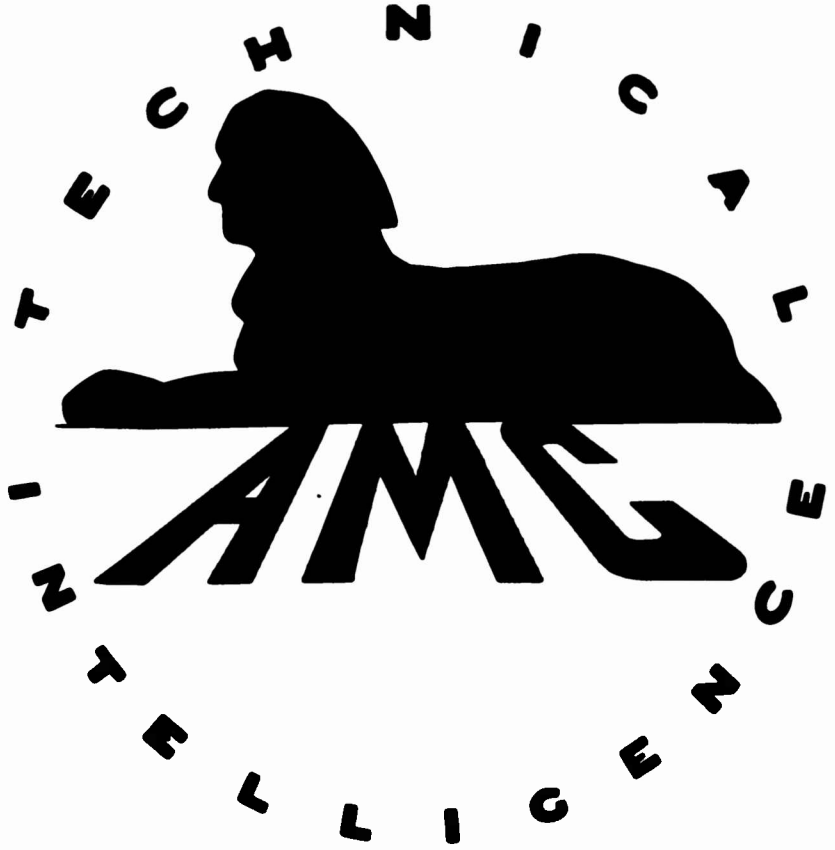
UNCLASSIFIED

AD NUMBER
ADA801540
CLASSIFICATION CHANGES
TO: **UNCLASSIFIED**
FROM: **RESTRICTED**
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; DEC 1944. Other requests shall be referred to Office of Scientific Research and Development, Washington, DC 20301.**
AUTHORITY
OSRD list no. 3 dtd 2-11 Jan 1946; OTS index dtd Jun 1947

THIS PAGE IS UNCLASSIFIED

Reproduced by

AIR DOCUMENTS DIVISION



HEADQUARTERS AIR MATERIEL COMMAND

WRIGHT FIELD, DAYTON, OHIO

The U.S. GOVERNMENT

IS ABSOLVED

FROM ANY LITIGATION WHICH MAY ENSUE FROM THE CONTRACTORS IN-FRINGING ON THE FOREIGN PATENT RIGHTS WHICH MAY BE INVOLVED.

WRIGHT FIELD, DAYTON, OHIO

REEL - C
1358
A.T.I.
33601

RESTRICTED

REPORT

Upon

Contract No. OEMsr-1057

Stanford University

by

Professor J. W. McBain

Short Title "Fundamental Study of the Structure and Characteristics of Soap-Thickened Fuels".

Scope Study of the structure and phase relations of thickened fuels in order to provide a more fundamental basis for understanding their properties.

General Field Gels, jellies and the theory of their structure.

Personnel Dr. Karol J. Mysels, fulltime since May 15, 1943.
Mr. Gerould H. Smith, part time since May 15, 1943.
Mr. H. Pomeroy, full time since May, 1944.
Dr. L. B. Rogers, part time since May, 1944.
Mr. R. H. Coe, full time since July, 1944.
Mr. R. Zentner, full time since July, 1944.
Mr. S. Marsden, full time since July, 1944.
Mr. G. Shields, part time since October, 1944.

Supervisor Professor James W. McBain.

RESTRICTED

STANFORD UNIVERSITY
DEPARTMENT OF CHEMISTRY
Stanford University, California

File No. 11-455
Contract OEMsr-1057
Problems C-3-10, 21
Liaison Officers:
Army: Brig. Gen. T.C. Rabrich
Navy: Comdr. J. H. Sides
Lt. Col. L. E. Marie (M.C.)

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

covering period July, 1944 - December, 1944

Distribution:

1	Harvard University (L.F. Fieser)
1	Standard Oil Development Co. (N.F. Myers)
1	The Texas Company (W. E. Kuhn)
1	Eastman Kodak Co. (E. K. Carver)
1	Harshaw Chemical Co. (K. E. Long)
1	Ferro Drier and Chemical Co. (G. H. McIntyre)
2	O.S.R.D. Mission, London
1	O.S.R.D. Liason Office
1	British Central Scientific Office
3	Canada, D.C.W. and S.
1	Australia, Munitions Supply Laboratory
3	British Petroleum Warfare Dept., New York
5	C.W.S. - Technical, Edgewood Arsenal
1	C.W.S. Laboratory - M.I.T.
1	Deputy Chief, C.W.S. - Technical Washington
1	War Department Liaison Officer with N.D.R.C.
1	Chief Division 11 (E.P. Stevenson)
1	Chief, Section 11.3 (H. C. Hottel)
4	Technical Aide (R.H. Ewell)

TABLE OF CONTENTS

SUMMARY 1

INTRODUCTION 1

CHAPTER I THE MAIN PROBLEMS STUDIED 4

A. Pure Aluminum Soaps 5
(a) The existence of pure soaps 6
(b) Polymorphism of aluminum soaps . . . 9

B. Free and Bound Acid 12
(a) Nomenclature and nature 12
(b) Experimental distinctions between combined, sorbed and free acid . . . 13
(c) The degree of binding of bound acid 15

C. Napalm. Its nature and Similarity to Disoap 16
(a) Composition 16
(b) X-ray diffraction 17
(c) Behavior in hydrocarbons 18
(d) Behavior with water 18

D. Significance of Various Methods of Determination of Moisture 20
(a) Free water 20
(b) Bound water 20
(d) Potential water 21

E. Gels and Jellies in Hydrocarbons 22

F. Additives in Soap-Hydrocarbon systems. . 24
(b) Use of solid fatty acids 26

CHAPTER II THE ALUMINUM SOAPS 27

A. The Precipitation of Aluminum Soaps and Factors Influencing the Results 27
(a) Our standard method of preparation 27
(b) Factors influencing the precipitation 29
(c) The effect of protective colloids in the preparation of Napalm 32

B. Extraction with solvents. 38
(a) Choice of solvent 38
(b) Apparatus 39
(c) Exhaustive Soxhlet extraction . . . 40
(d) Batch extraction under conditions approaching equilibrium 52

C. Extraction of Napalm 62
(a) Extraction with methanol ether and with acetone 63
(b) Extraction with isooctane 63
(c) Interpretation 64

TABLE OF CONTENTS CONT'D.

D. X-ray Examination of Aluminum Soaps. . . . 65
(a) General survey of x-ray diffraction diagrams 66
(b) Polymorphism of aluminum stearate and laurate 68
(c) X-ray evidence for the presence of some free acid 77
(d) X-ray evidence for molecularly bound acid 80
(e) The crystal structure of aluminum soaps 81

E. The Individual Aluminum Soaps 86

(a) Aluminum dilaurate. $Al(OH)L_2$. . . . 87
(b) Aluminum distearate $(Al(OH)Str_2$ . . 91
(b) Aluminum oleates 92
(d) Aluminum dicyclohexane carboxylate $Al(OH)(C_6H_{11}COO)_2$ 94
(e) Aluminum naphthenates 96
(f) Aluminum monolaurate $Al(OH)_2L$. . . . 98
(g) Napalm. 99

CHAPTER III ALUMINUM SOAPS AND WATER 102

A. The Role of Inorganic Impurities in the Water Sorption of Napalm 103

B. X-ray Diffraction by Dry Moist Aluminum Soaps 106

C. Application of the Sorption Balance to Aluminum Soaps 109

(a) Pure aluminum dilaurate $Al(OH)L_2$. . 110

(b) Aluminum dilaurate with bound or sorbed lauric acid 113
(c) Napalm 114

D. The Karl Fisher Method 122

(a) Aluminum dilaurate $Al(OH)L_2$. . . . 122
(b) Aluminum distearate with molecular stearic acid; the nonexistence of tristearate 123

E. Benzene Distillation. 126

CHAPTER IV THE SYSTEM ALUMINUM SOAP-HYDROCARBONS 128

(1) Definition and Differentiation of the of the Various Forms of the Aluminum soap Hydrocarbon System 130

TABLE OF CONTENTS CONT'D.

A. Aluminum Dilaurate-Cyclohexane 130

(a) Introduction 130
(b) Definitions and Background 130
(c) Experimental criteria 131

B. Application to Napalm and the Effect of Inorganic Impurities in Napalm 135

(a) Visual observations 135
(b) The existence of gel and jelly forms of Napalm in gasoline 136

(2) Transitions Between Dry Soap, Gel, Jelly and Sol 141

A. The Transitions from Dry Soap to Gel and Jelly 141

(a) Visual observation. 141
(b) Sorption of cyclohexane 147
(c) X-ray diffraction 151

B. The Transition between Gel and Jelly or Sol 153

(a) Visual observations 153
(b) X-ray diffraction 155
(c) The solubility of $Al(OH)L_2$ in cyclohexane, and its dependence upon the physical state of soap. 155
(d) Napalms. 160
(e) Reversion in thickened fuels etc. . . 164
(f) Relation between transition temperature and consistency 165

C. The Transition between Jelly and Sol. . . 166

(a) Viscosity measurements in sealed tubes 166
(b) Viscosity measurements in Ostwald viscosimeters 172
(c) Osmotic measurements, $Al(OH)_2$ in Benzene 176

(3) Thermodynamic Stability 180

A. Pure Soap Systems 181

(a) The dry soap. 181
(b) The gel. 181
(c) The sol 181
(d) The jelly 181

B. Fuel Thickeners in Hydrocarbons 182

(a) Ultimate time limits of storage . . 182

TABLE OF CONTENTS CONT'D.

(b) Temperature of dispersion 183
(c) Low temperature stability. 183
(d) Ageing or maturing 184

4 The Phase Diagram 185

5 Forces Operative when Thickening Fuels by Means of soap 190

A. The Two Types of Thickening 190

(a) The particles active in thickening aluminum soap jellies are not original soap but something resulting from the interaction of solvent and soap 192
(b) In water 195
(c) Specific effects of aluminum 194

CHAPTER V ADDITIVES WITH ALUMINUM SOAPS IN HYDROCARBONS 196

1. The Behavior of Pure Aluminum Soaps Alone, Mixed. and with Added Fatty Acids 197

A. Qualitative Tests 197

(a) Effect of solvent 197
(b) Effect of the physical state of the acid soap 197
(c) Effect of acid from which the soap is derived 198
(d) Effect of previous extraction of the soap 198
(e) Action of unextracted soap or of acid 198
(f) Effect of unsaponifiable from acetone extract of Napalm 199

B. Solubility of Aluminum Stearate in Isooctane 200

C. Additives in the System Aluminum Dilaurate Cyclohexane 201

2. Metathesis (Double Decomposition) of Aluminum Soaps with other Acids in Hydrocarbons . . .203

3. Additives to Napalm. 205

A. The Various Effects 205

B. Nomenclature 207

(a) Peptizer 207

TABLES OF CONTENTS CONT'D.

(b) Polar compounds. 207

C. Experimental 210

D. Results of the survey 211

(a) Effects on viscosity and formation of jelly. 211
(b) Effect of the various additives 213
(c) Other effects 221

4. Aluminum Cresylates and their Use in studying the Properties of Thickened Fuels 226

SUMMARY

1. The problem assigned was tied to the Napalm program; to study aluminum soaps, to identify the phases and phase transitions utilized in the hydrocarbon systems; to find how water is held by Napalm; to distinguish between free acid, sorbed or bound fatty acid and chemically bound acid; to compare different Napalms in pure solvents; to discuss gel and gel structure and the effective additives.

