Al(OH)L_2$ cannot undergo any of the reaction i to iii because of the absence of uncombined acid. Reaction of the type iv is also impossible since there is only one hydroxyl group per aluminum atom.

Thus interatomic dehydration of type v is the only one possible leading to an "anhydride" of aluminum dilaurate.



The weight of water formed in this reaction could be 2.03% of the dilaurate.

In case of our sorption or drying experiment we have never observed anything suggesting such a reaction. However, it appears that the hydroxyls can react in this way during the Karl Fisher water determination.

<u>Reaction between fatty acid and hydroxyl.</u> The only reaction between hydroxyl groups and fatty acids with regard to which we have definite information is type ii, the reaction involving mono soap. It seems to occur at temperatures of the order of those used in water determinations and gel testing and storage. This reaction has been discussed on p. 11, and in Harshaw's sixth monthly report etc. and is being studied further.

We have found no indication of reaction type iii between disoap and fatty acid but it is quite possible that it occurs under drastic conditions.

The reation type i between alumina and fatty acid is suggested in the literature (Craig British Patent 338,919 May 21, 1929) to explain the solution of freshly precipitated alumina in fatty acids. There seems to be no direct evidence that the fatty acids combine with colloidal alumina (as opposed to a peptization thereof) but it is quite possible that it occurs.

(e) The significance of various methods of determining moisture. In view of the above discussion it appears that the determination of moisture in Napalm includes water held as such by the soap and that held by the inorganic impurities.

Drying in vacuum or over desiccants at temperatures at which the soap is stable determines all the sorbed water; but at higher temperatures water of reaction between fatty acids and monosoap may possibly be included. Drying in vacuum does not determine water of reaction between hydroxyls. The Karl Fisher method determines the latter, presumably in addition to all the other above forms of moisture.

The Karl Fisher moisture determination method was applied to a sample of aluminum dilaurate through the kindness of a Shell Development Company. This sample was prepared and dried by evacuation at room temperature for one hour at Stanford University and forwarded in a sealed tube to the Shell Development Company at Emeryville. The result was 2.5± .4% moisture corresponding to 0.62 ± 0.11 moles of water per mol of $Al(OH)L_2$.

The only apparent source of such a large amount of moisture in aluminum dilaurate lies in the interaction of the hydroxyl groups with formation of the anhydride, and the amount which may be thus formed (2.03%) corresponds within experimental error to that found. A fraction of a percent of moisture may however have stemmed from other sources such as adsorption.

This study of the pure soap shows therefore that potential water stemming from interatomic reaction of hydroxyl groups does not form during vacuum dehydration at temperatures at which the soap is otherwise stable but forms during the Fisher determination

It is very unlikely that it could form or act as water in an aluminum soap gel, especially since aluminum dilaurate $Al\ OH.L_2$ may be recovered unchanged from hydrocarbon systems.

CHAPTER III

THE SYSTEM ALUMINUM SOAP-HYDROCARBONS.

(1) Introduction.

When an aluminum soap is introduced into a hydrocarbon it may show a variety of behaviors depending on its nature, the hydrocarbon, the temperature and often the presence of traces of foreign substances. In all cases of record it is readily wetted but it may be practically inert or may swell or dissolve, it may form a homogeneous mass or stable layers of different properties. The system may be clear or turbid, stringy or crumby, and after heating may return to substantially the same state or to a quite different one.

In order to clarify this picture, we used a well defined pure hydrocarbon: cyclohexane, and a pure soap: aluminum dilaurate. Additional variables could then be introduced one at a time and the concepts developed on these simple systems, tested on systems containing Napalm and gasoline.

The main subjects investigated were:

Definition and differentiation of the various forms and phases of the aluminum soap-hydrocarbon system.

Transition between these forms.

Their thermodynamic stability.

Their phase diagram.

Their structure, and comparison of aluminum with sodium and calcium soaps.

The effect of peptizers.

Our main tools in this aspect were direct observation of mixtures in sealed tubes or weighing bottles, the McBain-Bakr sorption balance, osmometry and viscometry.

(2) Definition and Differentiation of the Various Forms of the Aluminum Soap Hydrocarbon System.

(A) Aluminum dilaurate-cyclohexane.

(a) Introduction. A small sample(0.5 - 1%) of white powdery "original" aluminum dilaurate swells rapidly in cyclohexane at room temperature but does not fill the liquid completely. Upon standing two layers are formed, the upper clear and transparent, the lower opalescent and composed of small flocks. Upon heating, the flocks disappear and a homogeneous transparent system is obtained.

If the concentration of soap is higher (3-10%), the soap imbibes the whole liquid giving a rather homogeneous stiff opalescent mass, which upon heating becomes clear but retains at first some of its rigidity and at still higher temperatures flows freely.

To distinguish these forms we use the terms gel for the opalescent non coherent lump form, sol for the clear and freely flowing liquid form, and jelly for the clear, rigid and elastic form.

(b) Definitions. The term "gel" was introduced by Thomas Graham as a generic term to embrace all more or less solid systems of a colloidal nature. The term "jelly" is familiar in ordinary life as the clear elastic edible table jelly or gelatine. The jelly is therefore a distinctive variety of gel. The term gel is however often used, excluding jellies. We shall therefore distinguish between gels and jellies. Sol is merely Graham's generic term for colloidal solutions; that is, for flowing liquids containing colloid.

The accepted theory of jellies is that they consist of a continuous medium in which colloidal particles are suspended, these particles being more or less loosely stuck together to form an open structure, designated as ramifying or branching or brush heap, or interlacing or streptococcal-- differing from sols in that there are more bonds between particles and between their aggregates sufficient to make the jelly resemble a soft elastic solid.

In general it has been found that there is no sharp boundary between jelly on the one hand, and sol or colloidal solution on the other, but that there is a continuous transition. Sols are often distinctly elastic. Jellies often relax and flow slowly. Thus a limpid Newtonian solution of a colloid and a hard elastic transparent jelly are merely two extremes of the same colloidal solution. We use therefore often the term jelly-sol to denote both

On the other hand, many colloidal systems, called gels, consist of semi-opaque or turbid, non-cohering lumps, often in a clear liquid. X-ray examination shows that they often contain or retain crystalline material. For example, with sodium soaps, an aqueous <u>curd</u> or <u>gel</u> consists of a mass of perfectly crystalline curd fibers enmeshing a liquid present amongst them.

(c) <u>Experimental criteria</u>. We found three experimental methods for distinguishing between gel and jelly-sol.

<u>Their Appearance</u>. The jelly and sol(if made from pure materials) are perfectly transparent, showing no opalescence. The gel is strongly opalescent, and this opalescence is still very easily visible at 0.05% of soap.

When the gel is in contact with excess sol the separation between the two is easily visible and sharply defined.

The jelly under the same conditions forms no sharp boundary but only an ill-defined transition zone.

Their Mechanical Properties. The jelly-sol is continuous and either easily flowing or stringy(or both). The gel is crumby and, unless compressed strongly by centrifugation or surface forces, clearly discontinuous. The gel has a marked yield value even in great dilutions, the sol flows readily, and jellies do not appear to have yield values, their surface readily becoming smooth even when their flow is extremely slow.

The X-ray Diffraction of the Residue after Evaporation. A gel, jelly or sol may be frozen by rapid cooling and then exposed to vacuum until the solvent is completely sublimed. The soaps thus recovered when placed in cyclohexane at room temperature return rapidly to their original state forming a gel or sol-jelly. This is not in itself a criterion for differentiation but shows that some of the character of the original state is retained by the recovered soap.

These recovered soaps may be clearly distinguished by their X-ray diffraction patterns which are shown in figure 14(p.42). The soap recovered from gel retains most of the crystallinity of the "original" dry soap while that recovered from jelly and sol has become almost amorphous.

(B) Application to Napalm and the Effect of Inorganic Impurities in Napalm.

The distinction between gel and jelly forms established in case of a pure soap may be applied to Napalms, provided that a pitfall arising from the presence of inorganic impurities is avoided.

(a) Visual Observations. Mixtures containing 6-7% of Napalm (McGean Lot No.462) with various hydrocarbons were prepared at room temperature. In toluene a transparent yellowish very elastic stiff jelly was produced. This contained, dispersed throughout, weakly opalescent flocks which slowly disappeared.

In isooctane, under anhydrous conditions, a two phase system resulted even after two weeks storage at room temperature. The grains of Napalm were swollen to translucent lumps of gel in a slight excess of a thin liquid.

A sealed tube containing 5.5% of the same Napalm, dried by evacuation at room temperature for 1 1/2 hours, and 94.5% isooctane was observed while heating. The swollen lumps of soap, which after two days at room temperature occupied only about 30% of the mixture, gradually swelled to 50% at 38°C and filled the liquid at 45-48°C, becoming gradually more whitish and translucent. The intergranular liquid seemed to become somewhat more viscous in the later stages.

At 56-57°C the bulk of the substance became transparent with many small translucent flocks dispersed throughout it. This appearance was essentially unchanged after heating to 110°C, maintaining this temperature for 24 hours and cooling to room temperature, except that the flocks become more diffuse.

It was thought that the formation of a two phase system by Napalm in isooctane might be due to oxidation of the sample but the same result was obtained with Harmon Lot R11235 and Ferro Enamel Lot P Batch 184. Aluminum dinaphthenate(33024-R) obtained as such from Standard of California readily formed a coherent and quite translucent mass in this solvent.

Between the extreme behavior of Napalm as gel in isooctane and Napalm as jelly in toluene are ranged the other hydrocarbons in the following order: isooctene, cyclohexane, cyclohexene , benzene. The soap fills these liquids readily (except isooctene) and forms stiff systems which show gradually decreasing turbidity.

Mixtures of the two extremes, isooctane and toluene, give a progressive series passing from a two phase sol-gel system to a clear jelly. The attached photograph (fig.28) shows these systems one week after preparation.

When compared with this continuous series the turbidity of the cyclohexane system had a turbidity between that of the 30% and 40% toluene mixture and "test" gasolines between 20 and 30% toluene.

On the basis of their visual appearance these intermediate systems would have appeared to contain a large proportion of the gel form. We have found however that these apparent gels could be liquified i.e. changed to sol without a marked change in turbidity by adding small amounts of peptisers. Presence of 10% by volume of nitrobenzene in cyclohexane and isooctane caused liquifaction of mixtures containing 4% Napalm. In toluene the same addition caused an appreciable but much smaller softening. When compared with the series of mixtures of toluene and isooctane shown in figure 28 the addition of 10% of nitrobenzene had the same effect on turbidity as addition of some 10% of the toluene which caused no liquifaction. This led to a search for the impurities responsible for the turbidity.

(b) Separation of the Materials Causing Turbidity in Napalm. The peptized turbid sols or easily flowing jellies of Napalm give, upon centrifugation or prolonged standing, a small amount of a very fine whitish precipitate with simultaneous clarification of the supernatant mixture. In stiff jellies or gels this separation is of course prevented by the viscosity.

We isolated a larger amount of this insoluble component of Napalm from a 4% McGean Napalm (lot462) sol in a solvent composed of 5% by volume (8% by weight) of nitrobenzene and "Test") gasoline After agitation overnight a turbid but quite thin liquid is formed. The major part of the turbid matter settles out in one day and most of it in two weeks of standing. Centrifugation has the same effect in a few minutes.

The sediment was washed by repeated suspension and centrifugation in the same solvent to remove any entrained soap, then in isooctane to remove the nitrobenzene, and finally suspended in cyclohexane, frozen, and the solvent removed by sublimation. A white very fine powder was thus obtained corresponding to about 2% by weight of the Napalm.

It is believed that this product is the turbid component of normal Napalm hydrocarbon mixtures, because(i) the appearance of Napalm gels free from nitrobenzene is substantially the same as of those containing it before settling of the precipitate or after the sediment is redispersed by shaking. (ii) During the whole process the sediment came in contact only with neutral solvents.

(c) Properties of the Material Causing Turbidity. It is a white fine powder very difficultly wetted by water, difficultly wetted by dilute hydrochloric acid, easily wetted and dispersed in hydrocarbons. It forms a white "silky" suspension in cyclohexane and isooctane, and become almost invisible in benzene and toluene. It does not dissolve in the latter however, as may easily be ascertained by spreading the clear suspension on the walls, where it deposits particles; or by letting it settle and form a distinct though almost transparent sediment. Its refractive index must therefore be close to that of the aromatic hydrocarbons(n=1.501 and 1.495).

About 50% of the powder is soluble in water, and 60% in dilute hot hydrochloric acid. The portion dissolved in hydrochloric acid weighs after drying almost 100% of the original weight. The ash is about 50%.

If the powder is properly separated from the soluble soap by the above procedure, the hydrocarbon extract of acidified and heated aqueous suspension is negligible (0.4% of the powder), showing that the powder contains no insoluble soaps but only inorganic constituents, which are presumably sodium salts, basic aluminum salts, and alumina.

(d) The Existence of Gel and Jelly Forms of Napalm in Gasoline.

Thus, the visual criterion failed in case of Napalm and for this the explanation was apparent. The mechanical criterion distinguished readily between the extreme cases of toluene and cold isooctane. For intermediate mixtures it indicated the presence of jelly as the systems were coherent especially after some ageing, but to confirm this point and to show the distinction between gel and jelly in case of Napalm, X-ray diffraction patterns shown in figure 17(P.46) were obtained under closely comparable conditions with the following samples:-

(1) Napalm McGean Lot 462 untreated . The pattern shows rather sharp lines.

(2) Same soap placed in 11.5 weight parts of isooctane for three days forming a two phase system of a small amount of thin clear liquid and swollen murky lumps of soap, then dried by evacuation below room temperature. The diffraction pattern shows distinct lines, confirming the presenceof the gel phase.

(3) Same as 2, but heatedon the steam bath for one hour , forming a coherent mass of somewhat lower turbidity than(2.). Only halos are present and prove that the gel phase has given way to the jelly.

(4) Some Napalm placed in 11.5 parts of cyclohexane at room temperature formed a turbid mass. Frozen and dried by evacuation it shows a pattern of jelly, not gel.

(5) Same process as (4) but with benzene. An almost clear transparent mass was formed, and figure 17 shows again a pattern of jelly similar to that obtained from the turbid samples 3 and 4.

It must be noted however that the X-ray criterion may fail sometimes. A very crystalline pattern was obtained from the residue of evaporation of a peptized jelly formed by this same Napalm in 11.5 parts of a mixture of 10% nitrobenzene and 90% cyclohexane. Evaporation of this mixed solvent was very difficul the smell of nitrobenzene persisting after 24 hours of evacuation, and apparently a far-going reversion to gel took place in the meantime.

(3) Transitions Between Dry Soap, Gel, Jelly and Sol.

The molecules of aluminum soaps are asymmetrical in shape with their hydrocarbon chains and small central atoms. Yet most of their surface is uniform, being formed by similar CH2 groups. This may explain why once their orderly arrangement is disturbed they may remain in loose disorderly tangled structures for long periods

This lack of rapid reversibility characterizes most of the transitions in soap-hydrocarbon systems and renders their study difficult but may account for the usefullness of their properties

(A) The Transitions from Dry Soap to Gel and Jelly. We have observed these transitions both visually and by means of the McBain sorption balance.

(a) Visual Observation.

i. Aluminum dilaurate. This soap when placed in cyclohexane swells at room temperature for about a day, increasing in volume at first rapidly then more and more slowly and finally remaining unchanged for months. If the proportion of soap is small and the liquid is agitated frequently during the swelling, the particles of gel are discrete and suspended in the liquid. They settle under the influence of gravity to a well defined level and remain discrete and easily dispersed. Centrifugation compresses them to a lower level and it requires a stronger shaking to redisperse them. After centrifugation the compressed layer of gel may spontaneously and slowly rise somewhat but does not recover its original height. In other words the soap particles swell to gel particles which form a loose aggregate held together by friction between particles and enmeshing large - amounts of liquid.

If the suspension is not agitated during the swelling process the friction among particles and between them and the glass may be sufficient to prevent the gel layer from expanding and may force the swelling particles into more and more intimate contact until they lose their discrete character and the gel is very difficult to break up by shaking. If the concentration of soap is higher(5-10%) and the swelling gel layer fills the whole liquid, the capillary forces prevent it from expanding further, and cause the same intimate contact between them, and a stiff gel is formed which has a relatively high yield value but is short and brittle. If the process of compression has not gone too far, addition of more liquid and some agitation will cause the gel to redisperse again.

The above description is restricted to the case where the interstitial liquid is highly fluid, as is the case at room temperature with the "original" form of dilaurate. At somewhat higher temperatures or when a larger proportion of soap is amorphous(or in the case of a glassy soap) the gel particles are immersed in a more viscous plastic medium which hinders their relative movements so that they seem to lose their discreteness.