2. Beginning with carefully prepared aluminum soaps of pure fatty acids, the most important were found to be the di-soaps such as dilaurate $Al(OH)L_2$, di-stearate $Al(OH)Str_2$, dioleate $Al(OH)Ol_2$ and aluminum dinaphthenates. Tri-soaps almost certainly do not exist; preparations of that empirical composition are readily made up but none has supplied a test for pure compound.

3. The pure aluminum dilaurate $Al(OH)L_2$ in many respects typifies the behior of Napalm. The gross composition of Napalm is that of a di-soap, and although the mixed fatty acids differ from lauric acid, their average acid number is only a little more. There is a striking similarity between the x-ray diffraction pattern of Napalm and of aluminum dilaurate and a contrast with that of aluminum monolaurate and of aluminum oxide. The behavior towards hydrocarbons is in general similar, but of course much

better defined and constant with the pure dilaurate. Both sorb appreciable but very limited amounts of water although only the pure soap is readily dried to constant weight.

4. Pure aluminum dilaurate was carefully characterized by various physical chemical methods including the criteria demanded by the phase rule, and its crystalline structure was examined by means of x-rays.

5. 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.

6. X-ray examination of aluminum dilaurate and aluminum distearate show that they have the same polymorphic form. their side spacings are the same. The long spacings require that the fatty acid chains are placed end to end in pairs to produce the distance between the (001) planes, c sin β. The long spacings so nearly resemble those of the gamma sodium soaps that the aluminum atoms must likewise form a

double layer, the two fatty acid chains of each molecule of di-soap lying side by side. The difference in long spacings between laurate and stearate indicate monoclinic angle β equal to 48°, the same as one form of lauric acid. Aluminum dioleate is nearly amorphous but a sample supplied by Harshaw gave lines resembling the pseudo orthorhombic alpha sodium stearate. Aluminum naphthenates gave only halos.

7. When aluminum soap is prepared by adding soap solutions to an excess of aluminum chloride or sulfate solution, the precipitate contains a few percent of the fatty acid. All remaining fatty acid above that combined as di-soap is progressively extractable by inert solvents, being sorbed in the di-soap.

8. A definite answer can be given to the question so frequently asked as to the existence or non-existence of free acid in Napalm. From a practical standpoint, when Napalm comes into contact with a hydrocarbon, part of the acid above that combined as aluminum di-soap (or mono-soap), is freed in solution. The di-soaps, the main part of Napalms, are swollen or dissolved. Tri-soap is not present. Not more than a few percent of the acid is free. Most of that not definitely combined as di-soap or mono-soap is simply sorbed by the di-soap.

9. Aluminum mono-soaps are comparatively inert toward hydrocarbons.

10. Whereas pure aluminum dilaurate is readily and rapidly rendered anhydrous and its sorption and desorption of 1 or 2% of water is rapidly reversible; Napalms behave quite differently, and also differ at 50°C from 25°C. At 25°C they lose about 2% of water on drying, at first rapidly, then slowly over 24 hours. Napalms contain appreciable amounts of inorganic impurities capable of sorbing or combining with water. Napalms also contain volatile and non-saponifiable constituents.

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

12. 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.

13. 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 upon

concentration and temperature. Hence aluminum soaps in hydrocarbons are association colloids.

14. The viscosity of the hydrocarbon gels and jellies is 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 streptococcal arrnagement 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.

15. Peptizers act upon the linkages between the colloidal particles. It is shown by comparison of isomeric 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. With pure aluminum dilaurate $Al(OH)L_2$, the temperature of transition from opalescent gel to clear jelly may be determined precisely. It depends upon the form of the soap, the nature of the hydrocarbon and the presence of peptizer Factors reducing the swelling of soap increase the transition temperature.

18. Pure aluminum distearate is completely insoluble in isooctane at 30°C even in the presence of excess stearic acid. The order of increasing dispersion or solution of pure aluminum di-soaps is stearate, laurate, oleate and naphthenate. In general, the rate and amount of dispersion or solution may be increased by mixing with free acid or with unextracted soaps that contain sorbed acid. Conversely, the dispersion (swelling or solution of an unextracted soap is decreased by adding di-soap.

19. Ten Napalms of different manufacture differ greatly when tested with a pure hydrocarbon. Cyclohexane exhibits the greatest spread of properties. With isooctane, most Napalms, but not all, produce only noncoherent gel systems; Three formed jellies below 23°C, one at 28°C, others at 46°C to 53°C, and one at 65°C. The volume of the swollen soap after 50 hours at room temperature bears an approximately linear relation to the above gel-jelly transition temperature.

20. Additives have at least three independent functions in their effect upon soap hydrocarbon systems:- (a) to liquefy (peptize) or to stiffen the jelly or gel; (b) to accelerate or to retard the interaction of the soap with the hydrocarbon, to delay or shorten stir time and set time; and (c) to make the resulting jelly or gel more thixotropic or more dilatant (i.e. to increase or to decrease the apparent mobility with increasing rate of shear). These three functions may each be exhibited by

a suitablychosen additive (or combination of additives) in any desired direction. Then taking only the first two functions, an additive may be a liquefier and accelerator (xylenols, of which by far the best is 4-OH-12 dimethyl benzene; lauric acid and oleic acid) a liquefier and retarder (the lowest fatty acids), a stiffener and accelerator (wood rosin), or a stiffener and retarder (benzoic acid in small amounts, cyclohexane carboxylic acid). The effects may also depend on concentration; thus in larger amounts benzoic acid and lauric acid produce sols. Mixtures may be used to add to or counteract each others' effects. Additives operate in general through their effects upon the associative bonds between di-soap particles in the loose aggregates that produce the jelly structure. Thus a liquefier breaks these by satisfying them itself. In a few cases metathesis is also operative, as when benzoic acid reacts with di-soap or aluminum cresylate with fatty acids. Mixtures of additives may be used to add to or counteract each others' effects in any desired direction.

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 existence of several aluminum soaps as definite chemical individuals. The pure di-soaps in many respects resembled Napalm. Hence they were suited for a thorough study, both as regards preparation and properties, including influence of physical state on gelling behavior with solvents, and relations to moisture.

The progress of this work was reported in monthly reports and the work of the first year summarized in the Yearly Report of June 1944. The scope of this project has now been radically reduced and the present report is issued to summarize the main results obtained in the past 20 months.

The report then properly begins with a general discussion of the main problems studied, followed by a comprehensive study of the aluminum soaps, their relations to moisture, and their hydrocarbon systems alone and with additives.

References.

For the purpose of brevity the reader is frequently referred for details to our Yearly Summary Report of June 1944 quoted as "Yearly" and to some of our monthly progress reports of 1944 quoted by the month in which issued e.g. "October" referring to the report covering the period September 15 to October 15, 1944.

We also refer frequently to British Petroleum Warfare Board Memoranda (British P.W.B. Memo.); to "The Manufacture, Properties and Testing of Napalm Soap" by G. Broughton and A. Byfield O.S.R.D. Report No. 2036 of Nov. 17, 1943 as (Broughton and Byfield or as B.B.) and to Monthly progress reports of the Eastman Kodak Company and the Harshaw Chemical Company.

CHAPTER I

THE MAIN PROBLEMS STUDIED

In this chapter are collected the general discussions of the main problems which we studied while details of the experimental results and many minor problems are relegated to the subsequent sections.

We deal in turn with the existence of pure aluminum soaps, their polymorphism and the presence of free and bound acid. This discussion gives basis for considering the nature of Napalm and its similarity to pure di-soaps. Then we consider the significance of moisture determinations, the formation and structure of gels, jellies and sols in hydrocarbons, and the various effects of additives upon the latter leading towards control in any desired direction.

A. Pure 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.

Substance called aluminum soaps occupy the range of compositions intermediate between alumina and fatty acids. The possible formulas, according to the classical rules of valence are numerous and complex. Natural signposts in this vast region are the mono-, di- and tri-soaps representing one, two, or three acid radicals combined with aluminum.

The confusion originally existing in this field may be judged by the extreme opinions of Lawrence (British P.W.B. Memo No. 368) who claims that all three soaps exist and differ but little; and at the other extreme are those of Eigenberger (Kolloid Z. 91, 287 (1940), British P.W.B. Memo No. 450) who claims that none of these soaps exist but only an intermediate compound corresponding to the formula $St_2AL.O(ALStO)_6AL\ St_2$. Intermediate opinions are those of Professor Alexander (British P.W.B. Memo No. 370) according to whom the mono-soap is the only one to exist, and McBain's and McClatchie's (J.A.C.S. 54, 3266 (1932) studies pointing out the probable nonexistence of the tri-soap.

We have explored rather thoroughly the region of the immediate neighborhood of the composition of the di-soap and proved that the di-soap does definitely exist as a chemical entity, and that in fact it often forms in aqueous precipitates. On the acid side of it we could never detect any additional acid combined as tri-soap but proved that some acid may be bound in molecular form, probably by sorption. We also found some evidence that a mono-soap may exist but have not explored the whole region between di- and mono-soaps.

(a) The existence of puresoaps. 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 since 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 are a useful adjunct and 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 compounds of which the most general is that a chemical compound must act as a single component over some range of experimental conditions. The classical tests of sharp melting point, boiling point, or recrystallization without change of composition are practical realizations of this criterion.

Miller and Kendrick (J. Phys. Chem. I: 260-268 (1903).) in 1903 pointed 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. (p.62-4).

(i) Aluminum di-soaps. Our proof of the existence of aluminum di-soaps is based mainly on the preparation of the dilaurate Al $OH.L_2$ whose composition is very close to the theoretical (p. 87) and approaches it even more when changes of hydrolysis are reduced (p.47). It has a sharp melting point (p.88) and x-ray diffraction pattern (p.71) and upon partial solution in hydrocarbons may be recovered without change in composition (p. 160). The distearate behaves similarly (p.91-2, 73-6) and the solubility of stearic acid therefrom is less than 0.1% of the solubility of free stearic acid (p. 56). Thus it satisfies fully the criteria of a chemical compound.

(ii) Mono-soap. Our main argument for the existence of mono-soap is the appearance of a new x-ray diffraction pattern, different from that of either known forms of alumina or di-soap, in substances approaching the composition of $Al(OH)_2 L$. (p. 98). Its solubility is far less than that of a di-soap.

(iii) Tri-soaps. The preparation of this soap is described by A.S.C. Lawrence (British P.W.B. Memo 364 and 368) by merely reacting aluminum tri-isopropoxide and stearic acid. No tests of the products are however described (although the author noted that the physical properties of his mono-, di- and tri-soaps are very similar and their melting point about 200°C). Unless the substance itself is however tested

(and satisfies the phase rule criteria) its existence cannot be considered probable from a scientific point of view.

We have noted great differences in the properties of mono- and di-soaps and a melting point of 175-177°C for the distearate. Therefore the author's work describing his unpurified compounds does not appear convincing either, nor as already pointed out by Professor Alexander (Memo 370), does it support the existence of the tristearate.

In addition to the quoted work of McBain and McClatchie, which refers to both aqueous and anhydrous preparations, we have the following evidence for the nonexistence of tri-soaps in aqueous precipitates: the presence of hydroxyl groups determinable by the Fisher reagent (p.124), the solubility of the acid in acetone and isooctane (p.52 ff.) the sublimation of lauric acid (p. 113).

The anhydrous method of preparation of Dr. Lawrence will be repeated and the product tested as soon as an opportunity presents itself.

(iv) The Eigenberger compound. "AL $St_3O(Al\ OSt)_2 Al\ St_3\ Aqua$". The authors base their argument mainly on unchanged composition upon repeated solution of the soap in benzene in the presence of alcohol and precipitation with excess alcohol. Their tests do show that the substance behaves like a single component under that particular set of conditions. This is not sufficient however to show that it is a true compound. In order to establish this the same behavior must be shown under at least one different set of conditions. This the authors failed to do. It is therefore possible that they obtained a

constant mixture of decomposition products. (In the same way as by distillation an azeotrope is often produced and has a constant boiling point).

It must be noted that the test applied involves extremely drastic conditions of alcoholysis (and hydrolysis unless extreme care, not mentioned, was taken to exclude water). Our di-soaps would certainly suffer far-going decomposition by this process. This in no way detracts from their existence as definite compounds (because only elements have to act as single components over the whole range of usual experimental conditions), but it explains why Eigenberger and his collaborators failed to observe their existence.

From our own work we know but little about the region between the di- and the mono-soap and have no definite evidence either for or against the presence of intermediate compounds such as the one proposed by Eigenberger. For purposes of convenience the report is written on the simple assumption that compositions intermediate between the two soaps are due to a mixture of mono- and di-soap in varying proportions. Whether this is actually the case remains to be investigated

(b) Polymorphism of aluminum soaps. Thus far we have been able to account for the behavior of aluminum soap using classical concepts of chemistry such as valence, sorption, and polymorphism. This last phenomenon is encountered in aluminum soaps to an unusually high degree and is the main obstacle to their study. The soaps seem to exist in a continuous series of polymorphic forms differing both by physical properties and chemical reactivity and covering a very broad range from

extremely reactive and unstable to almost inert and indifferent and corresponding to the range from almost amorphous to quite crystalline. Yet the transformation of these forms into each other is extremely slow or negligible at room temperature. It is only through thermal or solvent treatment (recrystallization) that they can be transformed into each other. (p.89 and 154).

Our evidence for the identity of substances of widely different properties is based on the fact that they all give by thermal recrystallization the same "crystalline" form of sharp melting point and sharp x-ray diffraction pattern (p. 85, 90 ,160) or alternatively by solvent treatment the same very amorphous "recovered" forms (p. 89) without any possibility of change in composition. The presence of the same x-ray diffraction lines in all forms differing only by intensity of sharpness but not of position (p.71).

The difference of the various forms is shown by their appearance, swelling in hydrocarbons (p.89), transition temperature from gel to jelly (p.153), melting point (p. 88) and intensity and sharpness of x-ray diffraction lines(p.71).

In addition we found that an ordinary aluminum soap is composed of many fractions of widely differing properties as shown by the fractionation with cyclohexane (p.159) and probably by hydrolysis during acetone extraction (p. 47).

In other words in aluminum di-soaps the aluminum and fatty acid, while combined in the stoichiometric ratio, are united by bonds widely varying in strength.

This polymorphism varying from amorphous to crystalline should not be confused with the polymorphism of two different

crystal forms which we found for the distearate (p.76). The two polymorphisms are superimposed i.e. each crystal habit may exist in a variety of forms from almost amorphous to very crystalline.

B. Free and Bound Acid.

The fatty acid in the pure di- and mono-soaps of aluminum can be freed only by hydrolysis or alcoholysis or metathesis.

In addition aluminum soaps may (and usually do) contain further acid in molecular form either bound or sorbed; or free as such in mechanical mixture.

(a) Nomenclature and nature. The term "free" acid is frequently applied to any acid which may be extracted from the soap under a given set of conditions. Such methods in general determine the "freed" acid liberated under these conditions which is much more than the "free" acid present as such in the soap, and often greater than the sorbed acid.

The strict logical use of the term "free acid" is to denote only that acid, present in the soap, which has an activity equal to that of the pure acid. We have obtained evidence from x-ray diffraction (p. 77) and solubility studies (p. 55)

that such acid may actually be present in aluminum soap so that the term is certainly not useless.

Frequently however excess acid is not free but bound to or sorbed by the soap in molecular form and its activity and solubility may be reduced to a hundreth or thousanth of that of pure acid (p. 56). This binding may be either by formation of an acid soap or by solid solution or by sorption. Due to the polymorphism and heterogeneity of aluminum di-soaps we have been unable to distinguish definitely between these possibilities by solubility measurements (p.56) but these and x-ray data point to sorption. (p. 80).

The sum of free and bound acid may be properly referred to as "molecular acid" of the soap.

(b) Experimental distinctions between combined, sorbed and free acid. The simplest criterion is probably based on solubility in a solvent inert with respect to soap and capable of dissolving the acid. Then the acid if free has the same solubility as the pure acid; bound acid is soluble but has a lower solubility than pure acid, the form of the equilibrium extraction curve distinguishing between solid, solid solution and sorption; combined acid is insoluble. The practical application of this criterion presents difficulties due mainly to the difficulty of finding a proper solvent (p.39 , 51). The vapor tension of fatty acid in the soap at ordinary temperatures would be a perfect method of investigation but it presents obvious difficulties. (p.113).

All practical methods are, or may be, not inert with respect to the soap so that one must always be on guard to distinguish "freed" acid from actually "free" acid.

(i) Distinction between combined and excess molecular acid. Here it is only necessary to prevent decomposition of the soap and yet separate all the molecular acid by inert extraction. Low results may be due only to incomplete separation of the molecular acid while high results are due to decomposition of the soap. Most methods avoid significant errors from the first source by repeated extraction of the soap. Errors from the latter source are however more difficult to avoid.

It seems safe to state that in general the method giving the lowest result is the best one and has avoided decomposition to the greatest extent.

Alcohols (p. 38);and even acetone dried over Drierite (c.46) cause extensive hydrolysis of most soaps under conditions of exhaustive extraction. Isooctane seems to be the most satisfactory under these conditions. (p.49).

When non-exhaustive batch extraction is employed it is not possible in general to separate all the bound or sorbed acid but isooctane (p.57), dried acetone, and even sometimes quite moist acetone (p.59) seem to cause practically no decomposition of the soap. Methanol-ether mixtures (p.63), and moist acetone (British P.W.B. Memo 451), often decompose the soap.

(ii) Distinction between free and bound molecular acid. Here obviously only solvents which do not decompose the soap are acceptable but furthermore physical interaction between soap and solvent might free some of the bound acid.

If it were possible to treat a large amount of soap with a very small amount of isooctane for example, and determine to what extent it becomes saturated,the problem would be

simplified. The soaps however imbibe such large quantities of solvent that this method is not directly applicable. Treatment of the soap with an almost saturated solution of the fatty acid and observation of the direction of change of its content of acid is a substitute and has been used by us (p.56). The presence of small amounts of free acid in some soaps has thus been proven for the first time and later confirmed by x-ray evidence(p.77).

(c) The degree of binding of bound acid. Quantitative measurements of solubility of the fatty acid in extracting the soap give an indication of the strength with which the acid remaining in the soap is bound to it. A beginning has been made of such study of a few samples but the study is complicated by incomplete reversibility (p.53), and therefore imperfect equilibrium.

C. Napalm. Its nature and Similarity to Di-soap.

(a) Composition.

The bulk of Napalm is an aluminum soap whose composition corresponds to the same di-type as aluminum dilaurate.

(i) Non-soap constituents. About 7% by weight of Napalm may be readily extracted with acetone (B.B. p. 71-72) out of which about 2% is unsaponifiables or high iodine value (p. 63) and about 5% is molecular acid.

Napalms of ten manufacturers contain on the average at least (p.103) 1.7% of inorganic impurities (Harshaw Fifteenth Report Table V) and about 0.8% water.

(ii) The soap constituents. This leaves about 90% of the Napalm as soap. The fatty acids which go into the manufacture of Napalm have an average molecular weight of about 233 (B. B. p. 31) so that the aluminum content (as Al) of mono-,

di- and tri-type soaps of these acids would be 9.2%, 5.30% and 3.74% respectively; the corresponding ash values being 17.46%, 10.01% and 7.06%. If the remainder of Napalm were mono-, di- or tri-soap respectively the percent of aluminum in Napalm combined as soap would be 8.94%, 4.92% and 3.46% respectively. Actually the average found by Harshaw (ibid) for the ten representative Napalms is 4.92.

The agreement is fortuitous of course but nevertheless indicates that the bulk of a typical Napalm has the composition of a di-soap.

(iii) Differences from dilaurate. This di-soap in Napalm differs most obviously from aluminum dilaurate in the nature of its acid which is comprised of a variety of saturated and unsaturated fatty acids and naphthenic acids of higher and lower molecular weight than lauric acid; but their average, 233, is only 15% higher.

Napalm differs also from pure aluminum dilaurate by its content of: acetone-soluble unsaponifiable (p.63), some molecular (uncombined) acids (p.63) of which a very little may be free (p.64). (Both of the above being to a slight extent volatile (p.114)), and maybe some proteins (p.45).

(b) X-ray diffraction. The sharpness of x-ray diffraction patterns of Napalms of various manufacturers differs markedly (p.69-70), so does the sharpness of diffraction patterns of pure dilaurate, depending on the method of its preparation (p. 71). However, the overall pattern of characteristic forms of both is strikingly similar (p.67). This pattern may be contrasted with the differing patterns of aluminum monolaurate and of aluminum oxides.(p. 72).

(c) Behavior in hydrocarbons. The behavior of Napalms of various manufacturers in a given hydrocarbon differs markedly (p.143). Aluminum dilaurate prepared in different ways shows also great differences (p. 89). However both are capable of forming definite gels of opalescent discreet swollen lumps, jellies which are coherent, elastic and transparent, and liquid sols (p.135). Aromaticity of solvent (p142-3) and presence of "peptizers" (p.201 , 211) affects them both similarly. Both sorb avidly large amounts of hydrocarbon (p.147-150).

The general great affinity for hydrocarbon of the usual forms of aluminum dilaurate and Napalm may be contrasted with the relative inertness of aluminum mono-laurate in these solvents (p.99).

"Inert soap". In two samples of Napalm we have observed the presence of a substantial amount of a soap relatively inert to hydrocarbons which was absent from all other samples (p.146). This "inert soap" is not a mono-soap, however, according to its x-ray diffraction and composition (p.101).

(d) Behavior with water. Both aluminum dilaurate and Napalm sorb appreciable but limited amounts of moisture at high humidity, and are not greatly affected by variations of relative humidity in the middle range of about 20 - 80% R.H. (p. 111, 120).

The most pronounced difference between the two substances seems to be in the sorption of water a very low relative humidities (p.109); the pure dilaurate being readily dried, (p112)

but Napalm never reaching a definite dry weight (p.116). Part at least of this difference is due to its content of volatile substance. (p.114).

Thus, on the whole, aluminum dilaurate, $Al(OH)L_2$, is an excellent model for the behavior of Napalm and particularly of the di-soap which forms the bulk of commercial Napalms.

D. Significance of Various Methods of Determination of Moisture.

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. This is usually eliminated by drying during the manufacturing processes.

(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 in solid solution, or as part of the crystal structure as a true hydrate.

X-ray diffraction shows that the crystal structure is unaffected by hydration (p.107) but small amounts of water are sorbed reversibly (p.110) by surface forces.

Evacuation at low temperature or rapid drying at 100°C determines this water readily in the case of aluminum dilaurate (p.112) but Napalm loses simultaneously nonaqueous volatile components (p.114) and is affected by heat (p.115).

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

Reaction between fatty acid and hydroxyl groups such as:

(i) Alumina $Al(OH)_3 + HR \longrightarrow Al(OH)_2 R + H_2O$

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

(iii) Di-soaps $Al(OH)R_2 + HR \longrightarrow Al R_3 + H_2O$

Reaction between two hydroxyls forming an oxygen

(iv) Within a molecule

$$Al(OH)_2 R \longrightarrow AlOR + H_2O$$

(v) Between two molecules e.g.

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

Preparation of pure 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 reactions (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.

Intraatomic dehydration of type (v) is however possible and does occur in the Fisher moisture determination (p. 121). In the presence of excess fatty acid the di-soap might form additional water in the Fisher determination such as by reaction (iii) (p. 125).

In the benzene distillation method none of these reactions proceeds to a very substantial degree. (p. 127).

E. Gels and Jellies in Hydrocarbons.

Aluminum soaps may show the full range of behaviors from complete inertness to complete solution in hydrocarbons. Their interaction depends upon the nature of the soap (p.198) its polymorphic form (p.89),the nature of the hydrocarbon (p.135), the temperature (p.185) and the presence of additives. (p.101). However it appears that with any given soap or solvent or at any given temperature any typical behavior may be produced, within reason, by varying the other factors.