When a very amorphous form of dilaurate "recovered from jelly" is observed at room temperature, or the "original" dilaurate is obsesved at higher temperatures, the particles become clear as soon as wetted and are often completely invisible to the naked eye unless the liquid is drained off them. In larger particles strains may cause birefringence and make them visible in polarized light. Then the particles continue swelling at a rate determined by the diffusion of liquid while their strength de -

creases, the outer layers become fluid and there finally results a continuous transition from a firm jelly in the center to the thin surrounding sol without any definite boundary.

Similar observations may also be made on many other swelling substances, for example gelatine in water.

ii. Napalm closely resembles aluminum dilaurate, giving the same type of transition from dry soap to gel or jelly in various hydrocarbons but its particles are larger and the clear transparent condition is approached only in aromatic solvents.

Toluene and isooctene(or isooctane with undried Napalm) are typical. In both cases the lumps of soap swell.

In the toluene mixture the viscosity of the liquid between lumps increases rapidly and soon a coherent jelly is formed, holding opaque lumps in suspension. After some time the lumps themselves become transparent except for a translucent floccular outline which seems to disappear only very slowly.

In the isooctene mixture however the liquid between swelling lumps retains its mobility and as long as enough of it is present the lumps move with respect to each other with great ease. As the liquid is soaked up by the lumps the mass passes through a caviar-like stage when there is not enough liquid to allow free movement of lumps,and then gradually stiffens as the lumps soak up the free liquid, and become squeezed tightly against each other, but still showing their individuality by uneveness of surface and irregular lumpy fracture and non-adherence to each other. For some time after apparent coalescence , the lumps may be separated by shaking some of the gel in excess solvent. In time, however, they do coalesce completely,the gel becoming coherent and not being broken up by excess solvent.

In mixtures of isooctane and toluene one may observe the tremendous effect of small amounts of toluene upon the time of setting (as measured by the appearance of rigidity at edges of the gel). Fig. 28 is a plot of the logarithm of this time for mixtures containing 8% of Napalm McGean Lot 462.

Mixtures containing less than 30% toluene had showed prior to setting, the characteristic appearance of lumps floating in a thin liquid; while those having more than this proportion of toluene become sufficiently thick to prevent rapid settling as soon as the liquid is added.

(b) Sorption of Cyclohexane.

i. Aluminum Dilaurate. Figure 29 shows two sorption isotherms at 50° obtained on a single sample of "original" aluminum dilaurate. It may be seen that in both cases a smooth curve, convex to the ordinate, is obtained. There are however, marked differences between the two series:-

(a) at higher relative vapor pressure the soap sorbed much more cyclohexane during the second run. In the first experiment 100 parts of soap sorbed only 61 parts of solvent so that 62% of the total weight was soap. In the second, 100 parts of soap sorbed almost 400parts of solvent so that only 20% of the total weight was soap.

(b) In the first series the same equilibrium weights were obtained when a given vapor pressure was established either from above or from below; that is, the equilibria were reversible, without hysteresis. In the second series the sorption showed a marked hysteresis and the difference reached almost 20%.

Figure 28

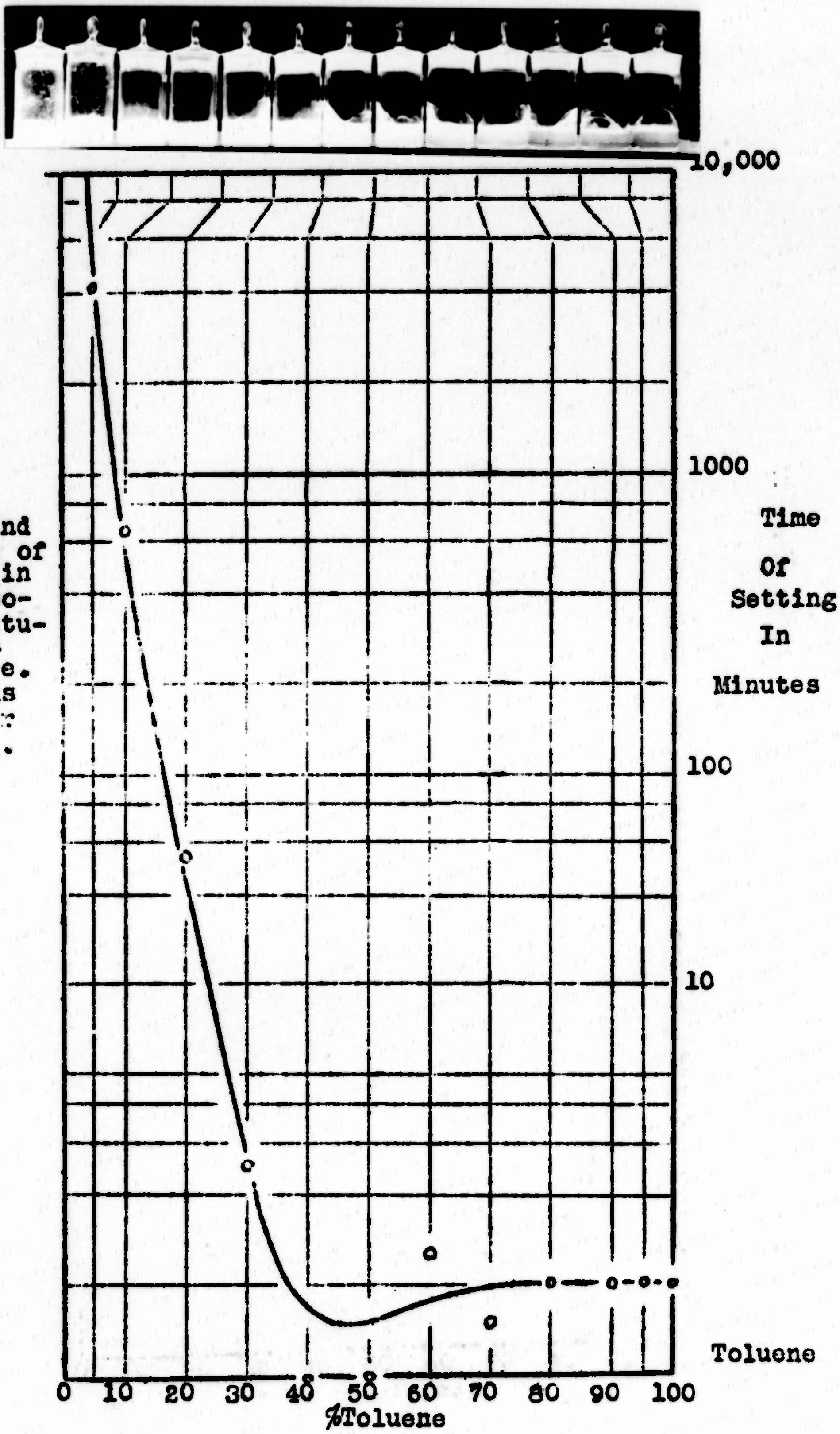
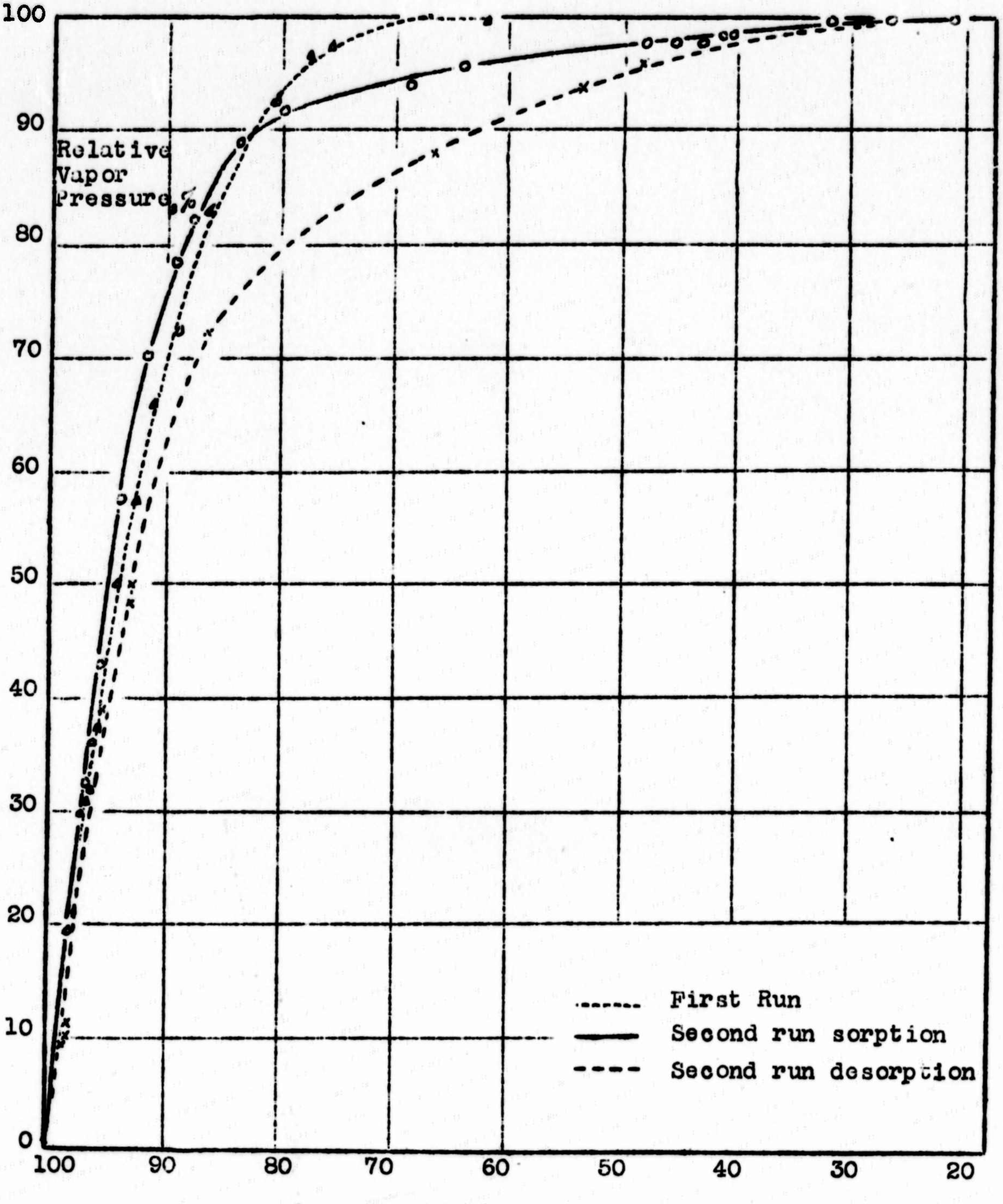


Figure 28

Set Time and appearance of 8% Napalm in toluene-isooctane mixtures. Room temperature. Photographs taken after seven days.

Figure 29

Sorption of Cyclohexane by Aluminum Dilaurate at 50°C



Percent Al(OH)L_2 by Weight

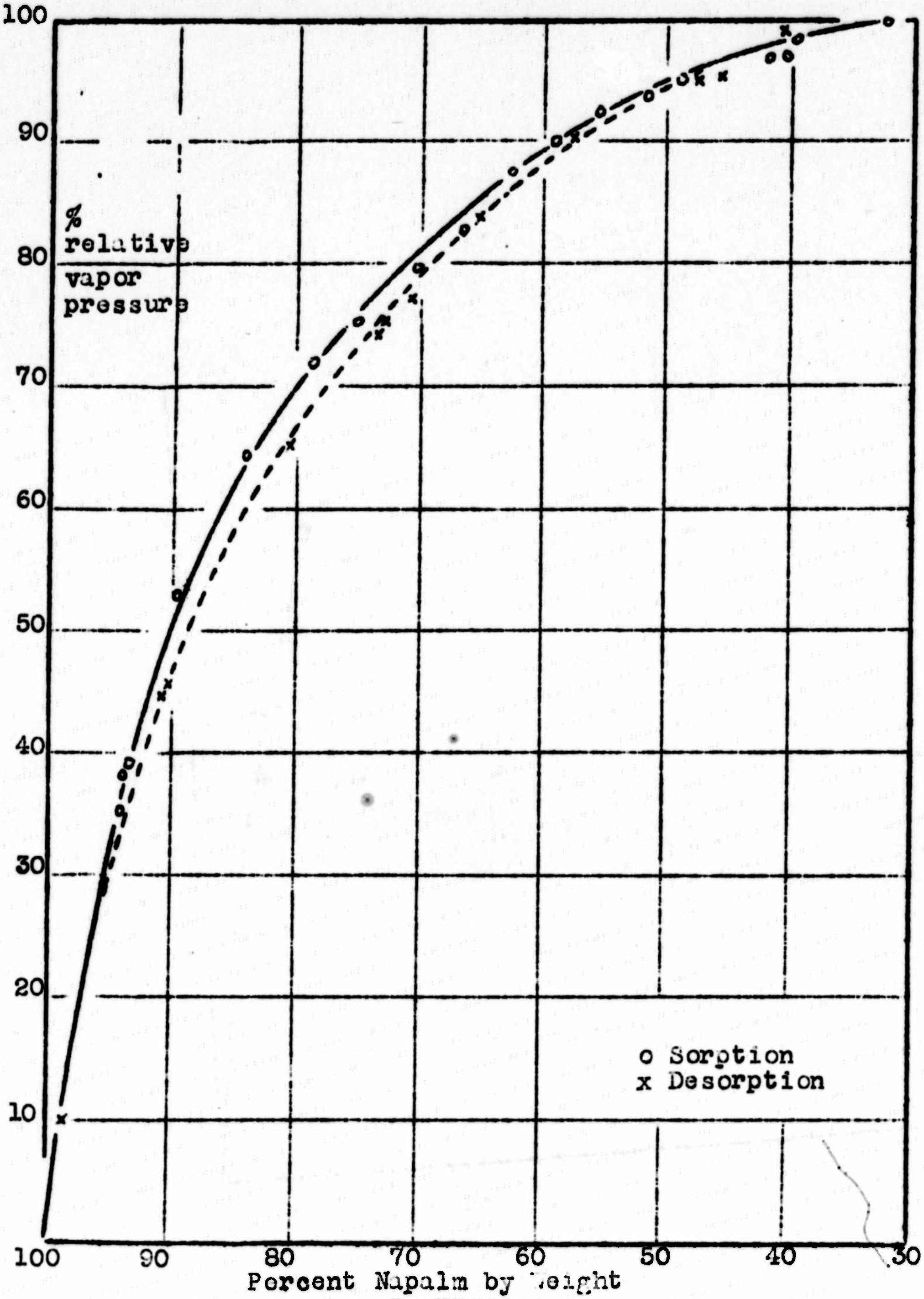
The method of thermostating was somewhat different in the two experiments but this can account for only a small part of the differences. An important difference was however observed between the two runs; in the first the soap remained a white powder composed of discrete particles; in the second it was transformed into a transparent coherent mass. It is not clear when and why the transformation occurred between the two runs but it seems clear that it corresponds to a change from gel to jelly in the state of the soap, the jelly sorbing incomparably more solvent and showing hysteresis.

The smoothness of the curve shows that the transition from dry soap to gel containing about 60% of soap is a continuous gradual change with no separation of distinct phases or formation of definite solvates.

The sorption isotherm for aluminum dilaurate and cyclohexane is very similar to that for rubber in benzene except that the rubber takes up more than twice as much for any given relative vapor pressure. In each case the sorption isotherm rises smoothly from 100% solid at zero pressure, and the hydrocarbon vapor becomes practically saturated when the solid contains roughly its own weight of hydrocarbon. Thereafter the vapor pressure asymptotically approaches 100% saturation while the solution is progressively diluted. The very slight lowering of vapor pressure throughout this region corresponds to the very high molecular weight and particle size respectively of the rubber and the aluminum dilaurate. At this end, the isotherm corresponds to the osmotic pressure whereas at the other extreme it corresponds to a swelling pressure with no break but only gradual transition thru out.

Figure 30

Sorption of Cyclohexane by Napalm Imperial NR 232 at 50°C



(ii)Napalm. The sorption isotherm of cyclohexane on Napalm Imperial NR232 at 50°C is shown in figure 30. Except for smaller hysteresis it presents the same general characteristics as the aluminum dilaurate (in the second run) and shows that the soap has to take up more than its own weight of hydrocarbon before the vapor pressure becomes as much as 95% of saturation.

These curves may be contrasted with the water sorption isotherm of Napalm given in figs. 26 and 27 , which show that a few percent of moisture were enough to saturate the soap and produce nearly 100% relative humidity.

2. Isobar and Hysteresis in the Sorption of Cyclohexane by Napalm

In the second chapter(p.71) we have described some experiment on hydration and dehydration of a sample of Napalm Imperial NR232 which lost up to 3.4% of moisture when kept at 50° exposed to water vapor of constant pressure of 4,56 mm. This final weight was taken as the weight of dry Napalm.