In general,as for example,the temperature is raised the soap swells more and more, forming a gel; and it may imbibe 50 or more volumes of solvent (p.156) although the structure of its crystallites seems to be unaffected thereby (p.151). Such a swollen soap may be an effective thickener for some

purposes but it lacks the coherence, elasticity and stringiness required for flame thrower use.

At a higher temperature the soap changes rather sharply (p. 153) to a jelly which is clearly distinguished (p.131) and has the required properties of coherence and elasticity. This change occurs in Napalms (p. 135) as well as pure soaps (p. 130) and affects markedly the structure of soap crystallites (p. 151). The jelly may be indefinitely stable (p.181) but is easily undercooled (p. 154) and its viscosity depends greatly upon its thermal history (p.168), showing that it is due to a slowly formed structure. (p. 171).

At still higher temperature the jelly passes gradually into a thin sol which shows the typical behavior of an association colloid (p.178) in which molecules of soap associate to ~~passing~~ primary particles, loose aggregates of which enmesh the liquid and determine its rheological properties.

Since fundamentally similar phenomena are observed(p.194)in aqueous systems as well as in nonaqueous systems of other soaps, particularly sodium and silver soaps, it is unlikely that the association be due to specific effects of aluminum such as coordinates between Al(OH) groups as postulated by Dawson and White (Flame Thrower Fuels O.S.R.D. Report 3506 April 20, 1944, p. 9 ff).

F. Additives in Soap-Hydrocarbon systems.

Additives, particularly xylenols, are widely used to lower the temperature at which an aluminum soap forms a jelly, and to lower its viscosity. Such additives are frequently referred to as polar compounds, but in fact no such simple relation exists as shown by the action of the isomeric nitrobenzene (p.208). Double decomposition between additive and soap is certainly the main factor in a few cases (p.203 ,216).

Metathesis has been apparently the basis of the proposal of forming a thickener by interaction between aluminum cresylate and oleic acid. We found this reaction to be too irregular to serve our purposes (p.226).

We found that "peptizing action",as symbolized by xylenols, is not a simple entity but is composed of at least three independent effects.

(a) Acceleration of jelly formation (set and stir time).

(b) Lowering of viscosity of the jelly.

(c) Increasing the falling off in viscosity with rate of shear.

These three effects are independent, and they are shown in varying degrees by various substances. Each has its opposite counterpart: (a) retardation of jelly formation, (b) increasing the viscosity of the jelly, and (c) reducing or reversion of the drop of viscosity with rate of shear. (p. 205, 211).

Even isomeric xylenols show great differences in their effects (p. 219).

It is therefore preferred to replace the term "peptizer" by the more general one of "additive" and to use such words as "retarder", "accelerator","liquefier" and "stiffener" for the various agents.

Any combination of these effects in either direction may be obtained by proper choice of the additive (p. 211) and it is apparent that the properties of Napalm may be improved or substantial economy in its use obtained by the simple device of dissolving an appropriate substance in the gasoline used.

The following appear promising from the present limited survey:

Extension of stir time which would relieve the difficulties reported in hand field mixing under tropical conditions, may be attained by addition of lower fatty acids.

Increased stiffness which may be desirabel in bomb filling,

might be attained by addition of commercial analogues of cyclohexane carboxylic or benzoic acid or of resins.

(b) Use of solid fatty acids. Xylenols cannot be packaged in the same container with Napalm since they transform it into a sticky mass. Solid fatty acids , particularly "lauric acid", although less effective than xylenols have the advantage that no interaction with Napalm may be expected below their melting point and before solution.

Other suggestions dealing with thickened fuels which were submitted by this group may be found in the last chapter of the Yearly Report.

CHAPTER II
THE ALUMINUM SOAPS

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

This section presents first, a brief discussion of our method of precipitating soaps; second, a summary of the factors involved; and third, the study of some soaps prepared by Harshaw to determine the influence of "protective colloids".

(a) Our standard method of preparation.

The influence of manufacturing conditions upon the properties of Napalm is a separate problem being studied by the Harshaw Company, and our work did not duplicate their 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. (Yearly 7).

This led to the adoption for our work of the reverse method, i. e. addition of a soap solution to an aluminum salt solution under standardized conditions. (Yearly 8). 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.

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.

The precipitate is then separated by filtration and washed with distilled water until free of chloride. It is then dried over P_2O_5.

All the samples prepared were extracted under standard conditions in a Soxhlet apparatus with dried acetone. This separates all the molecularly bound or sorbed acid and some of the most easily hydrolyzed combined acid.(p. 47) Samples were ashed before and after extraction and this, due to the absence of inorganic salts in our preparation, gave their aluminum content. X-ray diffraction patterns were obtained on most samples.

A few were examined more exhaustively by Soxhlet and batch extraction with acetone or isooctane and their behavior with water and hydrocarbons investigated, but these were too few to correlate with conditions of precipitation.

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

(b) Factors influencing the precipitation.

These factors in our method, particularly in case of the stearate, are as follows:

(i) The unextracted soap. The temperature of precipitation has a pronounced effect upon the physical characteristics of the product. 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. 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. (Yearly 9).

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 crystal structure of the stearate is of a different type depending on whether the temperature of precipitation is below or above about 60°C. The two types are discussed on p. 76 .

The laurate showed no such dimorphism in the range of 25° to 100°C.

The composition (ash) of both unextracted laurate and stearate varies rather irregularly and no generalization could be made.

(ii) The extracted soaps. The composition of the soaps after extraction under standard conditions was in general very reproducible and Figure 1 shows the main factors

involved. It remains essentially constant when the soap is prepared at any temperature between 0 and about 50°C. As the temperature of preparation is further increased, the "extracted" ash value correspondingly decreases gradually toward the value for distearate. This is shown by the heavy line.

Special experiments have shown that the "extracted" ash value may be either increased and decreased by suitable treatment subsequent to precipitation as well as by the temperature of precipitation.

In these experiments, the soap samples were precipitated under our standard conditions, and divided into two or three portions, each consisting of soap and mother liquor. One portion was processed by the standard method and the others were subjected to modified treatment before being processed by the standard method. The effect of any irregularities during precipitation was eliminated in this manner, and the effect of the special treatment brought into relief.

This effect is shown by the dotted lines in Figure 1 (Yearly p. 9 - 12, September p. 9).

Heating of the dry precipitate to 100°C decreases the ash of the extracted soap (Yearly p. 12).

The concentration of reactants has little effect. (Yearly p. 12).

Ageing (solidifying) the potassium stearate solution at 25°C prior to precipitation has the effect of markedly increasing the ash of the extracted soap as indicated by the stars in Figure 1. The aluminum chloride solution on the other hand shows no thermal hysteresis (Yearly p. 14).

Figure 1

The effect of conditioning aluminum stearate during preparation.

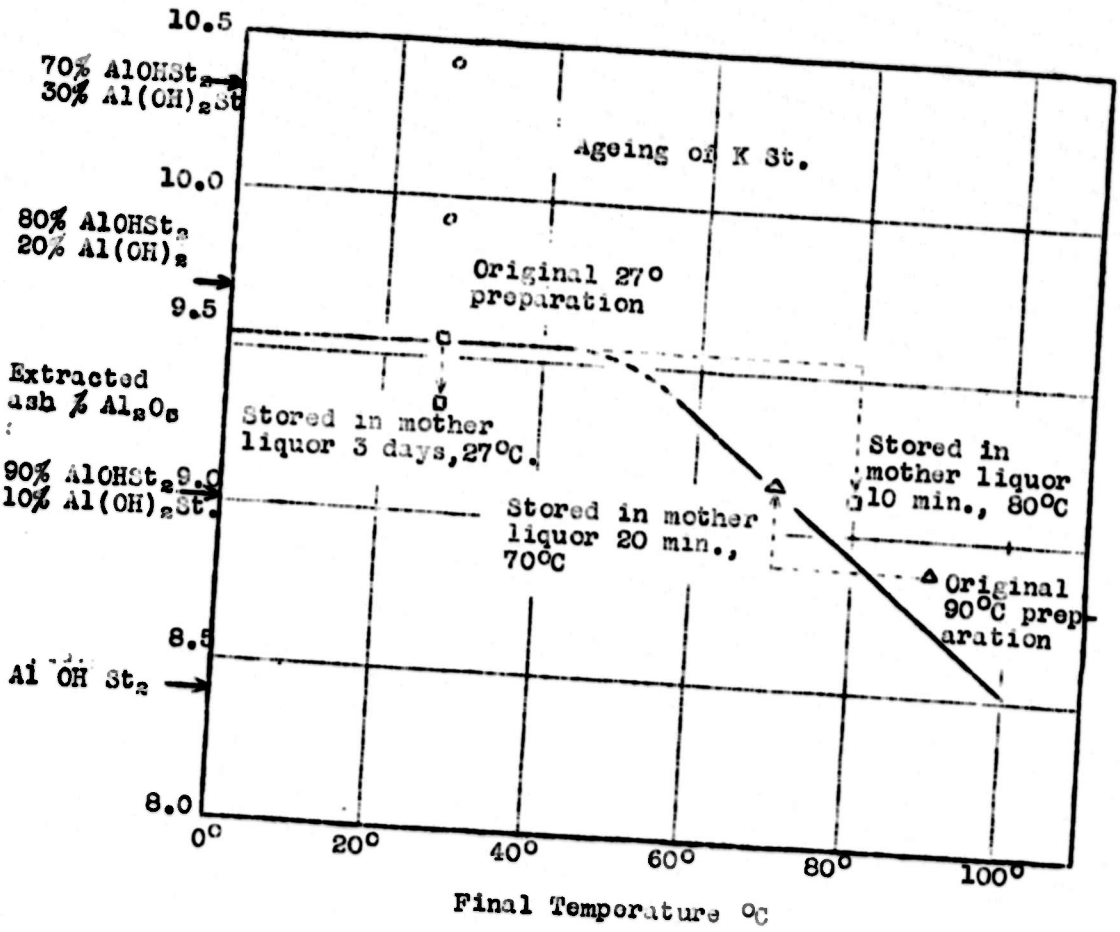
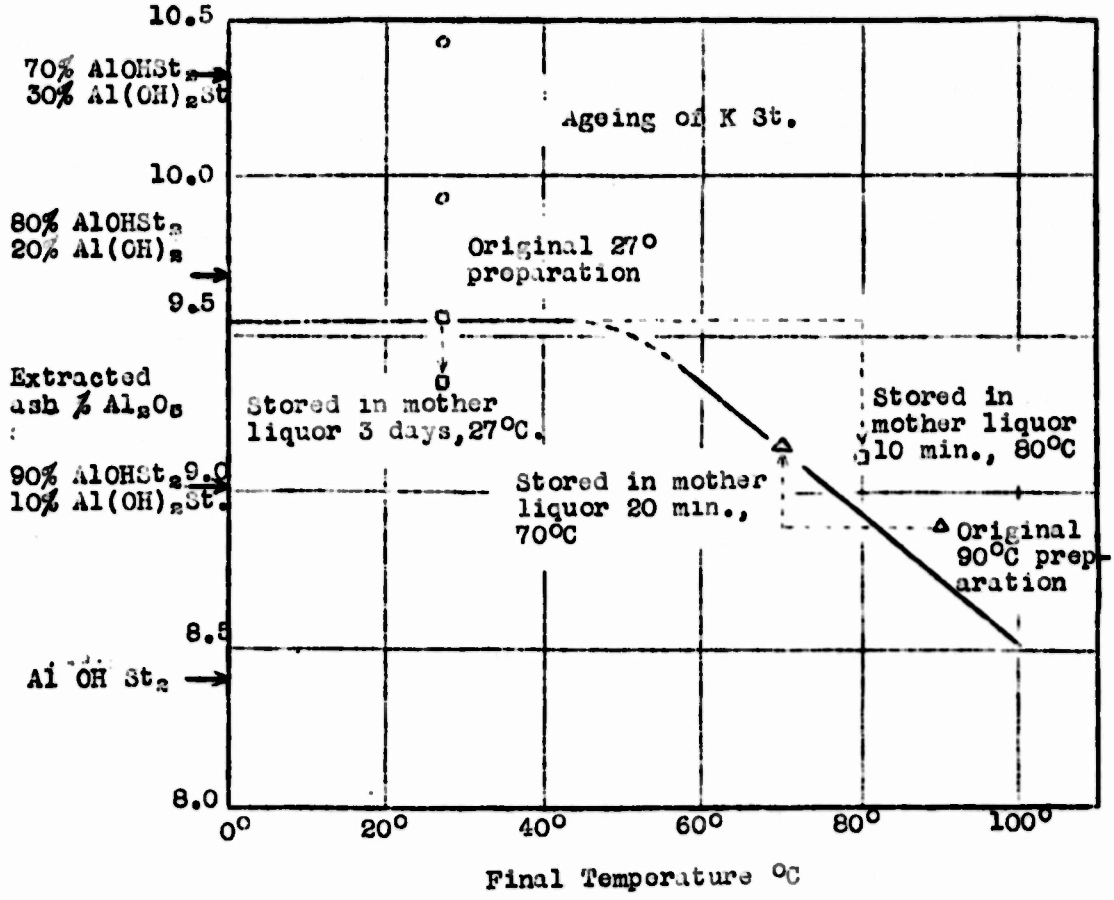


Figure 1

The effect of conditioning aluminum stearate during preparation.