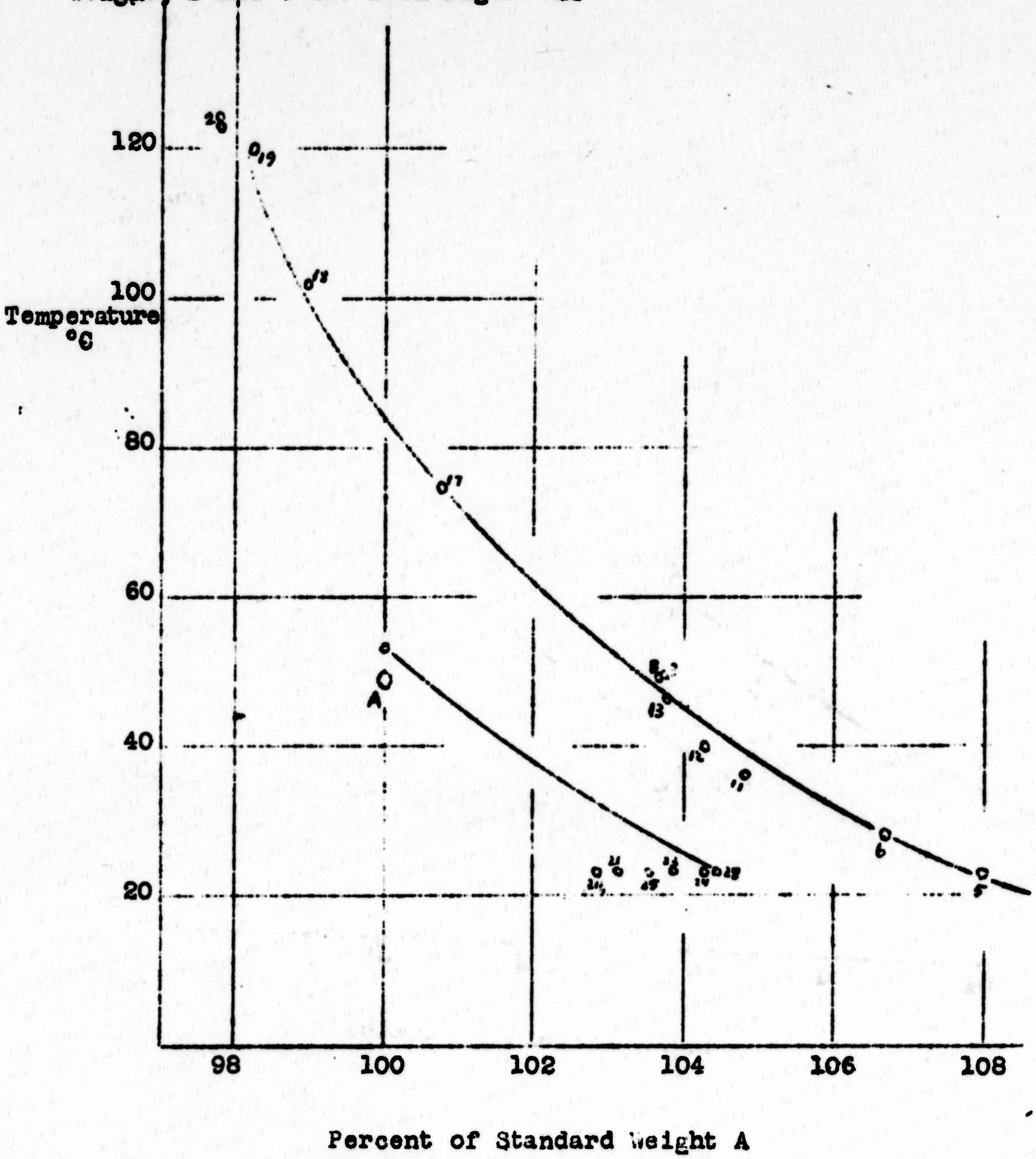
An ampule containing cyclohexane was then broken within the sealed system containing the McBain-Bakr sorption balance, and the above sorption isotherm(fig.30) of cyclohexane by this Napalm was determined.

At the conclusion of this run, an isobar was determined, the vapor pressure of cyclohexane being maintained constant at 27.5mm. Hg by keeping the lower end of the sorption tube at 0°C while the temperature of the soap was varied.

Figure 31 summarizes the results. It is a plot of the weight of the soap plus cyclohexane(and probably some water) as a function of temperature, using the weight of the soap dried as described at the beginning of this section as the zero point, marked

FIGURE 31

Isobar of sorption of cyclohexane by Napalm Imperial NR 232 at 27.5mm. Hg (vapor pressure of cyclohexane at 0°C). Numbers are elapsed time in days since starting isobar. A is the standard weight; B and 3 are from Figure 30



A on the diagram. The numbers next to each point indicate the period in days since the beginning of the experiment.

It will be seen that the amount sorbed at constant vapor pressure of cyclohexane decreases rapidly as the temperature of the soap is raised. This is to be expected, since the relative vapor pressure of the solvent at the temperature of the soap is reduced.

It may also be noted that there is a marked hysteresis at 23°C. When the soap is recooled back to 23°C, it sorbs less than half as much cyclohexane as it did before being heated. Thereaft it slowly sorbs somewhat more cyclohexane over a period of several days, as if the change produced by the heating were somewhat reversible, but even after a week it has sorbed only half as much as the original soap did at 23°C. Possibly restoration of a small amount of water is necessary to help sorption, as in the well known case of silica gel.

The dimihished affinity for cyclohexane, shown by the preheated Napalm, persisted in the experiment at thirty days, when the isobar was remeasured at 53°C.

Finally, when now the relative pressure of the cyclohexane was raised to 42% by warming the whole lower part of the tube to 28.7°C(which would likewise warm any moisture present), the Napalm being still at 50°C, the amount sorbed checked within half of one percent with that previously determined before that isobar was begun(figure 30).

It will be noted at the higher temperatures that the soap lost more weight, possibly water, than it sorbed cyclohexane,and the weight of soap dropped below the initial 100 % value,A.

(B) The Transition Between Gel and Jelly or Sol. A small amount of aluminum dilaurate placed in excess of cyclohexane at room temperature swells to an opalescent gel surrounded by a very dilute, very fluid sol. When this system is heated, the gel swells further while the concentration of the sol increases, then either before or after the gel has filled the whole liquid the opalescence disappears and a jelly or sol phase are present. This transition has been studied by viewing sealed tubes during heating and cooling and by determining the solubility of the soap in the sol. Before describing the observations, details of the procedure for preparing the sealed up system are given:-

Preparation of Sealed Glass Tubes. The preparation of sealed tubes for visual observation of phase behavior and viscosity measurements requires great care in order that the contents of the tube represent truly its nominal composition.

How important this care is may be best seen from the fact that the melting point of an aluminum soap may be lowered 20°C and its recrystalization prevented if it is sealed in a tube without thorough evacuation, and the presence of 0.1% of moisture may lower the temperature of transition to jelly by nearly 100°C.

For the observation of soap alone, a glass tube is drawn out into a large capillary sealed off at one end forming a funnel. A very thin glass fiber is placed in it and the lower part of the capillary filled with soap by vibrating and pushing. The upper part of the capillary is then cleared of adhering soap particles(which would otherwise decompose during the sealing operation) by means of a tiny cotton wad.

The thin glass fiber is now withdrawn leaving a channel through the packed soap for the egress of air, the capillary connected to the vacuum pump and evacuated slowly and thoroughly; after about 1/2-1 hour it is sealed off while evacuation continues.

For the observation of soap-hydrocarbon system, a pyrex tube about 8 mm.O.D. and some 10-15 cm. long and closed at one end, is sealed on to a 12/30 standard taper outer ground glass joint. After thorough cleaning and drying it is weighed(with a stopper), the soap is placed in its bottom by means of a thin glass funnel so as not to soil the walls, and the tube reweighed, thus giving the weight of soap contained in it. The soap is then dried by evacuation for 1/2-1 hr. in case of aluminum soaps,and at 230° over P_2O_5 in an Abderhaldor drying "pistol" in case of sodium soap. A correction for the weight of moisture lost is applied if hecessary.

The hydrocarbon(stored over Drierite,$CaSO_4$) is then added rapidly by means of a hypodermic syringe and the tube connected to the vacuum pump by means of the ground joint. It is carefully evacuated till the first bubbles appear in order to purge it of moist air and then surrounded by dry ice up to somewhat above the level of liquid. It is then evacuated completely and sealed off below the ground joint care being taken not to loosen any glass during the operation. The vapor pressure of the hydrocarbon is sufficiently reduced by the dry ice to prevent the appearance of any sign of cracking during the sealing operation.

Both parts of the tube are then reweighed together with the stopper and the increase in weight gives the weight of hydrocarbon added.

(a) Visual Observation.

1. Sensitivity. The disappearance of opalescence with rise of temperature may be determined visually to within 1 or 2 °C when proper side-illumination against a dark background and good temperature control are provided. The visual determination of the presence of soap in the gel form is believed to be sensitive to better than 0.05%.

The main experimental difficulty of this determination is to prevent variation of concentration in different parts of the tube. If the swelling gel is allowed to cohere or the soap is present in large lumps, its contact with the surrounding liquids is reduced and equilibrium may be obtained only by diffusion and is not reached practically during heating. Fortunately in the usual range(1-10%) the concentration has only a small influence upon the transition temperature so that reliable results can be easily obtained.

If the gel particles are allowed to settle, the height of the gel layer may be measured and the volume to which a gram of soap swells at that temperature approximately computed.

A typical log of a viewing experiment is shown in table VI.

TABLE VI

Log of Observations for Tube No. 60, An Anhydrous System Containing 2.77% Aluminum Dilaurate, 13-F209-110, in N- Heptane.

Soap gel layer = 1.2cm. Total height of tube contents = 8 cm. Soap particles discreet and opaque, white, settle rapidly. The sample will be heated to determine the gel-jelly transition.

Temp. °C	Hour	Remarks
25	3:10	Soap as described above.
30	3:20	Slight swelling.
40	3:40	Swelling rapidly- Soap in less opaque gel-height increase to 2 cm , total volume unchanged.
46	3:55	Gel losing opacity and becoming opalescent. Swelling slowly.
46	4:30	Gel has become opalescent, translucent, but not clear. Disperses and flows in blobs. Gel height 2.2cm.
48	4.45	Whole system setting up, not clearing,
48	5:00	System now rigid. White opalescence fading to bluish.
48	5:20	Translucent, clear , but has a definite bluish opalescent tint.
50	5:40	Fading.
50	6:00	Clear. Transparent.

Tube removed from bath and cooled to room temperature. After 1 1/2 hours the system had become turbid.

After standing overnight, the tube was milky and the gel became mushy on severe shaking.

Conclusions- 1) Transition temperature for gel-jelly = 50°C
2) Computed concentration of gel 18.5% at 25°C 11.2% at 40°C and 10% at 46°C.

By correlating many such observations the following conclusions are drawn and the phase diagram of figures 41 to 43 obtained.

ii. Reversibility. If the system is heated and then cooled it does not in general recover its initial appearance readily. Once a jelly is formed and has been heated above its formation temperature it may remain clear for months but if the transition temperature is only just reached, or exceeded by a few degrees, it may revert markedly to the gel, its opalescence increasing slowly. This suggests that the presence of invisible particles of gel plays a great role in the formation of gel from jelly in case of pure aluminum soap. This lack of reversibility renders these observations more difficult since they cannot be readily repeated on the same system.

iii. Effect of physical form of soap. The physical form of soap has a marked effect upon its swelling(as noted in TableI) and upon the temperature of transition into the jelly or sol form. At room temperature, the crystallised form of aluminum dilaurate swells to less than 1.2 volumes, the "original" to about 50 volumes; that recovered from jelly forms a jelly or sol without any heating. The solubility measurements reported below show that the original form contains about 15% of forms which pass from gel to sol between 21.5°and 25°C.

Thus for comparative observations it is important that the same sample of soap be always used.

iv. Effect of solvent. The solvent has a marked effect upon the swelling and the temperature of transition to jelly. The greater the swelling at a given temperature in the solvent the lower this transition temperature as shown in Table VII in which the behavior of systems containing 2.5% of "original" dilaurate is recorded.

TABLE VII

Transition Temperatures and Swelling of Anhydrous Aluminum Dilaurate-Hydrocarbon Systems.

Solvent	Swelling at 25 °Centigrade		Transition Temp. °C
	Computed concentration of gel,	swelling volume.	
n-heptane	18.5	6	50
isooctane	24.5	4	64
benzene	0		25
cyclohexane	2.0	50	40

(b) **The Solubility of Al(OH)L_2 in Cyclohexane, and its Dependence upon the Physical State of the Soap.** Under strictly comparable conditions the amount of aluminum soap dissolved in a given amount of cyclohexane is, over a wide range, practically proportional to the amount of soap present. The soap behaves as if it were a mixture of a very soluble and a very insoluble constituent. Yet the two groups of constituents have exactly the same melting point and form crystals yielding the same X-ray pattern.

This is analogous to an aged sample of phosphorous which consists partially of the white form, very soluble in carbon disulfide, and partially of the red form, insoluble in carbon disulfide, both forms being transformable into each other under proper conditions.

In these experiments samples varying from 10 to 125 mg. of "original"$Al(OH)L_2$ were weighed into 25cc. mixing cylinders, dried, 25cc. of dried cyclohexane added to each, and the mixtures placed on a slow mixer in an air thermostat. After given time intervals the sol was separated from the gel either by settling for four hours or by siphoning through a cotton plug. About 15cc. of the liquor siphoned off the gel was placed in a weighing bottle, weighed and its concentration determined by weighing the residue obtained by exposing the frozen sample to vacuum.

Two series of solubility determinations were made one at 25°C the other at 21.5°C. In each series the effect of time and amount of soap present was determined.

Figure 32 shows the concentration of the solution as function of the proportion of soap present. Over the ranges covered at each temperature/it is a straight line passing through the origin. Figure 33 shows the same results expressing the proportion of soap dissolved as function of proportion of soap present.

The proportion dissolved remains constant at each temperature but varies markedly with the latter and is within experimental error 23% at 25°C and 8% at 21.5°C.

Figure 32

Variation of Concentration of Cyclohexane Solution with Varying Amounts of $Al(OH)L_2$ Present. - 48 hrs. of contact.

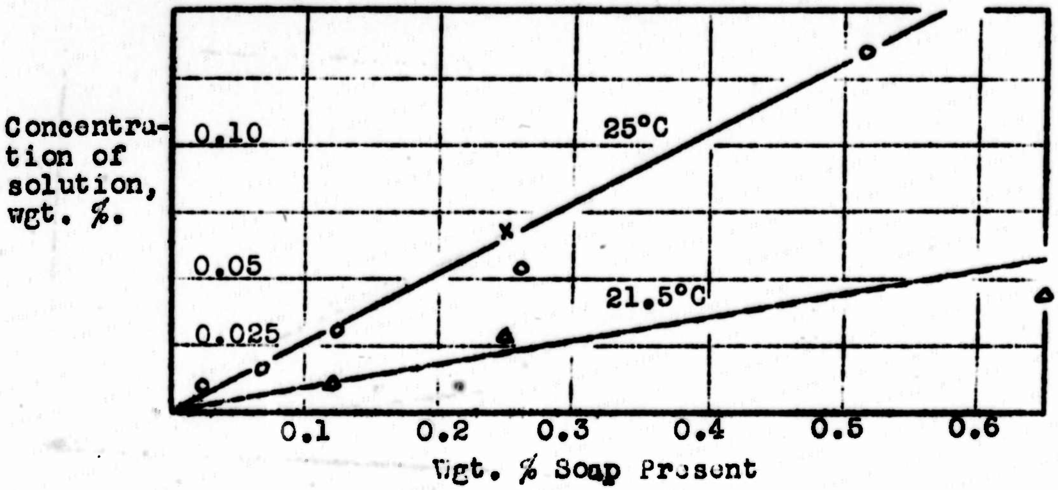
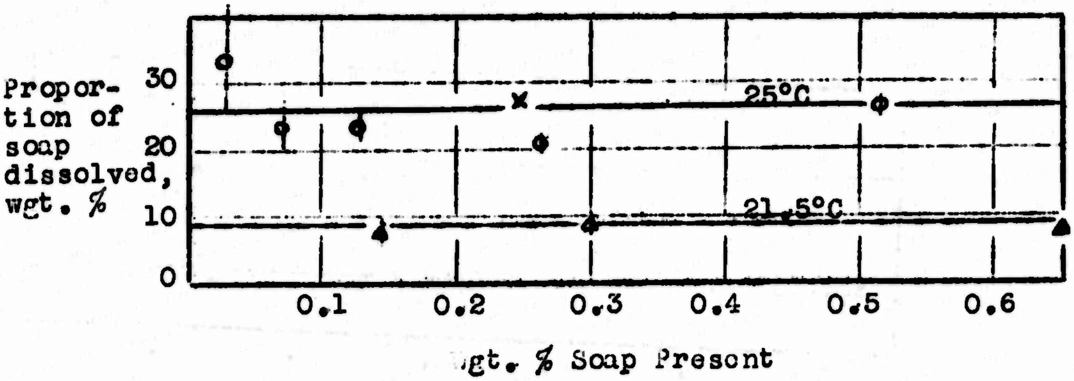


Figure 33

Proportion of Soap Dissolved for Varying Amounts of Soap Present . - 48 hrs. of contact.
(Vertical lines show experimental error)
x contains 1.2% HL



It was considered possible that the solution of only a fraction of the soap may be due to the presence in the soap of a trace of free acid which "might be able to peptize" part of the soap. This is made improbable by the identity of melting point of the original and the dissolved fraction. To obtain a definite disproof of this possibility, 1.2% of lauric acid(on the weight of the soap) was added to one of the samples of the above experiment and as shown on figures 32 and 33 did not produce any appreciable effect. The presence of small amounts of acid has therefore little influence upon the solubility of $Al(OH)L_2$ in cyclohexane.

Hence cyclohexane has separated the "original" dilaurate into a fraction readily soluble at 21.5°C amounting to about 8%, and one insoluble at 25°C amounting to 75%.

This fractionation could have separated either different chemical compounds or different physical forms of the same compound aluminum dilaurate. To find which hypothesis was true, the melting point and X-ray diffraction of the part soluble at 25°C (recovered after evaporation of the solvent was compared with that of the original sample and they were found identical. The recovered soluble part had a sintering point of 187-9°C and a and a melting point of 194-5°C while the original sample sintered upon first heating at 190-192°C and thereafter melted at 194.5 - 195.5°C. The X-ray patterns after recrystallization are shown in figures 13 and 14 respectively.

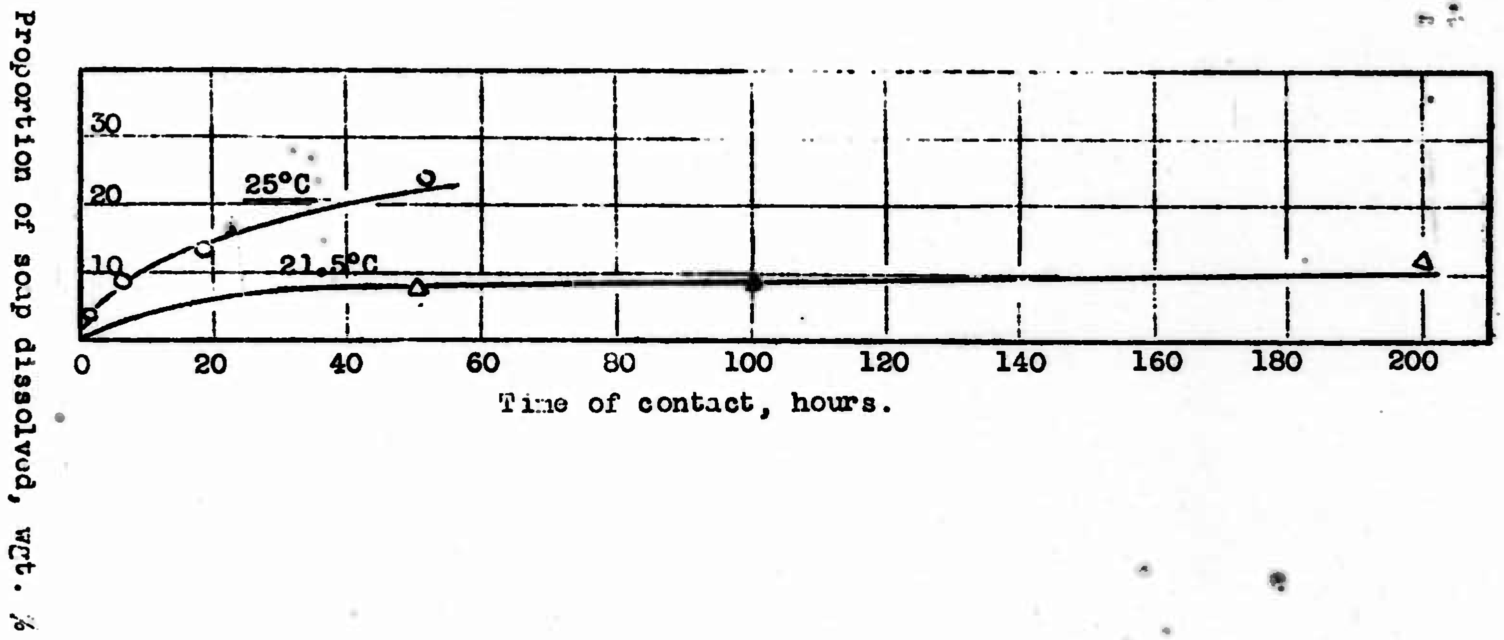
Thus the term solubility does not apply in its ordinary connotation to the system considered, while the "percent of soap soluble" in the sample is more useful. The rapid variation of this value with temperature suggests that this soap is composed of many fractions having each a very steep temperature solubility relationship.

Figure 34 shows the "percent soluble" as function of time. It may be seen that at 21.5°C equilibrium seems to be reached within two days while at 25°C despite a larger amount dissolved it may not yet be reached completely in that time.

Figure 34

Proportion of Soap Dissolved as a Function of Time of Contact in the System "Original" Aluminum Dilaurate $Al(OH)L_2$-Cyclohexane at 25 and 21.5°C.

(0.156-0.178% soap present at 25°C.)
(0.298-0.307% " " " 21.5°C.)



(C) <u>The Transition between Jelly and Sol.</u> We have found no characteristic separating sharply these two forms and the transition, as expected, is continual and gradual.

In case of aqueous sodium soaps it was shown by McBain and Laing in 1920 that a jelly may pass into a sol without change in refractive index, osmotic pressure, particle size, light scattering (opalescence), conductivity, E.M.F. or any property, other than mechanical, such as viscosity and elasticity. This demonstrated that the jelly was due to loose contacts between the colloidal particles that exist in the sols.

Since viscosity seems to be the main property in which these forms differ, we used it for their study.

(a) <u>Viscosity Measurements in Sealed Tubes</u>. In order to measure the viscosity of a system whose composition remained invariable over long times and wide ranges of temperature, we timed the rise, between two fixed points, of the vapor bubble in a sealed tube upon inversion. This method gave results of moderate precision but covering a wide range.

As expected, the viscosity is a function of the history of the system, and it is not easy to determine a true equilibrium value characteristic of the system for a given concentration and temperature. The hysteresis effects are, however, of marked interest in themselves and are still being studied. The results reported now must be regarded therefore as exploratory and not definitive.

(i). <u>Effect of Temperature.</u>

Out of a rather large number of observations which gave often widely varying results, it appears at present that the effect of temperature may be represented approximately by the curves of Figure 35. This is a semi-logarithmic plot showing the variation of viscosity for several concentrations as measured by the time of rise of the meniscus in tubes of about 6mm. I.D. in seconds per cm. All systems at sufficiently high temperatures are typical sols and their viscosity is little more than that of pure solvent. In the more concentrated systems, as the temperature is lowered and they become typical jellies, the viscosity increases first exponentially, and then much more slowly. At lower concentration, the slope of the exponential part seems less and the almost constant portion is not reached. The exponential part of these curves presents less marked hysteresis effects than the high viscosity part and is therefore somewhat more definite.

(ii). Effect of Concentration.

Figure 35 is replotted in figure 36 to illustrate the effect of concentration at various temperatures, showing a series of S-shaped curves.

(iii). Hysteresis Effects and Kinetics of Sol to Jelly Transition.

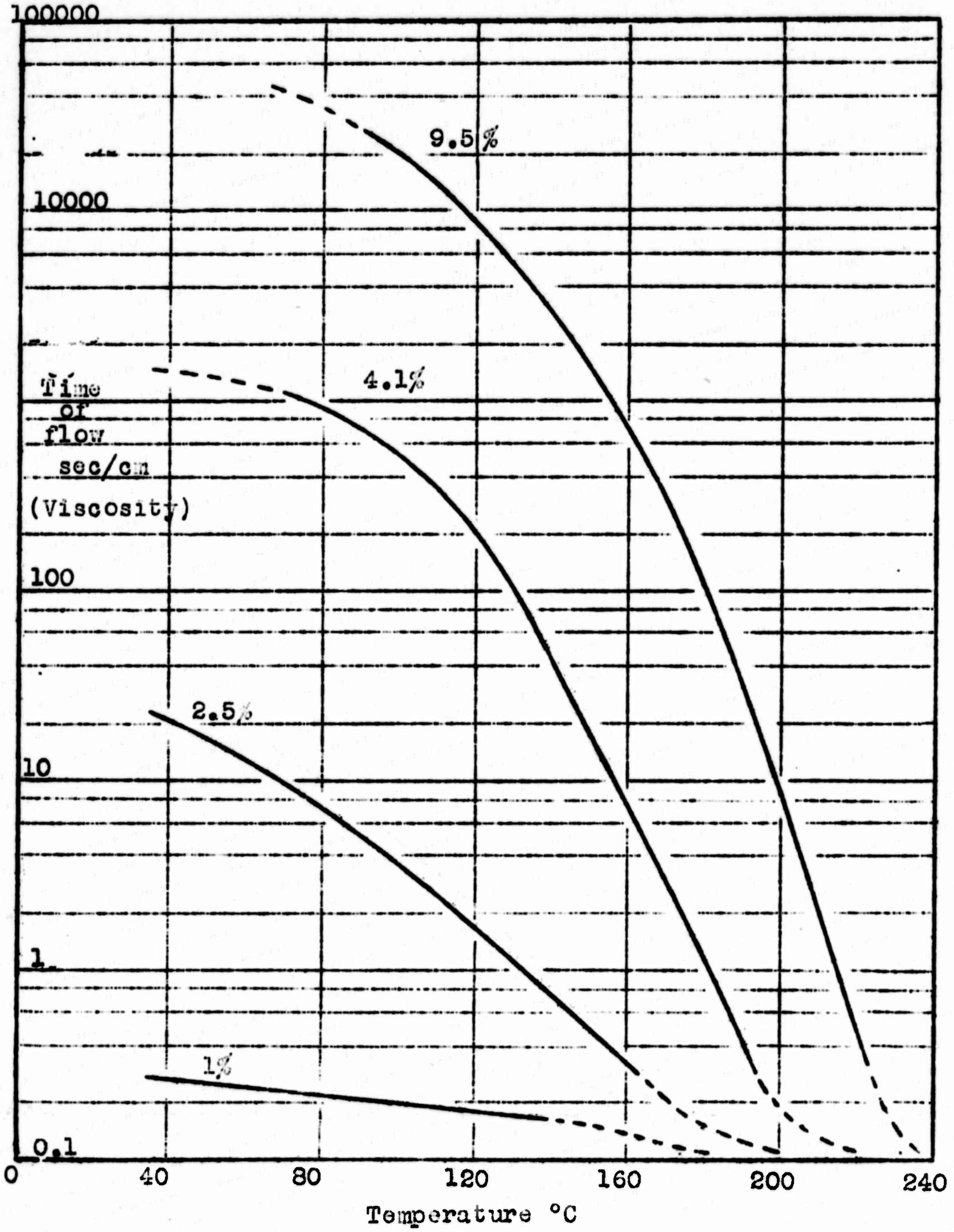
Two types of hysteresis were observed:- i) thixotropy; that is, reduction of viscosity by prior flowing especially by rapid flowing, and ii) supercooling, or "thermotropy"; that is, reduction of viscosity by prior heating.

Thixotropy was observed definitely only in more viscous systems having flow times of over 100 sec./cm., but this may be largely due to limitations of our method. When it was observed the healing was rather slow.

Thermotropy. It was observed that the viscosity is

Figure 35

Probable Variation of Viscosity of $Al(OH)L_2$ - Cyclohexane System with Temperature.



lowered by heating and recooling to the original temperature. Thereupon the viscosity slowly increases again. This rate of recovery seems to depend upon the temperatures at which [illegible] occurring. The initial viscosity after cooling therefore depends upon how fast the solution was cooled.

In one series of experiments the tube containing 4.1% $Al(OH)_3$ in cyclohexane was heated above 200° C, where it becomes a thin liquid, then cooled during the course of one hour at 82°C, kept at this temperature for a specified time which varied for each experiment, inverted, and to avoid all other hysteresis effects, the time of flow measured once only. Then the whole process was repeated. The results are indicated by the circles in figure 27. They show that immediately after cooling the time of flow was about 160 sec./cm but increased over five fold by keeping the tube for forty hours at 82°C.

If the cooling were conducted much more slowly, over a period of 41/2 hours, instead of one hour, the viscosity was definitely much higher as shown by the cross on the same figure.

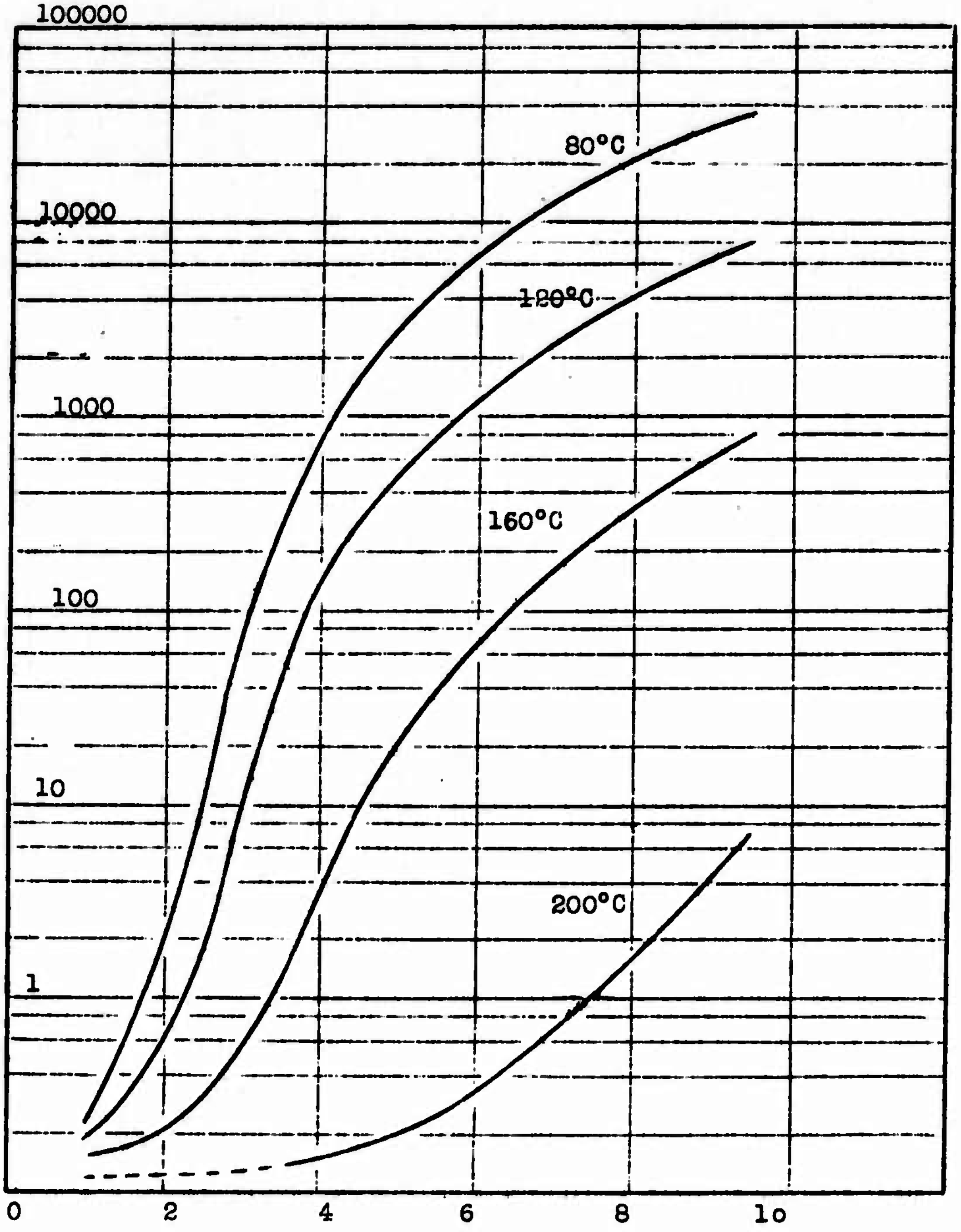
Flowing the tube a second time gave a lower viscosity due to the thixotropic effect as shown by the triangle in the figure.