The nature and purity of the "stearic" acid used has of course some influence upon the composition of the extracted soap (Oct. p. 33).

The crystal structure of the extracted stearate depends upon the temperature of both precipitation and extraction. Room temperature extraction yields extracted soaps having a structure similar to the corresponding unextracted soap. At the boiling point of acetone, unextracted soaps precipitated below 60°C recrystallize, however, and become similar to the unextracted one precipitated above 60°C. (See p. 75).

(c) The effect of protective colloids in the preparation of Napalm.

The Harshaw group prepared several soaps under strictly comparable conditions with and without the addition of various colloids during precipitation of the soap. They found that some of them had little, while others had a marked effect upon the gel-forming power of the soap. They expressed the hypothesis that these changes may be due to changes in the crystallinity of the soap of the same type as we have discussed previously for aluminum dilaurate.

Samples of these soaps were kindly made available to us and we determined their Kjeldahl nitrogen content and obtained their x-ray diffraction patterns under comparable conditions. Microphotometer tracings of these patterns are reproduced in igures 2 to 3 . The differences in crystallinity thus revealed are sometimes very marked and easily visible on these tracings. In some cases differences between the sharpness of

lines on the original diffraction pattern are less pronounced and escape the microphotometer but are still clearly visible to the naked eye. In other words, microphotometer tracings are less sensitive than the eye to the small changes in sharpness and fail to show them properly.

The results are therefore presented both in form of tracings and in Table I. The latter gives a subjective measure of the sharpness of the x-ray diffraction pattern as given by four different observers on arbitrary scales. All four observers agreed on the order of the pictures, thus showing the objective value of this estimation. The gel strength as determined by Harshaw for these soaps, their code number, the main point of the formulation and their nitrogen content are also given in this table.

It shows in all cases of colloids containing nitrogen that the N_2 content of the precipitated soap was increased, proving that it contained some sorbed colloid. This amount seems to correlate pretty well with the Gardner consistency of gels prepared therefrom.

This table shows also that differences in crystallinity, revealed by x-rays, often correspond to changes in Gardner consistency, the less crystalline soap giving a stiffer gel. There are, however, two marked exceptions. The BR - Al stearates, which differ from 360 to 510 grams in the Gardner test, give practically indistinguishable diffraction patterns. Similarly, the CPU Glue and Cetal samples give Gardner readings differing by 200 g., and the better one is somewhat more crystalline. Conversely, the CPU Glue, Ursolic Acid and Methyl

Table I

Comparison of relative crystallinities and Gardner consistencies of aluminum soaps prepared with and without protective colloids.

The crystallinities are rated subjectively by four observers on arbitrary scales, the lowest number corresponding to the most crystalline x-ray diffraction pattern.

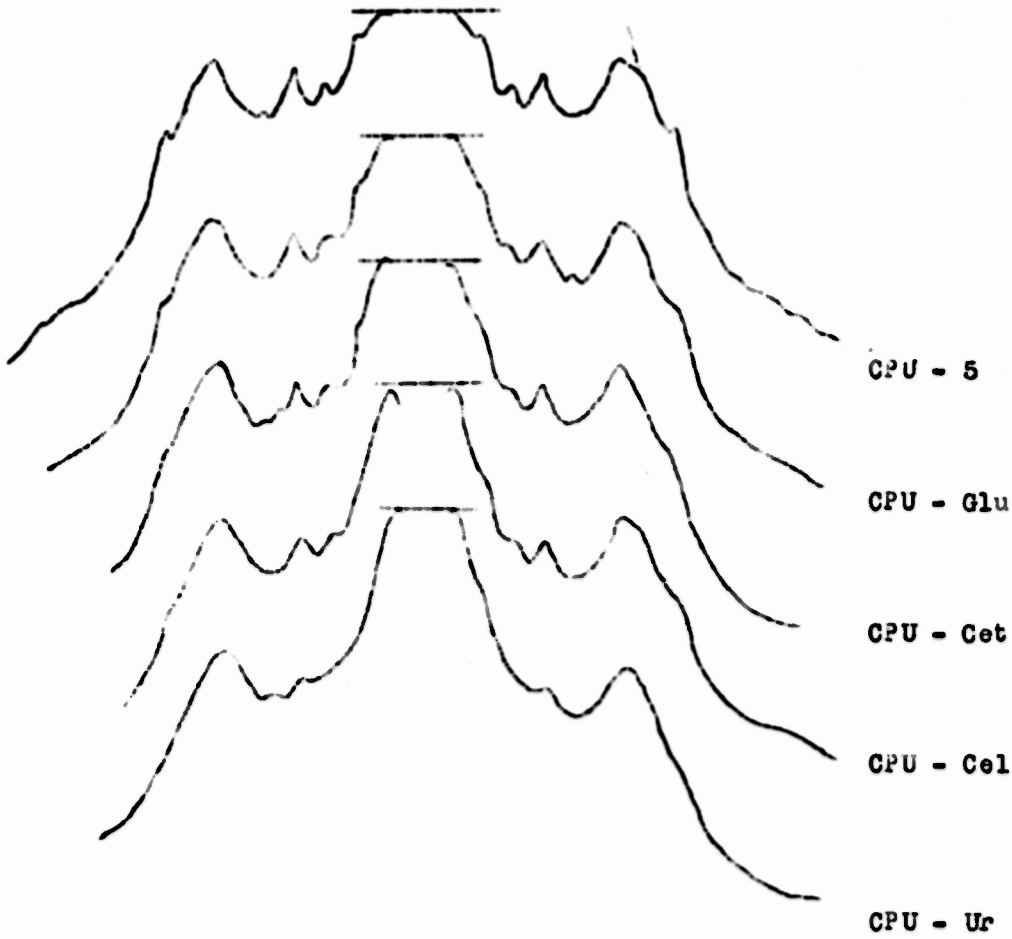
Method and fatty acids	Colloid	Code	Crystallinity				Gardner Consistencies			% Nitrogen
							44 hr 77°F	24 hr 150°F	2 hr 195°F	
Standard method Napalm acids	None	CPU-5	1	1	1	2	1025	880		0.3*
	Glue	CPU-Glu	3	2.5	2	3	1065	900		0.4
	Cetal	CPU-Cet	3.5	3	2.25	3	1265	1135		
	Methyl-cellulose	CPU-Cell	5	3.5	3	3	1275	1260		
	Ursolic acid	CPU-Ur	7	5	4.25	4	1250	1225		
Booke-Roberts method Napalm acids	Starch	BR-CPU-St	1	1	1	2	560	500		0.25*
	None	BR-CPU	1.5	1.5	1.25	2	530	440		
	Albumen	BR-CPU-Alb	5	3	2.25	3	1515	1410		0.7
	Glue	BR-CPU-Glu	5.5	3.5	2.5	3	1380	1140		0.5
Booke-Roberts Stearic acid	None	BR-Al-Stearate	1	1+	1	1			360	0.23*
	Glue	BR-Al-Stearate-Glu	1+	1	1+	1			510	1.6

* These values are believed to be significant because blanks run simultaneously on sugar and sugar plus 0.8% N(as $(NH_4)_2S\ O_4$) gave 0.0 and 0.8% respectively.

Microphotometer tracings of X-ray diffraction patterns of soaps prepared in presence and absence of protective colloids.

Sample to plate distance 5 cm.
Magnification 2x

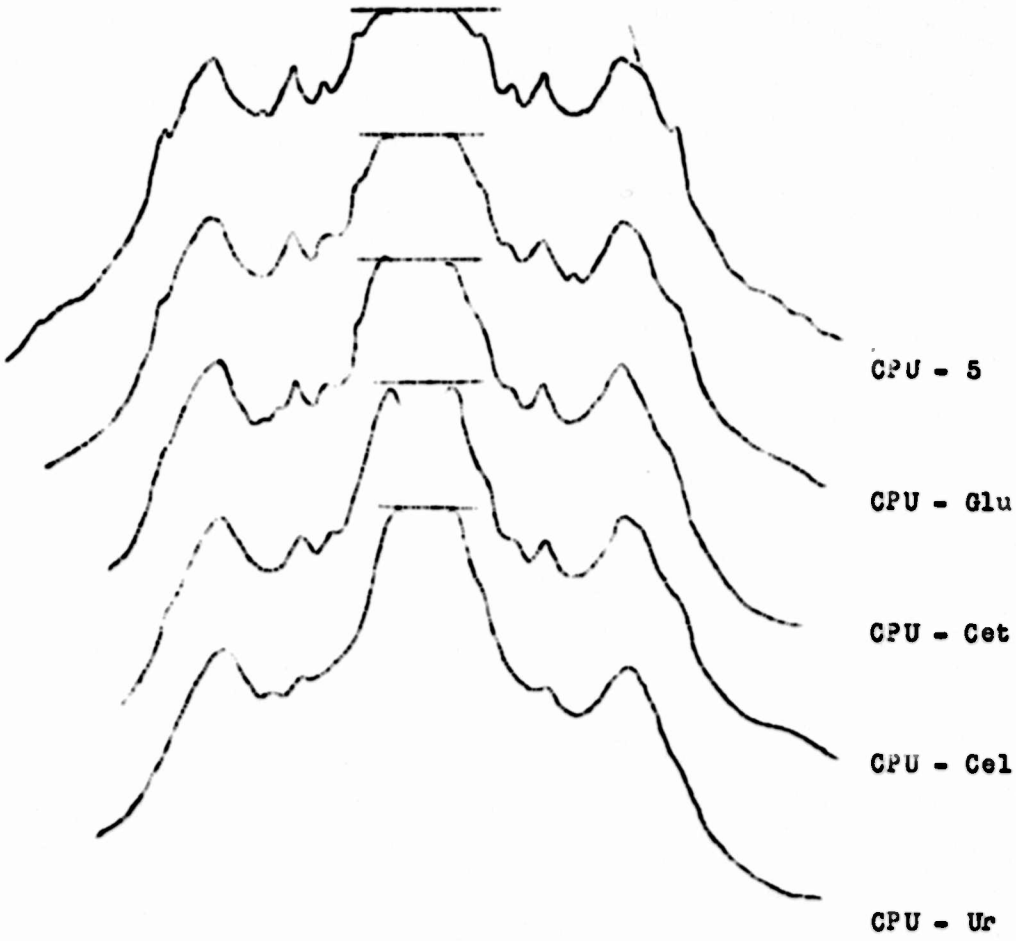
Figure 2



Microphotometer tracings of X-ray diffraction patterns of soaps prepared in presence and absence of protective colloids.