This behavior suggests that the structure of jelly causing viscosity is built up to an increasing extent as the temperature is lowered but that the rate of building up is more rapid at higher temperatures.

To test this hypothesis the tube was again heated above 200°C and then quenched by dropping it into cold water. This caused of course a local boiling and condensation within the system so that it became obviously inhomogeneous, some parts

Figure 36

Probable Variation of Viscosity of the $Al(OH)L_2$-Cyclohexane System with Concentration.

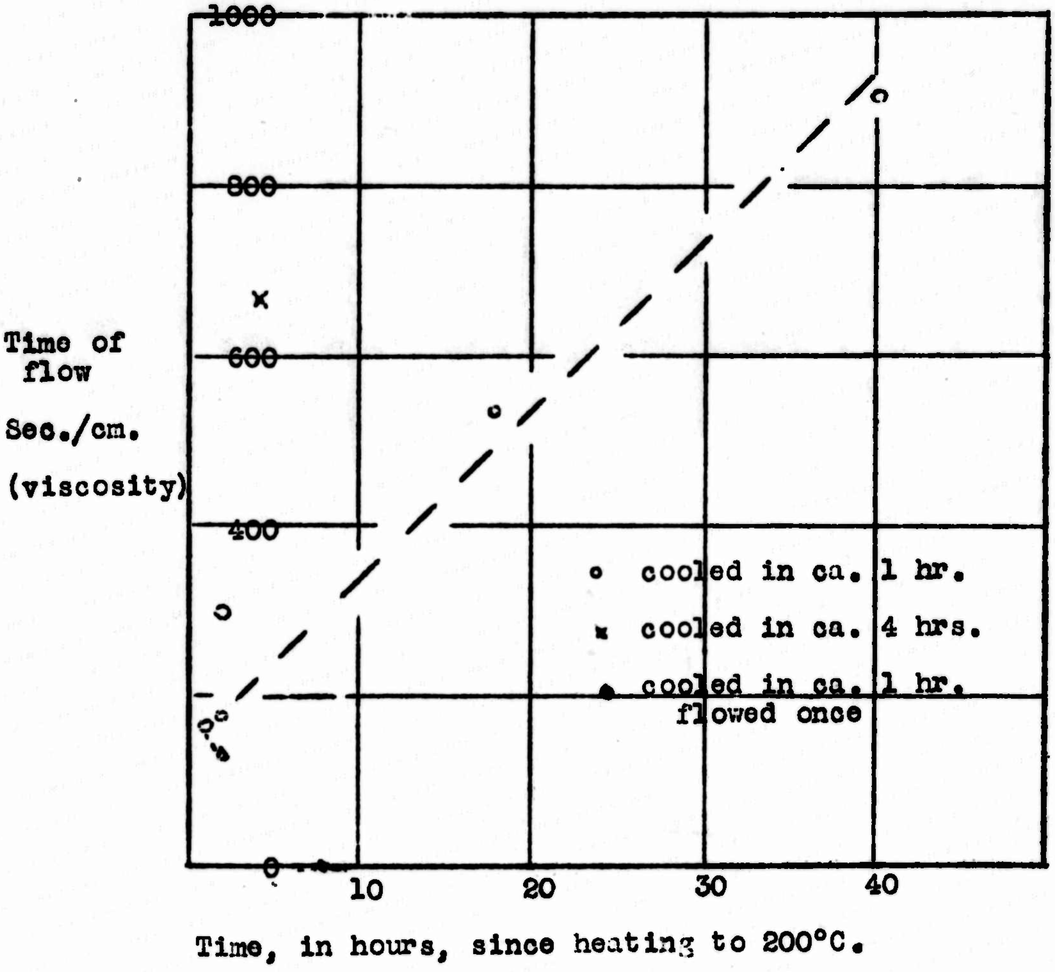


Concentration of soap, percent.

Figure 37

4.1 % Al(OH)L$_2$ in Cyclohexane

Viscosity at 82°C. after previous heating to 200°C., as affected by cooling rate, residence time at 82°C. and thixotropy



being much more viscous than others.

By next day, however this 4.1% $Al(OH)L_2$ in cyclohexane mixture became homogeneous; it was a slightly viscous liquid having a flow time of about 10 sec./cm. It was kept at room temperature and its viscosity observed occasionally over nearly 40 days until the tube was broken by accident.

The viscosity increased slowly at first, then more and more rapidly at an almost exponential rate, but after some twenty days the rate was again reduced. On a linear graph this would give an S shaped curve. On a semilogarithmic scale a rather regular pattern is obtained as shown in Figure 38, suggesting that the structure being built up is proportional not to the viscosity but to its logarithm. It appears further as if this structure was building up to a point where the time of flow would be about 1000 sec./cm. according to a rate of the first order. The smooth line drawn is calculated on this hypothesis.

When the time of flow became large, thixotropic effects again became disturbing and the points in the upper part of the curve are quite uncertain. The dotted line in Figure 38 shows the result of repeated rapid flowing of the tube in a centrifuge. The time of flow dropped appreciably below the smooth line and did not recover in a day. The recovery time from the thixotropic disturbance was much faster than from the thermotropic effect, suggesting that the two may affect different elements of the structure.

A further proof of our hypothesis was obtained when in case the temperature coefficient of the system appeared negative, the time of flow increasing from 153 to 430 seconds as the temperature was raised from 83° to 101°, showing that the structure was being built up despite the warming.

Whether the observed flats in the temperature viscosity curves are due entirely to very slow recovery from heating is not quite clear at present but seems unlikely.

b) *Viscosity Measurements in Ostwald Viscometers*. For more precise measurements over a limited range of time and temperature, the Ostwald viscometer is convenient. In order to obtain significant results it is necessary to prevent evaporation and to watch closely for lumps of jelly which may obstruct the capillaries. The results obtained upon successive measurements sometimes showed unexplained variations but these were always smaller than the rather large effects to be discussed. The values given are the average of five to ten successive measurements usually differing by less than 1% from each other.

In dilute solutions the *absolute viscosity* of the solution as measured by its time of flow must be compared with the viscosity of the solvent itself, which is the ratio of the viscosities of solution to that of solvent as measured by their times of flow in the same viscometer.

These measurements were made in benzene in which as already noticed, low concentrations of dilaurate form a jelly or sol at room temperature.

1) *Time Effect. The Transition from Jelly to Sol*. The viscosity of all freshly prepared solutions in benzene decreased with time as shown in Figure 39. This decrease continued for several weeks towards an equilibrium value, and is most notable in more concentrated solutions. It occurs at about the same rate whether the

Figure 38

Slow Recovery of a Quenched 4.1% Sol of Aluminum Dilaurate in Cyclohexane.

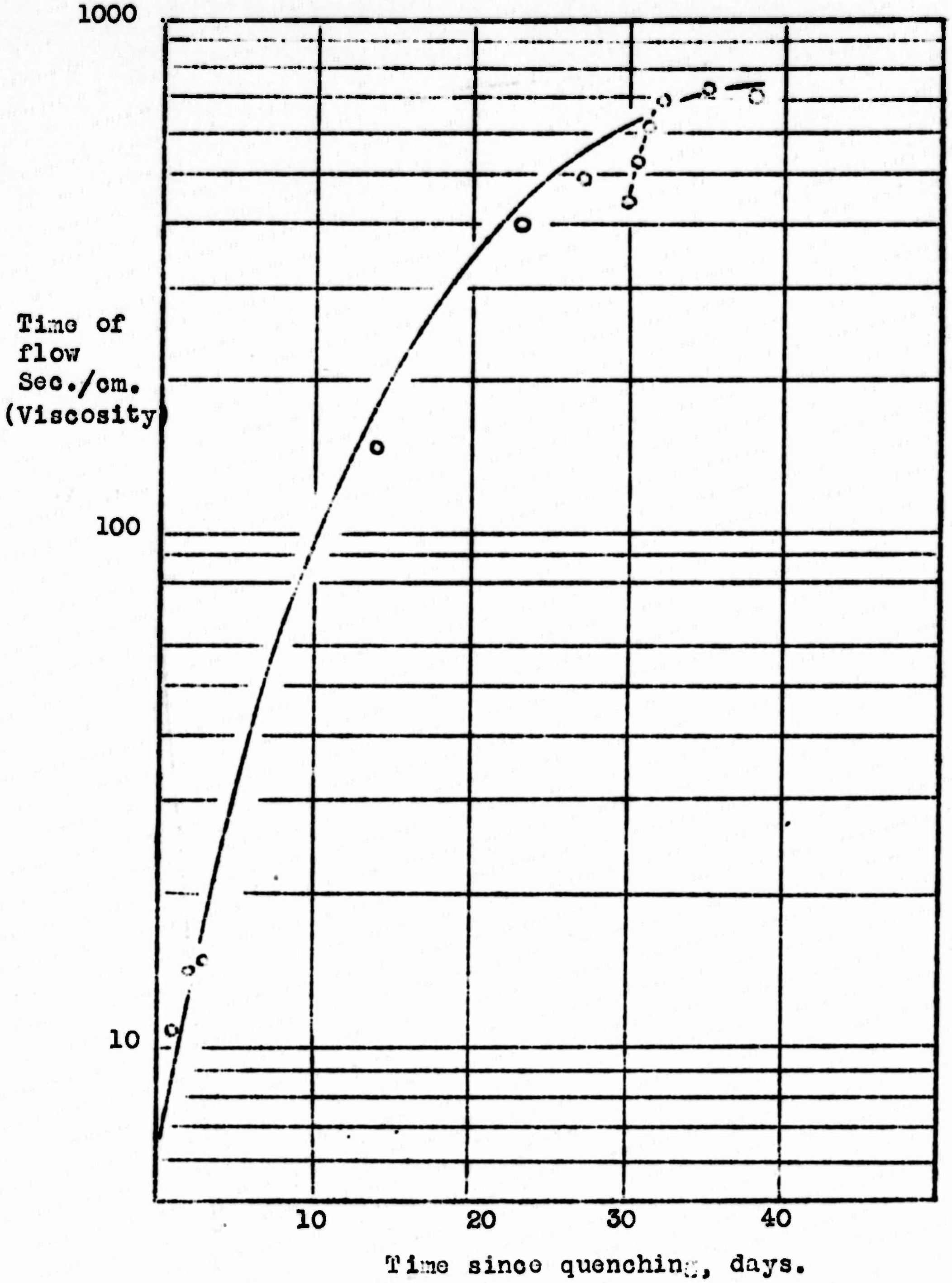
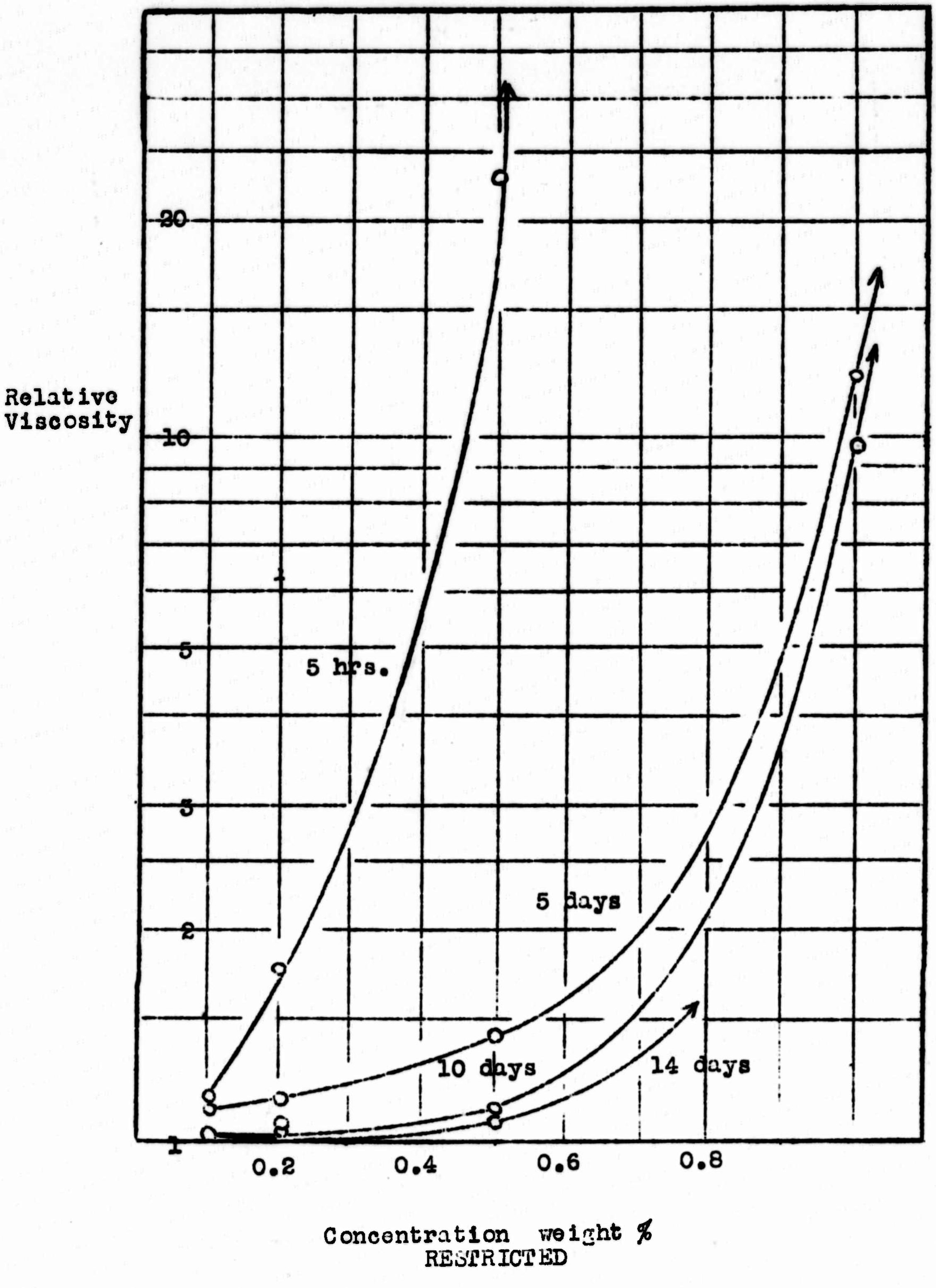


Figure 39


Relative Viscosity
20
10
5
3
2
1
0.2
0.4
0.6
0.8
5 hrs.
5 days
10 days
14 days
Concentration weight %

solution is stored in the viscometer and frequently measured or stored undisturbed in a glass stoppered bottle. Heating seems to accelerate the aging process. The comparative results were obtained over short periods of time during which this aging effect is negligible.

ii) *Effect of Concentration.* The viscosity increases with concentration, at first rather less than the usual logarithmic relationship, but at high concentration the increase is many times greater than logarithmic. This is shown in Figure 39.