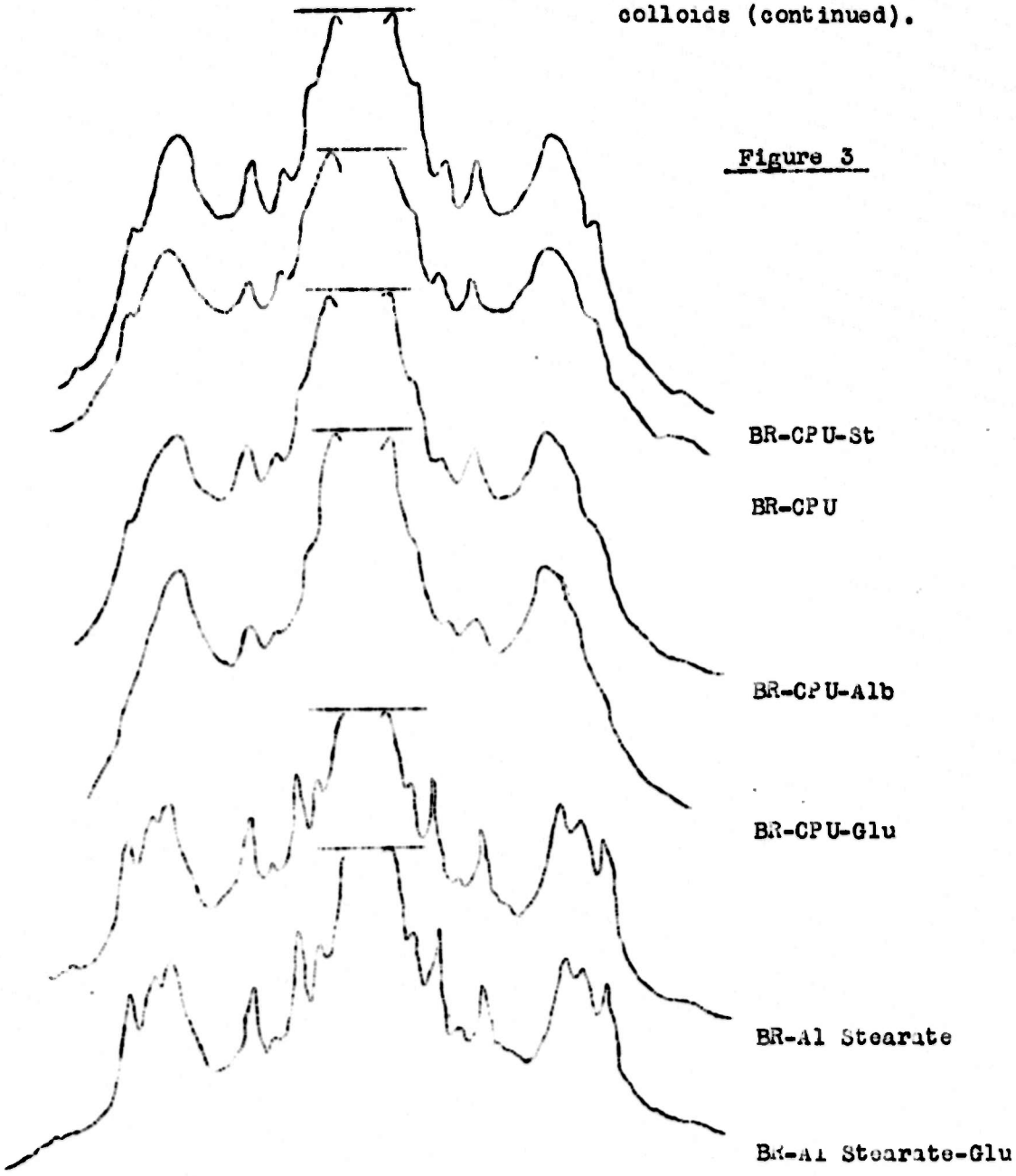
Sample to plate distance 5 cm.
Magnification 2x

Figure 2



Microphotometer tracings of X-ray diffraction patterns of soaps prepared in presence and absence of protective colloids (continued).

Figure 3



Cellulose give markedly different diffraction patterns but almost the same Gardner value.

Discussion. Thus factors other than the overall crystallinity of the soap shown by x-rays are also involved in the effect which the protective colloids have upon gel strength.

One of them may be the relative amounts of soaps of various degrees of crystallinity. We have shown (See p. 158) that aluminum dilaurate, as prepared was not homogeneous but composed of many fractions of different crystallinities yet having the same composition. It is probable that the same holds true for most aluminum soaps. It is possible that protective colloids may change the distribution of fractions of varying crystallinity in a manner which affects the gel forming ability without markedly affecting the x-ray diffraction or vice versa.

Another possible factor may be the effect of the colloid itself coprecipitated with the soap upon the gel. The nitrogen determination showed that 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 viscosity in the same way as paper pulp or other fibers, but with much greater efficiency due to the finer dispersion.

B. Extraction with Solvents.

Differences in solubility of components of a "soap" throw light upon its constitution. They may be utilized for their separation and preparation and particularly for the differentiation between molecular and combined acids. However the choice of a proper solvent, of proper conditions of time, agitation, separation etc. presented many problems, some still unsolved.

Our attention was directed mainly along two lines; exhaustive Soxhlet extraction under controlled conditions, and batch extraction in which a state of equilibrium was sought.

(a) Choice of solvent.

Alcohols are unsuitable because they may alcoholize soaps. (Yearly p. 15, British P.C.B. Memo 381).

Acetone is a good solvent for fatty acids (Nov. p. 66) and if perfectly dry would probably be inert with respect to soaps. It seems however in practice impossible to dry acetone sufficiently to get completely unambiguous results (Yearly p. 15 - 17) and it is probable that some authors who like Lanning thought that they were using really dry acetone, were mistaken (Nov. p. 71). We used this solvent nevertheless in most of our work after drying it over "Drierite" (anhydrous Ca SO_4) as it appeared in some other respects to be the best.

Hydrocarbons are good solvents for fatty acids (Nov. p 70) and having no reactive hydrogens or hydroxyls will not decompose the soaps. Due to their low hygroscopicity they are furthermore easily dried. Their ability to swell and dissolve aluminum soaps limits their usefulness. We found that the paraffins particularly isooctane could nevertheless be used at room temperature and below with the less reactive soaps such as aluminum stearate, since the latter was completely insoluble even in the presence of stearic acid (December p. 1).

(b) Apparatus.

We have modified the classical Soxhlet apparatus to obtain better control of the variables, particularly the contact between liquid and solid, and the temperature at which the extraction proceeds, while maintaining the solvents in continuous contact with a drying agent. (Yearly p. 18-22).

For conditions approaching equilibrium solubility after various attempts (Yearly p. 58) a precise technique was

finally evolved based on contact of soap and solvent in specially gasketed screw cap vials, centrifugation for separating the phases, and titration of the supernatant liquid. This method was described in detail in the October Report p. 39 - 42 and used since with only minor modifications.

(c) Exhaustive Soxhlet extraction.

When a soap containing about 2 3/4 equivalents of acid per aluminum is extracted with acetone, the general picture is always the same. It is illustrated by the typical curves of Figures 4 and 5 .

There is rapid leaching of acid from the soap by the first liter or so of the solvent until a composition approximating that of the di-soap or sometimes higher by less than 20% is reached. This is followed by much slower but definite extraction thereafter for the next 5 - 10 liters.

(i) The effect of the temperature of precipitation of the soap is shown by curves for two stearates in Figure 4 . It will be seen that both the initial rapid extraction and the subsequent slow one is much lower for the soap prepared at 100°C.

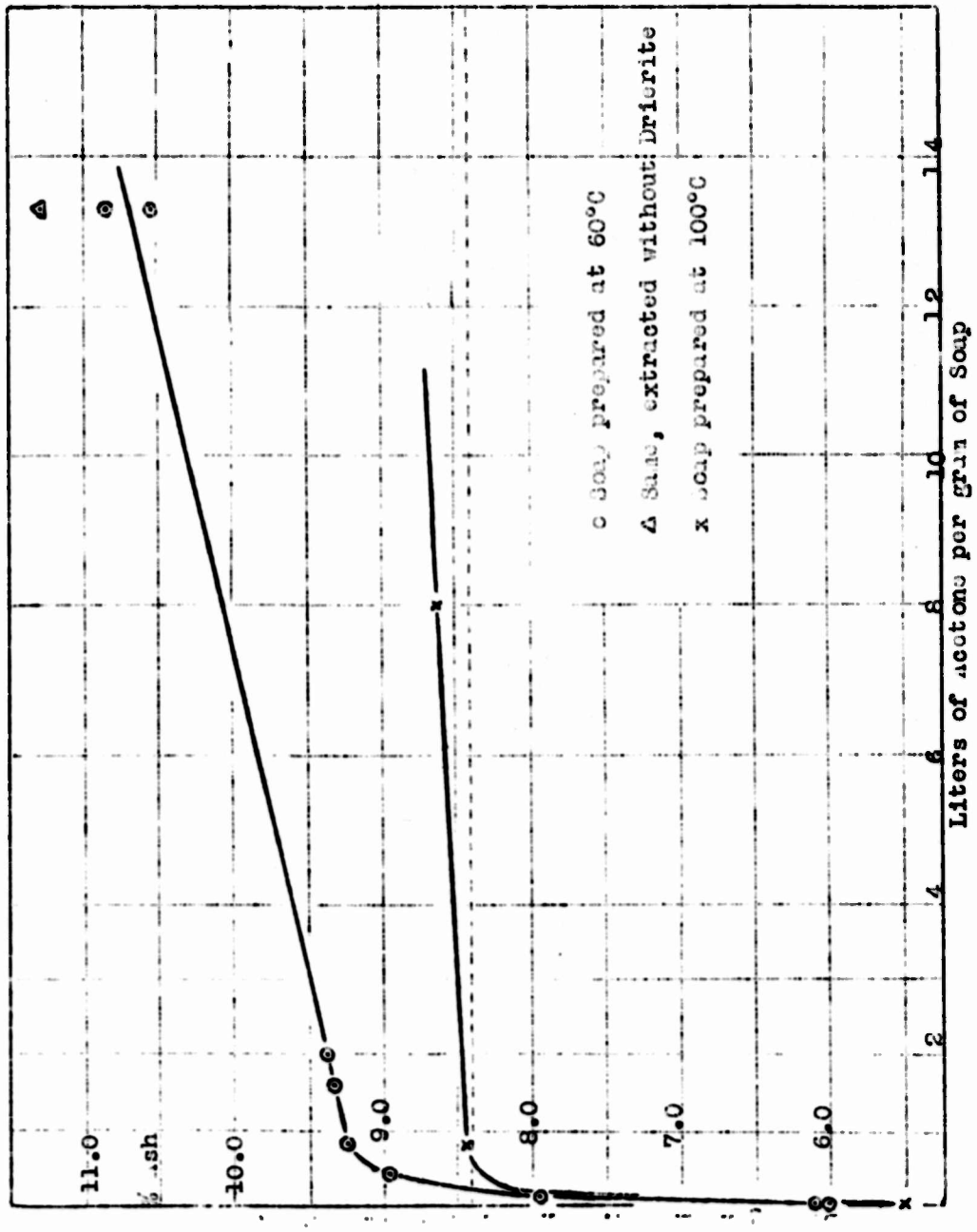
We failed however to find a corresponding effect of the temperature of precipitation for the oleate (Nov. p. 48).

(ii) Effect of the temperature of extraction.

Figure 5 shows the results of extraction of a single sample of aluminum laurate at three temperatures from 2° to 53°C using varying amounts of acetone.

Figure 4

Variation of ash content of aluminum stearate during exhaustive extraction with dried acetone.



It may be noted that at higher temperatures both the rapid and the slow part of the extraction extract higher amounts of acid.

The curve thus obtained at 0°C. is believed to be more accurate than the one presented in Figures 20 and 21 of the Yearly Report of June 1944.