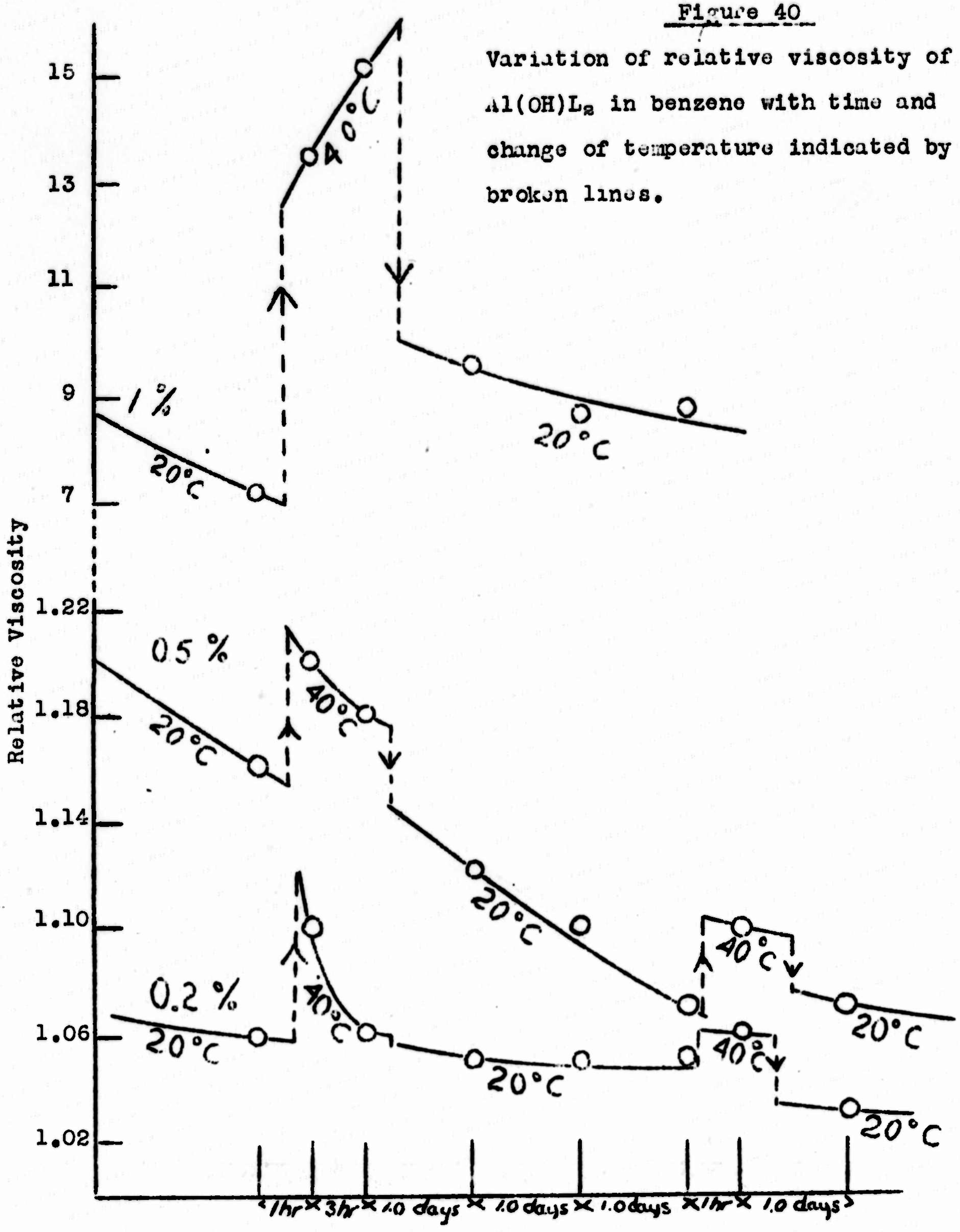
iii) *Effect of Temperature*. The remarkable effects of heating and cooling solutions of aluminum dilaurate are shown in graphs in figure 40. Raising the temperature from 20°C to 40°C results in all cases in an increase of *relative* viscosity with respect to pure benzene. The 1% solution even shows an increase in *absolute* viscosity with rise of temperature.

This behavior resembles two other well known cases, that of methyl cellulose in water and of nitrocellulose in alcohol, which gels upon increase in temperature. There is furthermore a marked contrast between 1% and more dilute solutions. Solutions containing 0.1 to 0.5% of soap showed a rather rapid decrease upon remaining at 40°C, and upon cooling back to 20°C they showed a lower viscosity than before heating, and upon a later second heating at 40°C, a smaller rise. This indicates that the aging process was accelerated by heating and was in the direction of lower viscosity, even while heating itself raises the relative viscosity.

The 1% solution increased in viscosity while at 40°C and returned to a viscosity at 20° higher than previously, and then

Figure 40

Variation of relative viscosity of Al(OH)L_2 in benzene with time and change of temperature indicated by broken lines.



decreased but slowly. This suggests that this more concentrated solution may have a different organization at the higher temperature at 40°C. The primary particles are far smaller, and there must therefore be a reorganization of the effective aggregates.

c) Osmotic Measurements, $Al(OH)2$ in Benzene. Osmotic observations were made with the glass osmometers described by R.H. Wagner(Ind. Eng. Chem. August 1944 16 , 520) and supplied by the Scientific Apparatus Company of Bloomfield N.J. The cellophane membranes were swollen in water and aqueous zinc chloride, the water then being replaced in successive stages, through dioxane to pure benzene.

1% solutions of aluminum dilaurate in benzene are liquid at all temperatures; the osmotic pressure changes from less than 1mm. at 18°C to 75 mm. at 25°C , and 190 mm. at 40°C. Hence the average degree of association changes from about 8000 molecules at 18°C to about 30 at 40°C. In 0.001% solution the number of molecules per average particle is only about 6, independent of temperature. Hence the particle weight of pure aluminum dilaurate in benzene solution varies reversibly between several thousand and several million depending upon concentration and temperature.

Aluminum dilaurate in benzene has therefore been proven to be an association colloid.

In contrast, cellulose derivatives, rubber, etc., are polymeric colloids. Their particle or molecular weight in solution is assumed to be independent of temperature and of concentration, and it is derived by extrapolating the actual measurements to infinite dilution. Association or physical linking, which must occur in real concentrations, is commonly ignored. Soaps in water are now universally recognized as the prototype of association colloid. The tendency to association increases rapidly with increase in molecular weight. For example, colloid forms from molecules of soap with six or eight carbon atoms only in concentrated solution. It forms above 0.01N for twelve carbon atoms, and already at 0.0006 N for oleates with eighteen carbon atoms. The tendency to associate appears to be the rule with higher molecular weight compounds of suitable shape. Innumerable synthetic detergents illustrate this.

The typical picture with polymeric colloids such as polystyrene(Bartovics and Mark,J. Am. Chem. Soc. 65, 2319 (1943) may be outlined in two sentences:

Osmotic pressure of polymeric colloids. The osmotic pressure divided by concentration increases rapidly with concentration.

Viscosity of polymeric colloids. The specific viscosity divided by concentration tends to increase, sometimes greatly, with concentration.

The picture with aluminum dilaurate may be summarized in three sentences:-

Osmotic pressure of Al(OH)L2 in benzene. The osmotic pressure divided by concentration decreases very rapidly with concentration at room temperature $(Al(OH)L2)_{30}$ for 0% → $(Al(OH)L_2)_{4000}$ for 1%; although at 50°C it remains constant at $(Al(OH)L_2)_{30}$.

Viscosity of $Al(OH)L_2$ in benzene. The specific viscosity divided by concentration tends to increase with concentration.

This becomes enormous when 1% concentration is reached.

Viscosity of (Al(OH)L_2 with temperature. In contrast to osmotic particle weight which decreases for 1% from $(Al(OH)L_2)_{4000}$ to $(Al(OH)L_2)_{30}$ with rise of temperature, the specific viscosity of 1% increases about two fold.
The contrast therefore appears in the relative increase of osmotic pressure for polymer particles and the great decrease for the aluminum soap. Again, both polymer size and resultant viscosity are independent of temperature, whereas with soap the particle size decreases so greatly while the viscosity doubles.

Interpretation.

It is clear that the important properties of these aluminum soap systems are those of an association colloid, not a polymer colloid.

The greatly enhanced viscosity at the higher temperature has to be accounted for by far smaller particles but more extensively or effectively linked in very loose aggregation.

It may be concluded with certainty that the observed viscosity of hydrocarbon soap systems is a structural viscosity.

To clarify this it may be recalled that Einstein showed that for a given amount of colloid within the liquid, the degree of subdivision or particle size is without important influence upon the viscosity. Furthermore for sodium oleate in water, it was shown by M.E.Laing McBain (J.Chem.Soc. London 1910) that a sol and a jelly of the same composition and temperature possessed primary particles of the same size as shown by osmotic properties and conductivity, etc.; they differed solely in rigidity and elasticity. The mechanical properties of the jelly are not due to the primary particles as such but to their loose ramifying aggregation which effectively immobilizes much of the free solvent. This explanation remains as that appropriate for aluminum dilaurate in benzene.

4. Thermodynamic Stability.

The question of thermodynamic stability of the various forms and state of a system is of fundamental importance since spontaneous changes within it proceed always from less to more stable states. Thus if a jelly is the stable form under a set of conditions, and we observe a gel or a sol under the same set of condi- we may be certain that if they change, it will be towards the jelly.

Of course we are not interested in the absolute thermodynamic stability with respect to ultimate products of evolution which in our system might be carbon, hydrogen and some low molecular weight basic salt of aluminum but in the relative stability of those states which can form spontaneously under ordinary conditions.

Conversely experimental observation of such changes as described in the preceding section is the simplest method of obtaining the relative stability of the initial and first state. We can thus summarize these observations as follows:

1) **The Dry Soap.** The most crystallized form is the stablest of the various forms of aluminum soap. This is always true when crystalline and amorphous forms of the same substance are compared below the melting point of the solid. It is further confirmed in our case by the higher melting point of the more fully or coarsely crystalline material, so that a less crystalline soap could melt into a liquid which, at the same temperature, would crystallize in contact with the more crystalline form; by its lesser swelling in cyclohexane and higher transition temperature to jelly.

ii) *The Gel*. The gel form of swollen soap is stable with respect to both the jelly and the dry soap-sol mixture over a limited range of temperatures below the transition temperature to jelly, since (a) the jelly often reverts spontaneously to gel at lower temperatures and (b) the soap even in the most crystalline form we were able to obtain, swells markedly at temperatures 5-15°C below the transition temperature and remains in this swollen condition for several days without becoming a jelly.

iii) *The Sol*. It is stable at sufficiently high temperatures since it forms spontaneously from the gel or jelly on heating and except for pyrolysis no further change should be expected.

iv) *The Jelly*. It is truly stable at temperatures intermediate between those where the gel and sol are stable. It is possible that the jelly may be stable only above a certain concentration (of the order of 2% for $Al(OH)L_2$ in cyclohexane). At lower concentrations the gel and sol seem to be the only stable forms. A jelly might be formed spontaneously at these lower concentrations by cooling the sol but it would be unstable with respect to gel.

At higher concentrations e.g. 5-10% $Al(OH)L_2$ the jelly forms spontaneously from gel upon heating to 50°-55°C and from sol by cooling below 150-100°C. The first transition is rapid and sharp, the second slow and indefinite but certain. This shows that in this region the jelly is stable with respect to both gel and sol.

The existence of stable gels and sols has been demonstrated previously on other colloidal systems but this is believed to be the first demonstration of true thermodynamic stability of a jelly

v. *Conclusion.* From a practical point of view it appears that only the jelly form has the desirable properties of stringiness and plasticity while the gel is too crumbly and the sol too fluid.

The proof of thermodynamic stability of jelly shows that it is not a priori impossible to prepare thickened fuels having an indefinite storage stability.

5. The Phase Diagram.

A phase diagram should represent the regions of conditions of temperature, pressure and composition under which various phases of a system exist. It is usual to represent on such diagrams conditions of thermodynamic equilibrium under which the most stable phases in each region are separated by permanent plane surfaces, or, as Gibbs called them, "coexistent" phases. Only very incomplete equilibrium phase diagrams can yet be drawn for aluminum soaps and hydrocarbons.

For metastable systems, non-equilibrium phase diagrams showing the region of temporary existence of metastable phases may also be drawn and may have definite application.

In such metastable systems it is often difficult to ascertain when a new phase begins to form if the surface of separation is not plane. For example the presence of a trace of gel in a large amount of jelly is easily seen but the presence of 10% or 20% of jelly or sol in a gel of swollen soap would be very difficult to detect if the soap fills the liquid completely. It is only when a supernatant liquid is visible that the presence of the sol or jelly and the existence of a two phase region may be easily ascertained. This accounts for the lack of definite boundaries of the two phase regions of the diagrams presented.

The available evidence indicates that for aluminum soaps in hydrocarbons the phase diagrams for the various metastable states differ greatly.

For the stablest form of $Al(OH)L_2$ available, the "crystalized" one, a large two phase zone between gel and sol forms is present below about 40°C and the gel-jelly transition temperature rises

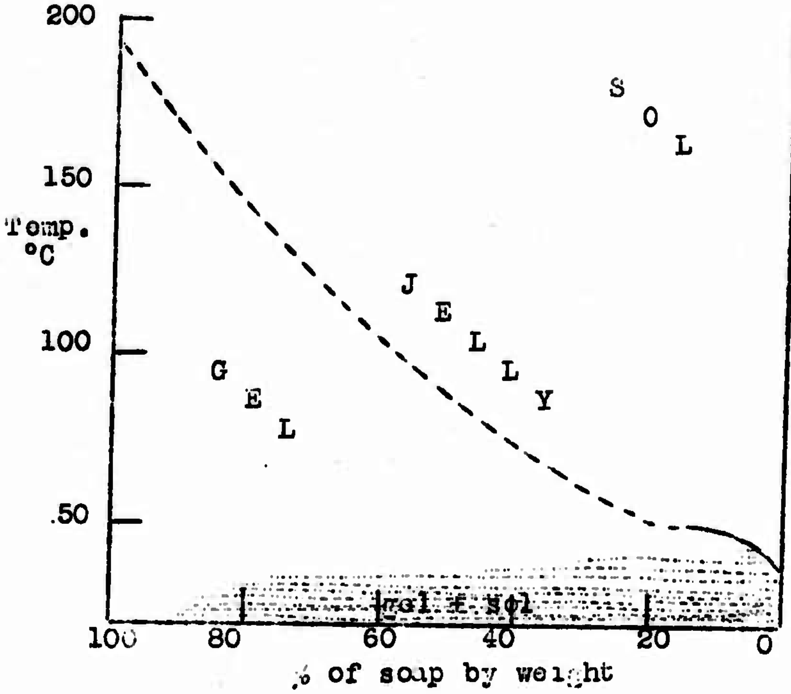


Figure 41

Outline of Phase Diagram of the System "Crystallized" Al(OH)L_2-Cyclohexane

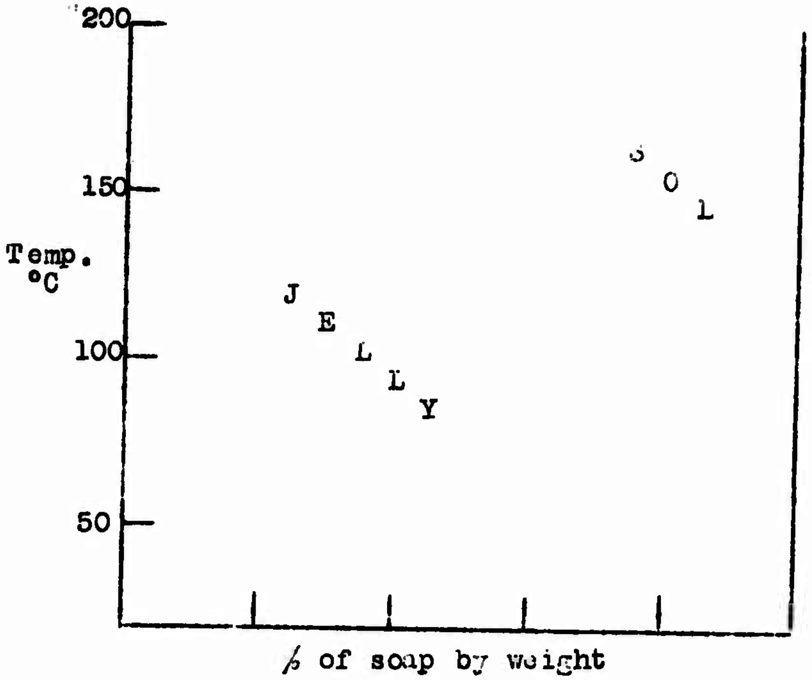


Figure 42

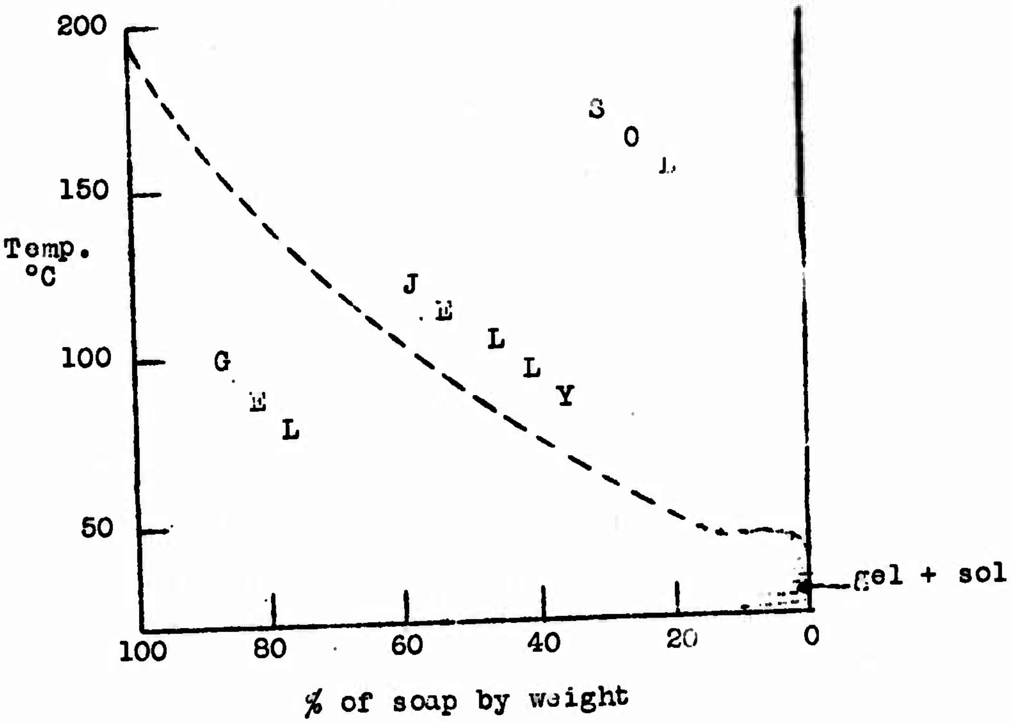
Outline of Phase Diagram of the System "Recovered from Jelly Al(OH)L_2-Cyclohexane to about 50°C as indicated in figure 41. The exact position of those lines and their extension to higher concentrations remains to be investigated.