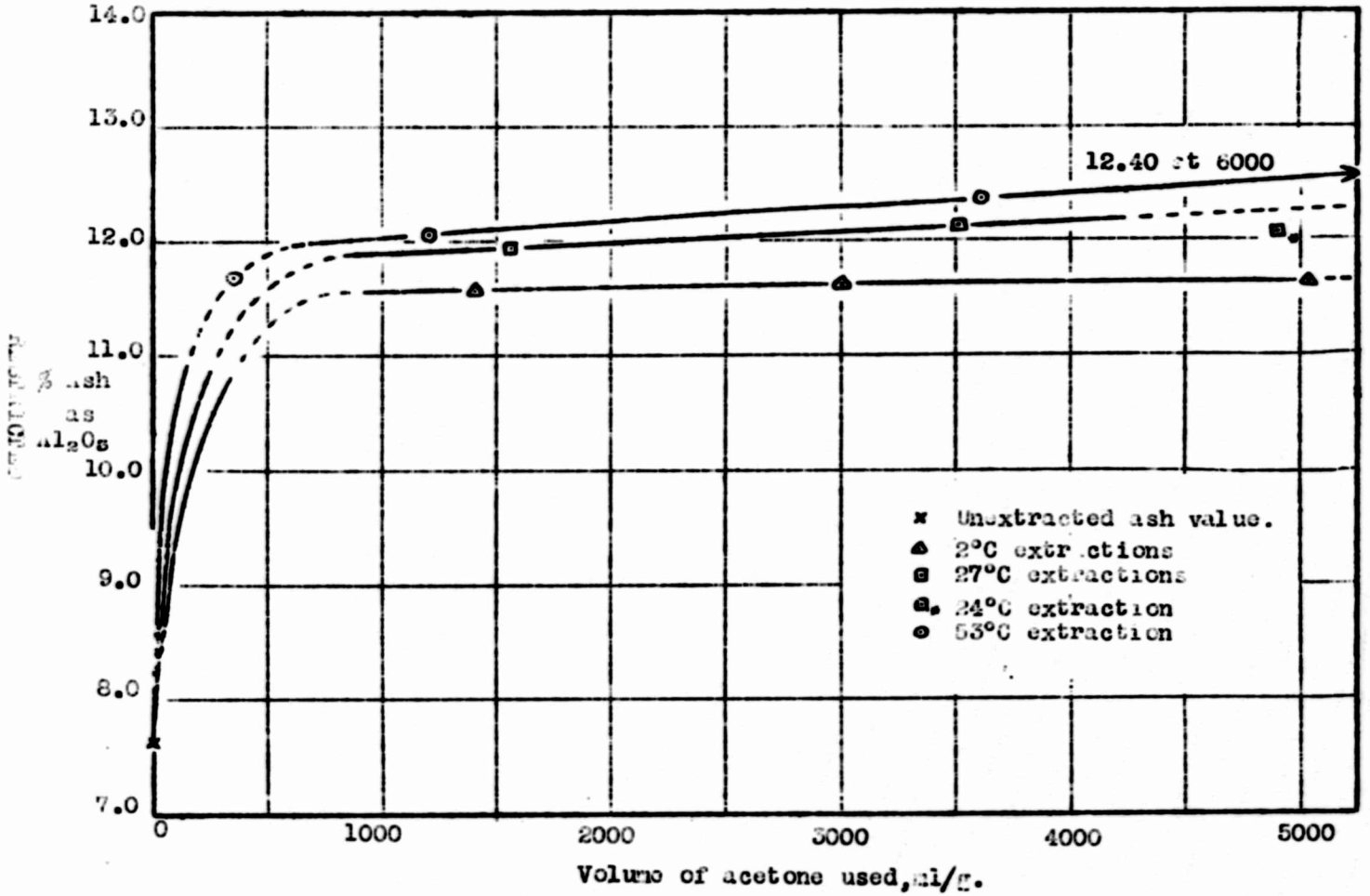
(iii) Variation of humidity at constant temperature. Figure 6 shows the results of a similar series of extractions was carried out on the same sample of laurate at 53°C. in which the humidity in the boiling flask of the extractor was controlled by the use of compounds of different drying powers. Comparison has been made among $CaSO_4$, K_2CO_3 and Na_2SO_4 whose hydrates have dissociation pressures which increase in the order listed.

The general character of the curve did not appear to be affected by the drying agent. However, the amount extracted in both portions of the curve again increased with increasing humidity.

(iv) Effect of the fatty acid from which the soap is derived. Figure 7 shows the result of extraction under comparative conditions of aluminum oleate laurate and stearate. The ordinates of this figure are in terms of moles of acid per aluminum rather than ash as in the preceding figures. The acid is most easily extracted from the oleate and with most difficulty from the stearate.

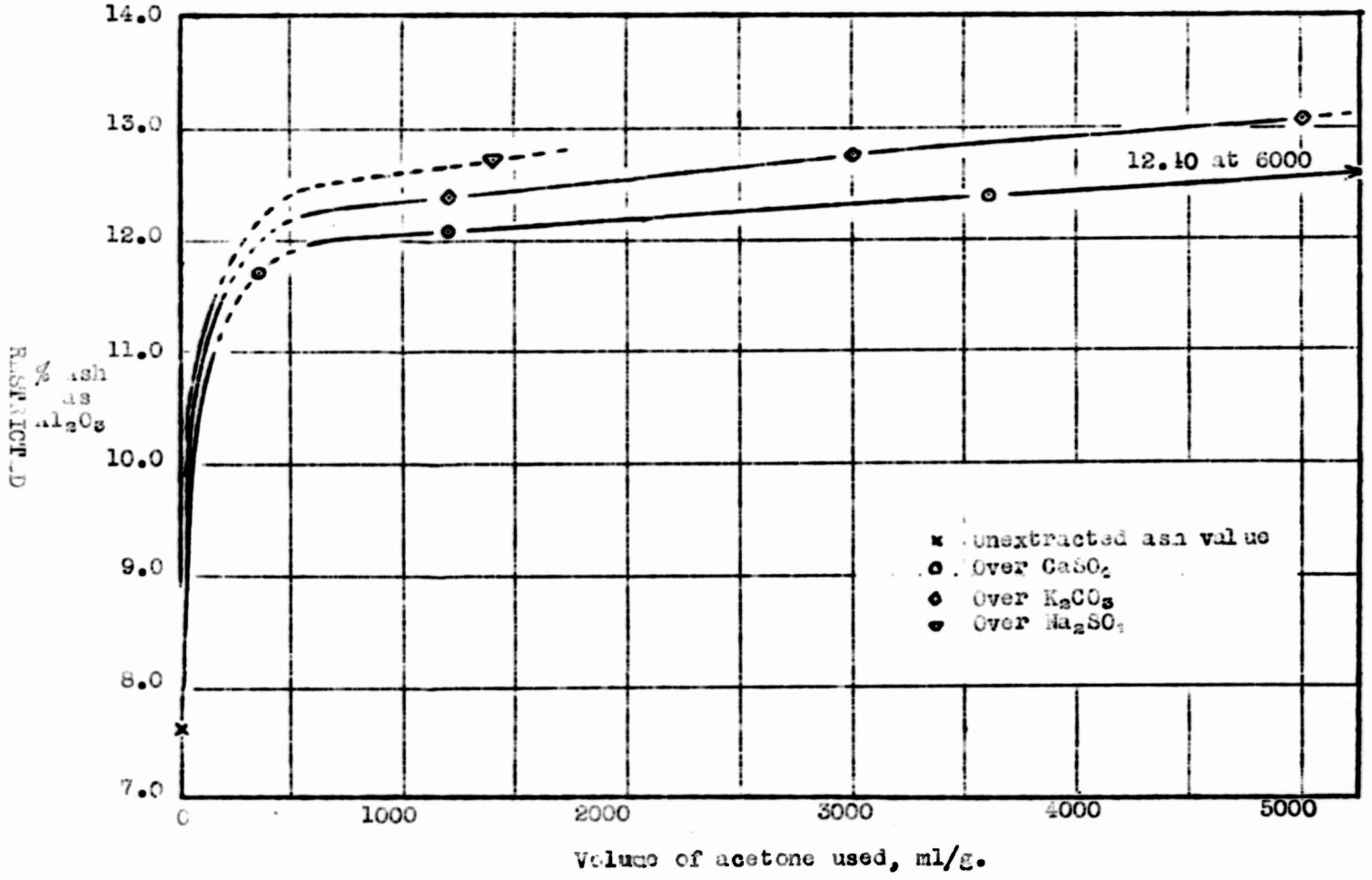
Figure 5

Variation of ash content of aluminum laurate during exhaustive extraction with dried acetone at three temperatures of extraction.



Variation of ash content of aluminum laurate during exhaustive extraction with acetone at three humidities.

Figure 6.

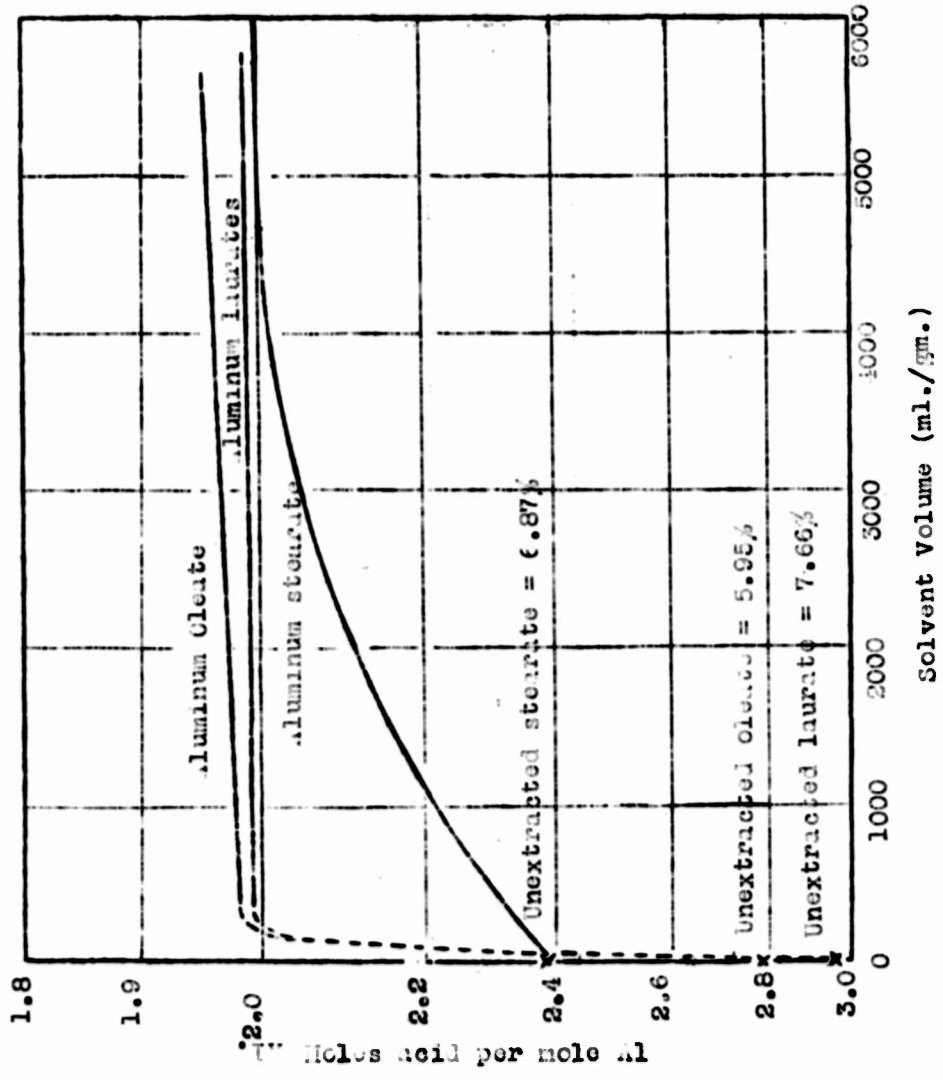


RESTRICTED

RESTRICTED

Figure 7

Modified Soxhlet extraction curves at 0°C of aluminum oleate, laurate and stearate with Drierite dried acetone.



(v) Discussion of Soxhlet extraction curves using acetone. As a working hypothesis we too assumed that:

1. 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

2. The constant slope section of the curve represents degradation of this soap due to a small but continuous hydrolysis by traces of moisture.