For the most unstable form of soap, that recovered from jelly or sol, there are no two phase regions but only a continuous transition between the jelly and sol states, as indicated in fig. 42.

For the "original" aluminum dilaurate which is a mixture of many forms of various stabilities the two phase zone is narrower and the known part of the gel-jelly transition line some 10°C lower than for the crystalline dilaurate (fig.43).

Figure 43

Outline of the Phase Diagram of the System "Original" $Al(OH)L_2$-cyclohexane.



6. Characterization of Peptizers; Their Lack of Relationship to Polarity as Measured by Dipole Moment.

The term "Peptization was introduced in 1864 by Graham to denote the liquefaction of a gelatinous material, whether jelly or gel, by the addition of a small quantity of another substance (see likewise Hack's Chemical Dictionary 1937). It thus involves reversal of coagulation or of gelatinization by means of an added peptization agent. It consists of loosening the bonds between adjacent particles, by substituting solvent or peptizer to satisfy the broken linkages.

Thus peptization, properly speaking, is but a special case of liquifaction of gel to jelly or sol, or jelly to sol, a transformation produced by the addition of a small proportion of a peptizer. We have seen that the same or similar changes may be produced by changing the temperature of the system, its history, the state of the soap, or nature of the solvent.

Agents whose presence in small amounts peptizes aluminum soap in hydrocarbons are now of great practical interest, and can correctly be termed 'peptizing agents".

It is generally assumed that a peptizer must itself be appreciably soluble in the liquid medium. If so, water might (a) act through liberation of fatty acid, or (b) through itself being solubilized by the soap in the hydrocarbon. The peptizer must have some affinity for the colloidal material. For example, it may be strongly sorbed on the surface of the colloidal particles, both freeing them from each other and exposing soluble groups to the solvent. Sorption is often favored by low solubility or by the presence of polar groups in the peptizing agent, although sorption is likewise often specific. The peptizing agent may itself be either colloidal, as with soaps, or not, as with phenol or fatty acid in hydrocarbons.

In water, acids and alkalies and salts often act as peptizing agents. Hence peptizing agents are frequently referred to as "polar compounds". This term has two meanings, the first of which embraces ionic compounds or electrolytes. This definition is not relevant in hydrocarbon systems. The second usage defines polar compounds as those which possess a permanent dipole moment. For example the dipole moment of water in Debye units is 1.8 , that of acetic acid is 0.74, that of toluene is 0.4-0.5, and benzene has none. Only unsymmetrical molecules can be polar in this sense, no matter what "strongly polar groups" may be present

Most of the known peptizers for aluminum soaps are polar in Debye's sense. A simple experiment serves to test whether a dipole moment is necessary or whether this was just a coincidence

The three dinitrobenzenes, ortho, meta and para, have the same composition, but different structural formulae, with dipole moments of 6.0, 3.7-3.8, and 0-0.32 respectively. Thus the polarity of the ortho-dinitrobenzene is very exceptionally large, that of meta large, while that of para is small or perhaps negligible. Hence we compared their efficacy as peptizers as follows, showing that there is little to choose between the most polar and the least polar in their reduction of the viscosity of Napalm jelly:-

Para-dinitrobenzene is only slightly soluble in benzene (about 2.5%) and even less in more paraffinic hydrocarbons.

Therefore 2.3% by weight solutions of the three dinitrobenzenes as obtained from Eastman Kodak were used. Gels containing six grams of Napalm (McGean No. 462) per hundred cc. of these solutions and of pure benzene were prepared under strictly comparable conditions.

At first the ortho, meta and para and the control benzene jellies were in the stated order; but next day all three dinitrobenzenes had lowered the viscosity comparably, that of the benzene jelly being unaltered. After 48 hours the times for equal amounts of flow under gravity were:

para . (least polar)	1
ortho (greatest dipole)	1.19
meta (large dipole)	1.65
benzene control	2.70

and after five days,

ortho	1
para	1.1
meta	2.0
benzene	3.1

This shows definitely that polarity in Debye's sense is not a determining factor in peptization.

One may also speak of polar groups within a molecule as measured by calculated dipole moments ascribed to each bond or group. Thus the nitro-aromatic groups in all three nitrobenzenes would have the same polarity, even though in p-dinitrobenzene the two polarities being symmetrically disposed neutralize each other. If this definition were to be applied it should be remembered that the carbon-hydrogen bond itself is to be considered as a strongly polar bond and hydrocarbons, such as paraffins, which have no peptizing action would have to be considered as being also polar molecules, thus rendering the term meaningless.

Therefore polarity, however defined, does not seem to be directly or simply correlated with peptization.

7. Forces operative in thickening fuels by means of soap.

One of the ultimate goals of this research is a clarification of the nature of the factors causing the useful rheological properties of thickened fuels. It appears probable that a small amount of soap can produce a great increase in viscosity of hydrocarbon because the molecules of soap associate to form primary colloidal particles and these particles then stick together in loose ramifying aggregates to form a brush-heap structure enmeshing and immobilizing large tracts of the solvent. This is essentially the same mechanism which operates to form jellies of sodium oleate in water.

There is not enough information available yet to decide upon further details of this picture, but a few remarks may be made.

i The particles active in thickening aluminum soap jellies are not original soap but something resulting from the interaction of solvent and soap.

Höppler (Fette und Seifen 49, 700-708 1942) in the study of mineral oil thickened by calcium soaps was led to the conclusion that a colloidal dispersion of calcium oleate in oil was formed. The calcium oleate retained most of its original characteristics in the finely dispersed state, particularly its melting point. Above the melting point of the soap a dispersion of liquid droplets was present, showing little or no thickening. Below the melting point of the soap it became a colloidal dispersion of fine fibrillar crystallites of the soap which by interweaving enmeshed the liquid and caused high viscosity with but small dependence on temperature. This view was supported by measurement of viscosity on a sample of $CaCl_2$ grease above and below the melting point of the soap (83-84°C). His results are reproduced in figure 44, which shows at this temperature a large discontinuity and dislocation between two flat portions. It may be noted that the viscosity scale is logarithmic, so that the discontinuity corresponds to about a 15 fold change.

To determine whether this hypothesis could be applied to our system, the viscosity of two $AlOHL_2$-cyclohexane mixtures was measured in the neighborhood of 196°C, which is the melting point of the pure soap. The results shown in figure 45 prove that this system shows no discontinuity in the viscosity curve at the melting point of the soap. Thus Höppler's theory, which may or may not be true for calcium greases, is not generally applicable to hydrocarbon systems thickened with aluminum soaps. In these systems, particularly in that containing 9.5% of aluminum soap, the viscosity is much higher than that of the pure solvent, and decreases uniformly about 3-fold per 10°C rise in temperature. The soap is therefore exerting a marked influence, but not through building up a scaffolding or felt of ordinary soap crystals.

This agrees well with the view that soap molecules associate to colloidal particles which then stick together in loose aggregates, enmeshing and immobilizing large tracts of solvent, but also shows that the colloidal particles are not original soap but something that results from the interaction of solvent and soap.

ii In water association of alkali soap molecules is due to the great affinity of water molecules for each other

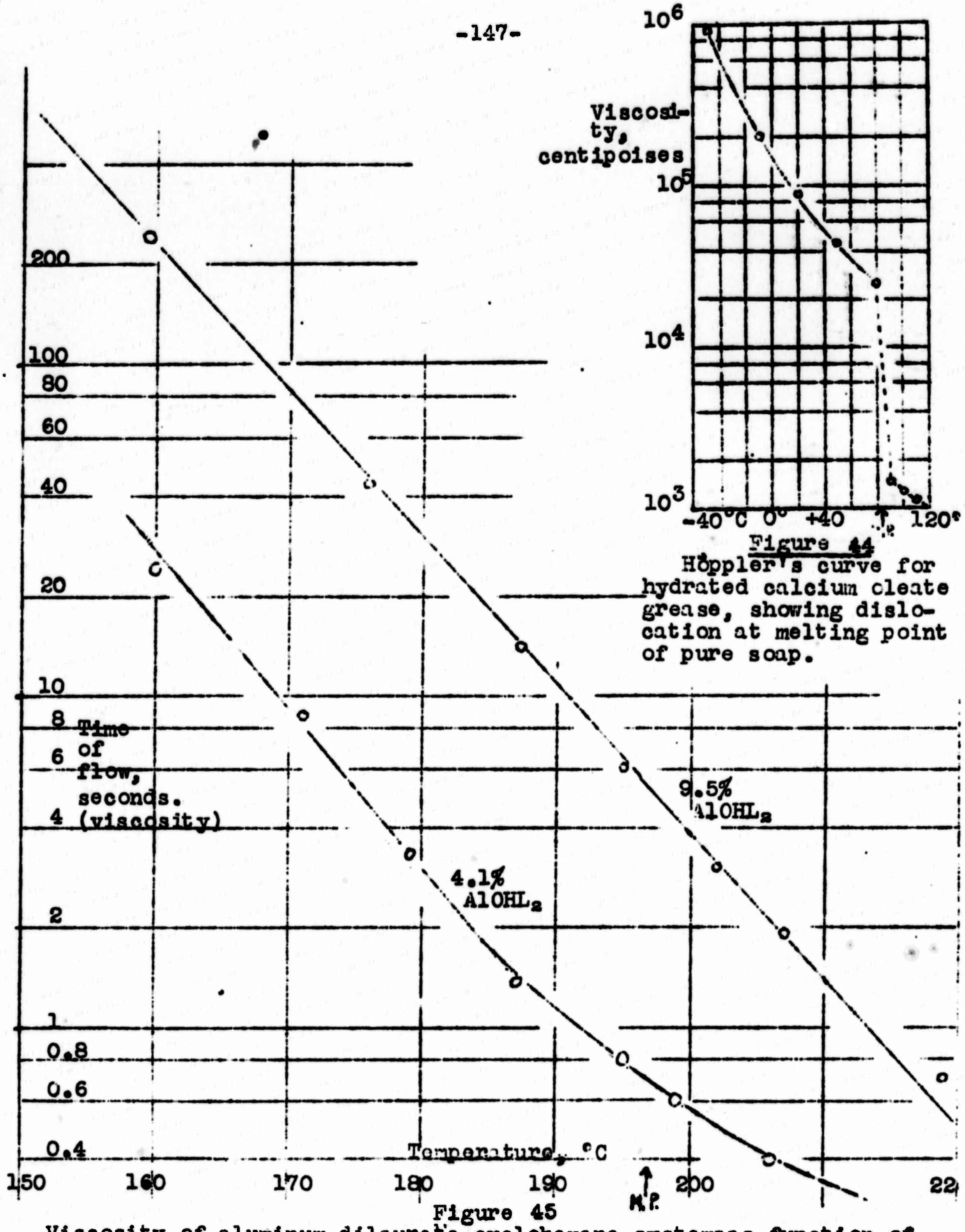


Figure 44
Höppler's curve for hydrated calcium oleate grease, showing dislocation at melting point of pure soap.

Figure 45
Viscosity of aluminum dilaurate-cyclohexane systems as function of temperature, showing no discontinuity at melting point of soap.

and for the polar groups, as compared with their affinity for the hydrocarbon end of the soap. The soap is held in solution because of its polar groups, while the hydrocarbon ends are expelled from the water and forced together.

In hydrocarbon solvents the reverse picture may be true. The affinity of the solvent for the hydrocarbon part of the soap may hold it in at least partial solution, while the polar groups are expelled therefrom and are strongly attracted to each other.

iii Specific effects of aluminum.

Specific effects due to the coordinating tendency of the aluminum ion may well exist, but it is believed that these are not of primary importance. The same fundamental phenomena that are observed with aluminum soaps, i.e., formation of swollen gels, transparent jellies and thickening in general, are also observed in hydrocarbon systems with sodium stearate or silver soaps. In the latter cases an explanation of this behavior by coordination seems precluded and it is altogether probable that the forces causing such similar behavior are essentially the same.

Observations on silver palmitate were published by J.W. McBain and W. L. McClatchie, J. Phys. Chem. 36, 2567 (1932).

The work on sodium stearate hydrocarbon system has been mentioned in our September report and has since been confirmed and expanded in this laboratory outside this contracted and reported below.

8. The system sodium stearate-cyclohexane.

Dry sodium stearate, finely powdered gamma cystalline form, swells somewhat in cyclohexane at room temperature. The particles become slightly translucent and markedly birefringent. Sorption experiments show that they fix only a few percent of cyclohexane at 50°C as shown by the isotherm reproduced in figure 46.

As the temperature increases, sodium stearate swells more, at first slowly, then rapidly in the neighborhood of 90°C reaching some ten volumes at 95°C, filling the liquid completely if less than that amount of liquid is present.

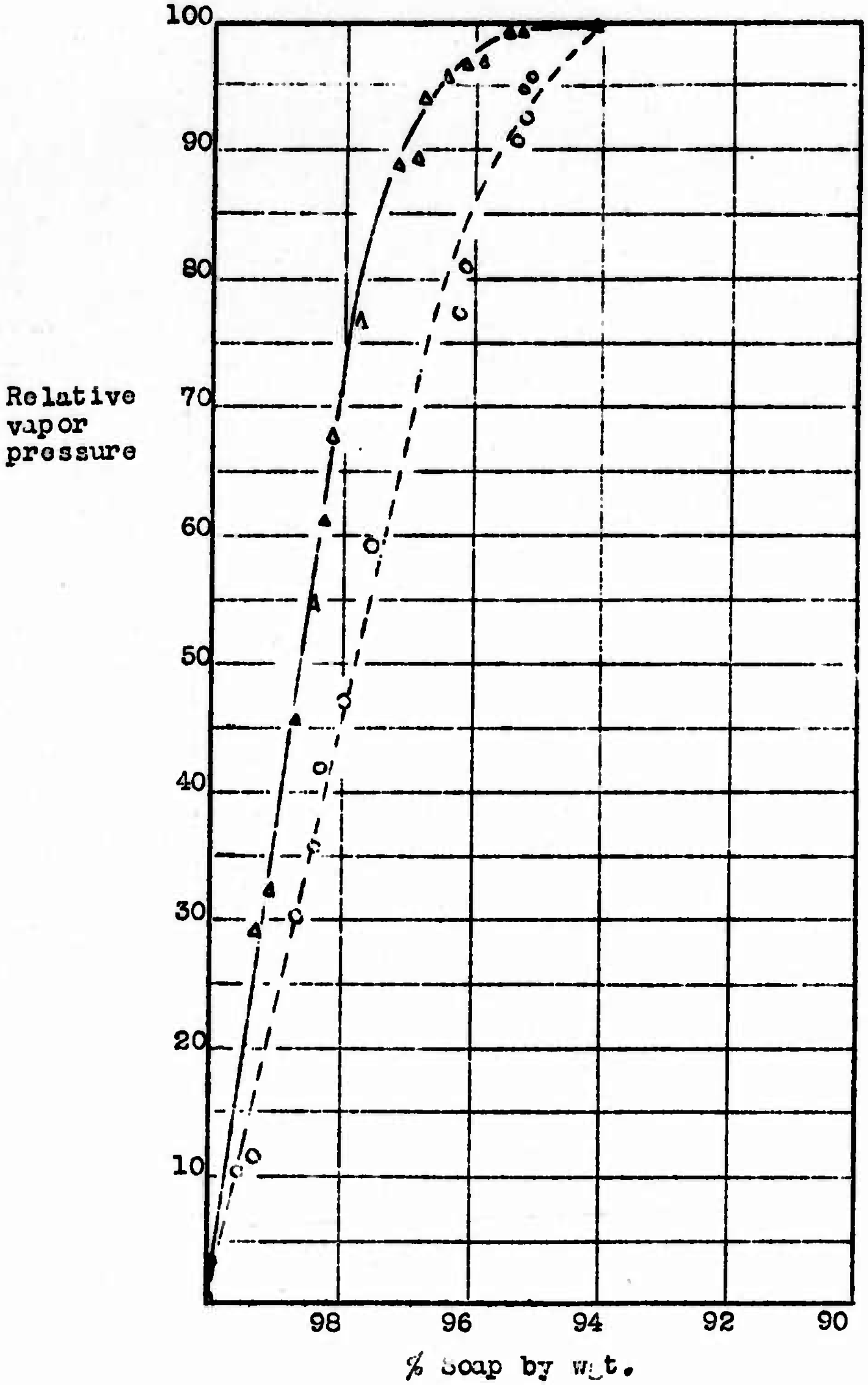
In systems comprising less than 50% of soap, a sudden change to a liquid crystal form occurs sharply at 98°C, the opaque swollen soap becoming translucent and homogeneous and remaining strongly birefringent.

At a still higher temperature, the birefringence disappears in systems containing less than 25% of soap and an isotropic sol or jelly is obtained; but as the temperature rises much above 240°C and the critical region of cyclohexane is approached, the soap precipitates again as a dense flocculent layer and settles to a compact layer.

At higher concentrations the various forms are more difficult to determine but the isotropic region is raised much above both the melting point of the soap (288°C) and the critical temperature of the solvent (281°C). In fact, systems containing 45 to 85% soap are waxy liquid crystals at 310°C, the highest temperature investigated.

Figure 46

Sorption of Cyclohexane by Sodium Stearate, NaSt, at 50°C.



A summary of these observations is presented in the outline of a phase diagram in figure 47.

Reversibility. The 98°C transition is irreversible; the system does not recover its initial appearance. For example a system containing 5-10% of soap which is a white powdery, easily settling suspension at room temperature before heating, becomes a syneretic birefringent swollen gel at room temperature after heating.

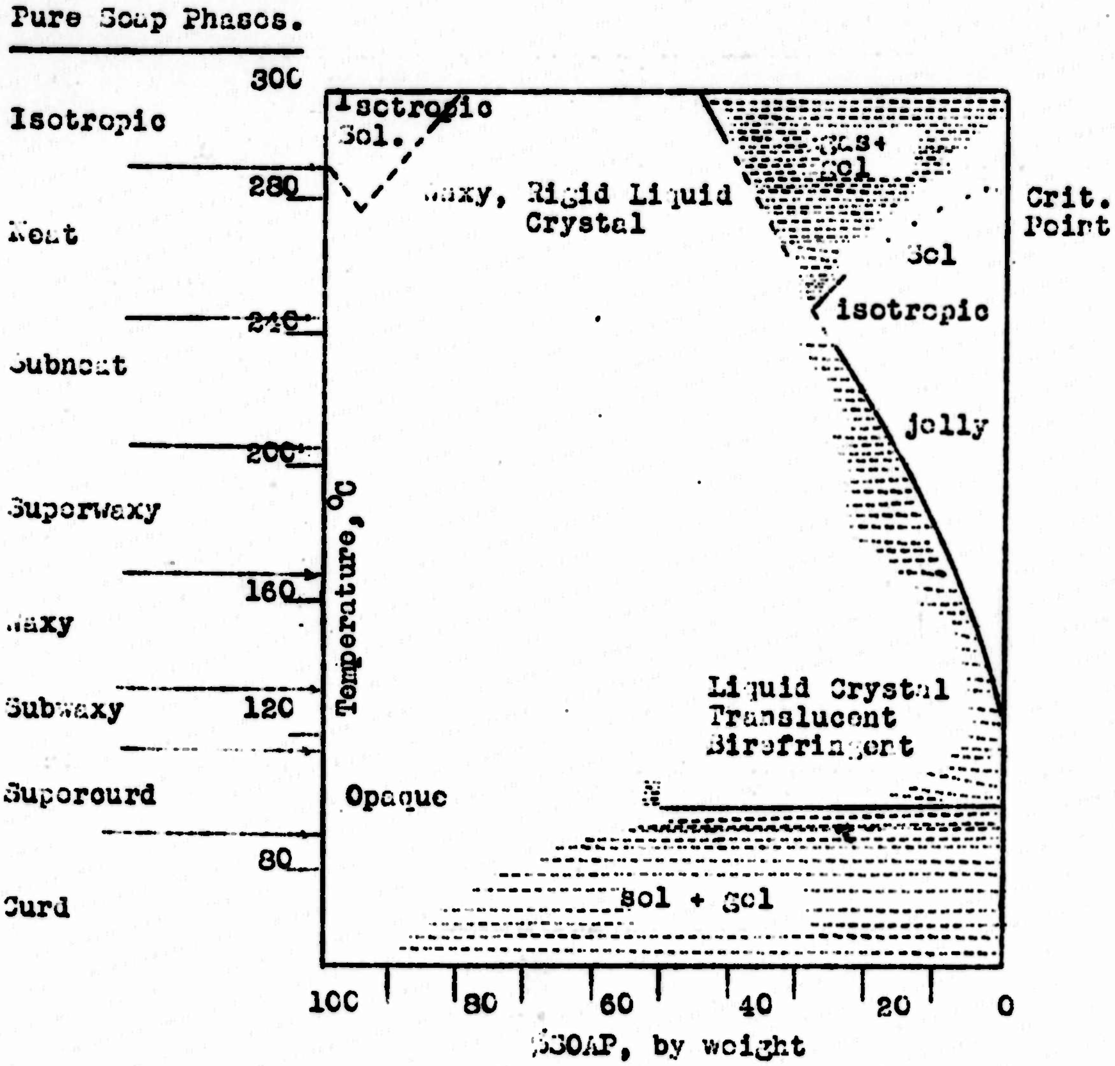
The original form is the more stable. This may be seen from the lower solubility in cyclohexane and the occasional reversion of the other forms.

The thin isotropic sol obtained in dilute systems at high temperature gradually solidifies to a stiff transparent jelly upon slow cooling which may exist without syneresis from 120-50°C, and then syneresis occurs upon further cooling.

Effect of water. Only a few exploratory observations on the effect of small amounts of water have been made. They showed that the presence of 0.1% of water lowered the temperature at which an isotropic sol is formed from about 220°C to 110°C, and upon cooling caused the appearance of a white curdy phase and a transparent liquid crystalline phase, both completely absent from the anhydrous system. The presence of 1% of water further lowered the isotropic temperature to 95°C, and it caused curding of the whole system.

Figure 47

Temperature-Composition Phase Diagram of the Anhydrous Sodium Stearate- Cyclohexane System.



CHAPTER IV

SUGGESTIONS SUBMITTED

In this chapter are collected together submitted suggestions dealing mainly with practical applications, and not directly related to our main problem "The Fundamental Study of Aluminum Soap." A considerable amount of experimental work has been done on the use of metallic sodium, and some on the use of Agripol (Norepol) in thickened fuels, while other aspects were submitted simply in the form of ideas without performing any experimental work.

A. The Use of Metallic Sodium.

A small amount, 0.5% to 10% of an alkali metal such as sodium or potassium, dispersed finely throughout the body of an incendiary gel, makes it ignite spontaneously on contact with water and prevents its extinction by this agent. It should then greatly increase the destructive properties of an incendiary.

The alkali metals may be used either naked or enclosed.

(a) Use of naked sodium. A report summarizing this work was submitted on November 8, 1943. It showed that the incendiary qualities were excellent, as expected, minute particles of sodium acting as a water-activated match. The rheological properties of gels were affected, a marked increase in rigidity occurred at room temperature, and liquefaction often at higher temperatures. Gels which did liquefy at higher temperatures, often recovered at room temperatures. However, it was possible to obtain gels which neither liquefied nor settled when heated 24 hours to 150°F, or kept several weeks at 120°F.

This work was transferred elsewhere at that point, and the exact conditions necessary for always preparing stable gels have

Five percent of metallic sodium enclosed in gelatin capsules failed to produce any visible difference in the properties of a 6% Napalm gel after 2 weeks at 150°F, as compared with a sodium free blank. (McGean Lot 462 in Specification Gasoline). Nor was any difference visible after 8 months of storage in the laboratory.

This shows that the gelatin is completely effective in preventing interaction between sodium and Napalm.

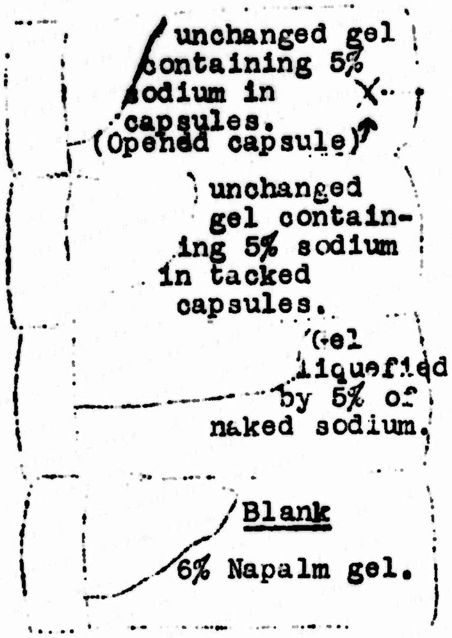
Figure 48 shows four samples of Napalm gel of the same composition (except for sodium and capsules), comprising a blank, two gels containing 5% of sodium in capsules and one containing the same percentage of naked powdered sodium. All had been kept 4 days at 150°F. It will be seen that the one containing naked sodium is largely liquefied while the former three gels show no appreciable differences.

The incendiary action of sodium is modified by enclosure in gelatin. However it is still very advantageous.

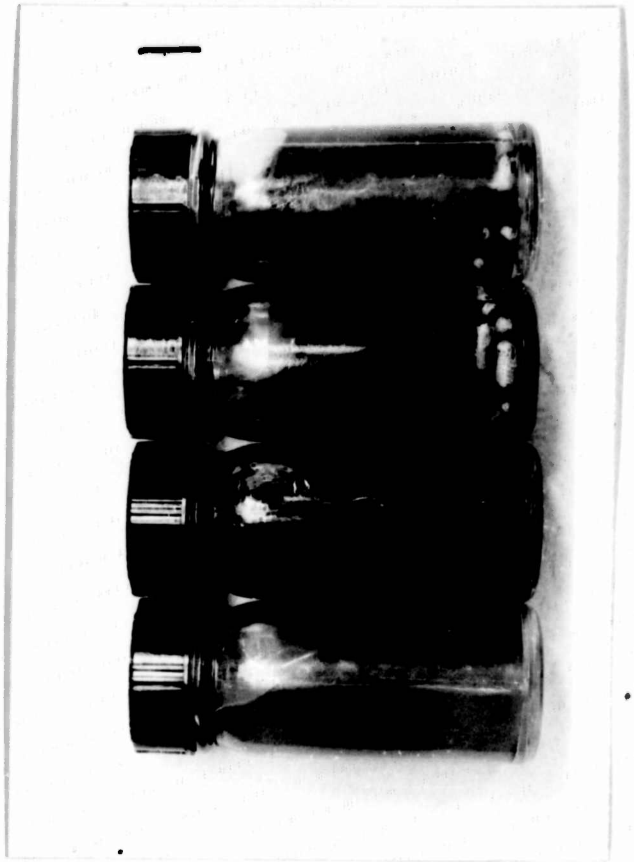
A capsule containing sodium ignites within 2-4 minutes when dropped into water. When surrounded by Napalm gel the time is longer and ignitions after from 3 to 45 minutes were observed. A stream of water causes more rapid and sometimes instantaneous ignition. Thus while naked sodium ignites instantaneously on contact with water, capsules containing sodium show merely delayed ignition. Furthermore while naked sodium in general burns in place, the capsule often acts as a micromortar, projecting ignited particles to some distance.

When the gel burns the gelatin is weakened and finally carbonized. Part of the sodium may burn but in general it becomes covered with carbonaceous matter. If water is used in an attempt

FIGURE 48



Outline showing important features of the adjacent photograph.



Photograph of samples containing 6% Napalm gel (McGeon, Lot No. 462 in specification gasoline) with and without sodium naken in capsules which have been kept for 4 days at 150°F.

to extinguish the burning gel it can interact instantaneously with such sodium which ignites immediately the way it would if naked, and thus it prevents extinction.

After the gel has burnt out spontaneously, a substantial proportion of sodium remains unchanged, buried in the carbonaceous residue, and this inflames spontaneously if water is sprinkled thereon. This new effect is almost absent in case of naked sodium. It makes handling of burnt out incendiaries much more hazardous.

The sodium metal enclosed in the capsule does interact with moisture contained in the capsule originally and perhaps also with some diffusing from the gel through the gelatin. A slow stream of small bubbles therefore slowly escapes from the capsule and may occasionally cause the latter to open and expose the Napalm gel to direct action of the metal. One such opened capsule with the corresponding formation of gum is visible as a black spot in the top bottle of Figure . This accidental opening was completely prevented by tacking the two parts of the capsules together by Duco cement without preventing the escape of hydrogen.

To summarize: the experiments described show that gelatin capsules can be used successfully to prevent interaction between Napalm gel and metallic sodium while maintaining the incendiary advantages of the latter. Large scale testing of this variant and evolution of a practical large scale method of producing gelatin membranes (or other membranes such as for example nitrocellulose or other plastic) around sodium are beyond the facilities of this laboratory. It is recommended that they be handled elsewhere.

B. Preparation of Thickened Fuel by Mixing Two Thinly Fluid Gasoline Solutions.

At the beginning of our program, we had available only one sample of Napalm (Nuodex PD2712?) which was very slowly and incompletely soluble in gasoline and had very little gelling power, due, presumably, to oxidation.

It was found that when the thin supernatant liquid from a mixture of 3% of this oxidized Napalm was mixed with a solution containing 50% of Agripol (Noropol) a gel was formed rapidly. The stiffest gel resulted when the final mixture contained 2% of Napalm and 17% of Agripol. Reducing the Agripol content reduced the stiffness and favored syneresis. Increasing the soap content increased both stiffness and syneresis.

The best gels were stiff, elastic and stable for over a year at room temperature but rather short.

After unoxidized Napalm was received, work on this aspect was discontinued but if field requirements call for thickening, produced rapidly by mixing of fluids, it may be a promising alternative to Dr. Alexander's method. Since the effect is almost immediate, a solution of Agripol might be useful to convert thin fiercely-burning flame thrower fuel into thickened fuel as desired.

C. A Possible Role of Protective Colloids in Napalm.

It has been found both in Britain and by Harshaw that the presence of small amounts of various proteins and of starch during precipitation of an aluminum soap markedly increases the viscosity of its hydrocarbon gels. This is interpreted as a "protective colloid action" changing the physical state of the soap. Usually, however, any protective colloid must itself be stable in the solvent in question. Hence such an action could occur only during precipitation in the aqueous medium.

We would like to suggest the possibility of an alternative or supplemental effect to account for this result. The substances used are probably to a large extent sorbed or occluded by the precipitated soap, and upon drying may form very fine films or fibers which may then bind together adjacent particles. When the soap is placed in hydrocarbons these substances, completely insoluble but finely dispersed, may produce an increase of viscosit in the same way as paper pulp or other fibers, but with much greater efficiency due to the finer dispersion.

D. The Use of Naphthenic Acids of Higher Molecular Weight.

It has been noted that the formula for manufacturing Napalm includes the use of low molecular weight naphthenic acids. It was believed that the use of higher molecular weight naphthenic acids would give metallic soaps having greater thickening power. This was confirmed by preparing barium soaps of relatively pure high and low molecular weight naphthenic acids and thickening gasoline with these soaps. Another sample of commercial naphthenic acid was tried and found to be too diluted with unsaponifiable material to suitably thicken gasoline. However, sufficiently purified naphthenic acid of high molecular weight can readily be made available.

E. A Possible Approach to the Problem of Reducing Hygroscopicity of Napalm.

It was learned with great interest that work was in progress on reducing the hygroscopicity of Napalm by coating its particles (Broughton and Byfield, The Manufacture, Properties and Testing of Napalm Soap, O.S.R.D. Report 2036, p. 61). The approach seemed to call for a coating which is permeated slowly by water to reduce the rate of absorption of moisture by Napalm.

It is suggested that the same method might be effective through a different mechanism.

Napalm has a very large surface which is presumably quite active in absorbing almost any available substance. Absorption of any one substance will often reduce the affinity of an absorbing surface for any other substance. This is particularly true for substances having similar structure, e.g. possessing polar group, etc. Moisture is very easily absorbed and very detrimental. However if a substance, preferably polar, having little or no effect on gelling properties is allowed to be absorbed by this surface the affinity of Napalm for water should be appreciably reduced.

In other words, coating of particles by a substance capable of being adsorbed should affect favorably not only the rate of moisture absorption but also the equilibrium moisture content of the soap.

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ABSTRACT:

Aluminum soaps are studied in order to identify the phases utilized and to find how water is held by Napalm and its function in their hydrocarbon gel system. Well-crystallized pure dilurate is inert towards paraffins and even cyclohexane at ordinary temperatures, whereas when the same pure dilurate is more amorphous or glassy it readily swells and forms a true gel. The mono-soaps are comparatively inert toward hydrocarbons. Napalms contain appreciable amounts of inorganic impurities capable of absorbing or combining with water. Osmotic examination shows that a solution of aluminum dilurate in benzene is a sol.

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Incendiary mixtures