This latter 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 by the above experiments (Fig. 6) and has been confirmed by extracting a sample of the soap used in obtaining the upper curve in Figure 4 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. away outside the figure).

The former hypothesis had to be revised however upon closer examination in experiments conducted with the single sample of aluminum laurate and shown in Figures 5 and 6 .

The slope of the flat portion of the curve is small enough so that extrapolation to zero solvent volume would appear to be justified and would be expected to give the composition of the original unextracted soap, containing no free and loosely held acid. If this were the case, extrapolation of all four curves should yield the same intercept because the composition of the soap before extraction is always the same. However, the actual experiments show that the extrapolated values differ by much more than could be

attributed to experimental error as shown by the dotted lines of Figure 8 .

Figure 8 definitely shows that during the modified Soxhlet extractions with dried acetone (except possibly at the lowest temperature) something happens in addition to rapid extraction of free and loosely held acid and slow uniform hydrolysis. A small fraction of the di-soap is subject to a relatively rapid hydrolysis before the constant, slow rate portion of the extraction curve is reached.

Extrapolation backwards thus appears to determine both the amount of mono-soap present in the original soap(if any) and that formed by rapid hydrolysis. This latter amount increases with both temperature and humidity.

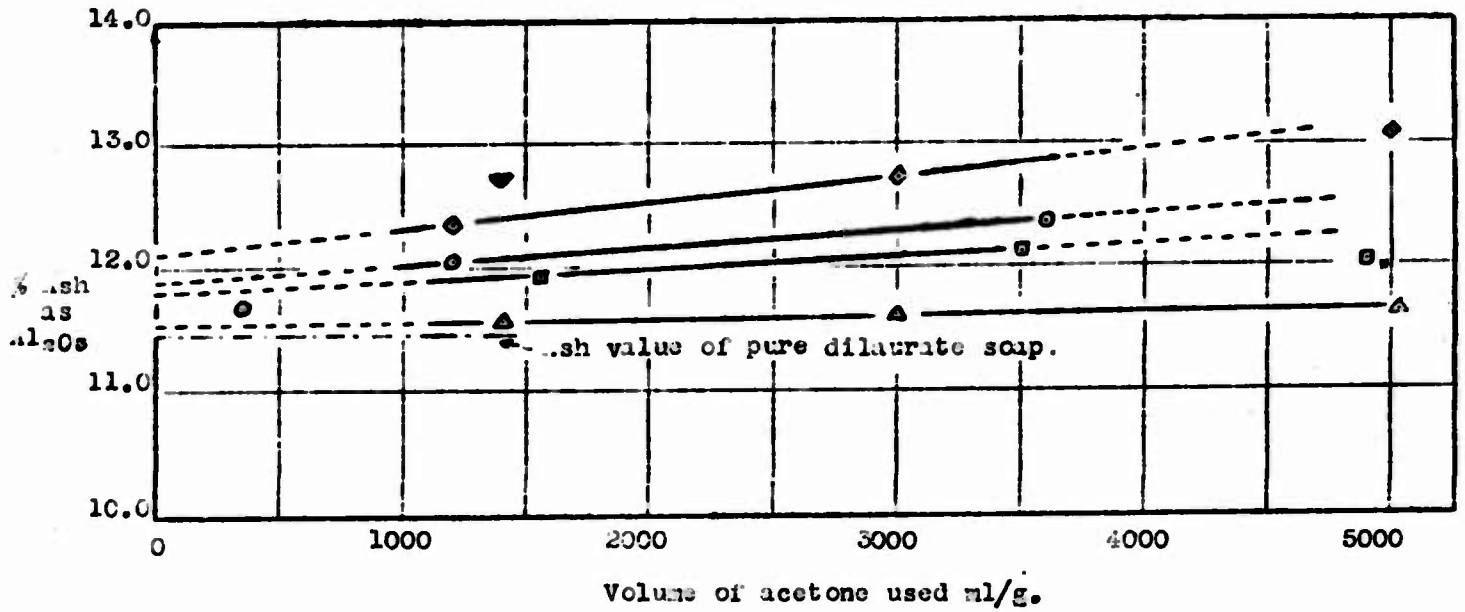
It is of interest that when the extrapolated intercepts of Figure 8 are plotted against the rate of slow hydrolysis, which is measured by the slope of the extraction curve between 1.2 and 4 liters per gram, the points fall on a straight line which extrapolates exactly to the composition of pure aluminum dilaurate as shown by Figure 8 . In other words this extrapolation shows that if extraction proceeded at a temperature where hydrolysis (during the slow rate part) was negligible, then the extracted laurate would have exactly the composition of a dilaurate $Al\,OH.L_2$.

(vi) Present interpretation. This leads to the conclusion that during exhaustive Soxhlet extraction with acetone, even dried with Drierite, there is first and foremost a relatively rapid extraction of molecularly bound acid and

RESTRICTED

Figure 8

Extrapolation of the extraction curves from Figure 5 and 6



RESTRICTED

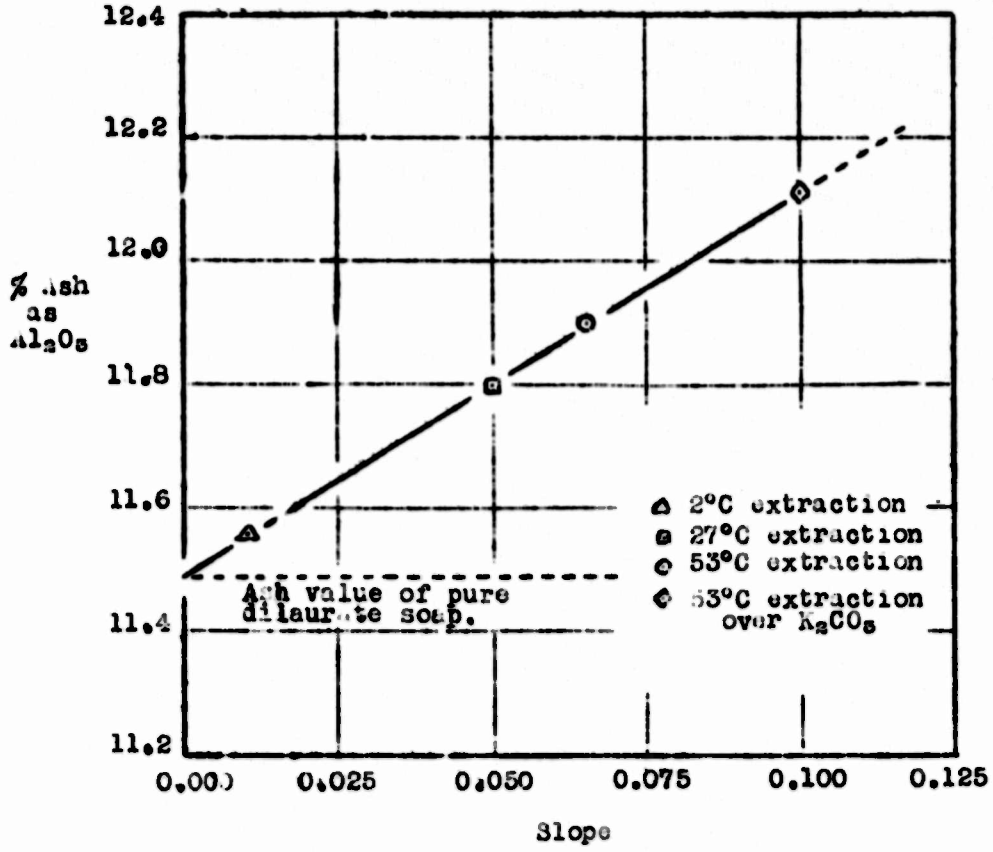
practically simultaneously rapid hydrolysis of a small fraction of the soap. These are followed by slow hydrolysis of further portions of the soap. In other words, a small fraction of the dilaurate is rapidly hydrolyzed even at 2°C. Another is slowly hydrolyzed at 2°C and accounts for the slope of this line. Slightly more di-soap is rapidly hydrolyzed at 27°C. than at 2°C. Thus the fraction subject to rapid hydrolysis does not influence the slope of the flat portion of the curve but only its intercept. The same may be said for the whole series of curves, including those pertaining to variation of humidity at constant temperature.

Variations in the readiness of hydrolysis of the many fractions of an aluminum dilaurate is in harmony with the facts that aluminum soaps are composed of many physically different fractions of the same chemical composition(p.159) and that aluminum stearates prepared under various conditions are hydrolyzed at different rates when extracted under identical conditions. (Fig. 4).

(vii) Use of Isooctane. The use of this solvent is still in the explanatory stages but shows real promise for the preparation of di-soaps. Our general method of preparing pure di-soap has been the precipitation of a soap containing a large excess of fatty acid followed by extraction of this acid under conditions minimizing hydrolysis. This has always been troublesome heretofore when using acetone as the extracting agent, since this solvent cannot be dried completely. The fact that the excess fatty acid is, in part at least, bound tenaciously to the soap requires extraction

Figure 9

Plot of intercepts versus slopes of Figure 8.



with large volumes of solvent and preferably at a high temperature, both of which increase greatly the danger of hydrolysis.

In order to evade this difficulty, we began using Soxhlet extraction with dry isooctane. Its main drawback is that at high temperatures it jellies and dissolves the soaps, and even at low temperature the soap obtained after evaporation of the solvent is not as light and fluffy and easily dried as after the use of acetone. Furthermore it seems to require definitely larger amounts of solvent and longer extraction times. This may be in part due to poorer contact due to the swelling of the soap.

Extraction of a small sample of aluminum laurate in our modified Soxhlet extractor at room temperature with 1200 ml. per gram, gave a product having an ash of 11.64% compared with a theoretical ash for the di-soap of 11.52% and opposed to an ash of about 11.9% obtained under the same conditions with our driest acetone.

Extraction of a larger sample of some soap under similar conditions gave an ash of 11.31% showing incomplete extraction.

Extraction of a stearate in an ordinary Soxhlet apparatus left a clear jelly in the thimble (since extraction proceeded at the boiling point of isooctane). This jelly however after drying had an ash of 8.47% compared with 8.52% corresponding to the theoretical distearate, showing that in spite of extreme conditions only the excess of acid present above that required to form di-soap was removed.

Extraction at room temperature with 1500 ml/gm gave an

the soap and solvent, and one corresponding to the final state. It is therefore proper to represent each experiment by an arrow connecting these two points.

These arrows show what happens when a soap and solvent of given composition are in contact. This method of representation is shown in Figures 10 to 14 . When the composition of the soap is calculated, it is shown by a circle; when determined by ashing, it is shown by a cross. When acetone is used as a solvent the arrows are drawn as straight lines, and when isooctane is used they are crosshatched.

The points of similar arrows are connected by a heavy line which delineates a curve at which the soap was in contact with the solution of that final composition, even if true equilibrium was not obtained. Occasional variation of the shaking time from 12 hours to 4 days did not affect these lines appreciably.

The constant state thus reached does not correspond to a strict reversible equilibrium because the same composition-solubility curve is not obtained when approached from either side as may be seen in Figure 12. The lower "extraction" line measures, nevertheless, the degree to which the remaining unextracted acid is held by the soap of this composition under the experimental conditions, or it may show that there was too little solid in proportion to liquid to produce a greater degree of saturation. However, this last possibility is removed in some of our experiments by the simple device of taking an extracted residue and exposing it again to a

lower concentration of fatty acid in the same solvent. This is shown by a series of successive arrows, the beginning of each lying vertically under the end of the preceding arrow. This always takes out further fatty acid, showing that it was there, but sorbed or bound. The process stops when pure di-soap is reached, but since moisture produces more fatty acid by hydrolysis, some mono-soap is produced when very large amounts of acetone are used (i.e. as in Soxhlet extraction).

Four samples of soap were studied by this method. Three (Nos. 2, 11 and 45) were prepared from Eastman stearic acid. The fourth (No. 42) was prepared from less pure "Kahlbaum" acid and was less significant, and is discussed in Section I of the Monthly Report for November.

(i) Extraction with dried acetone. Sample No. 11 was also used in the upper curve of Figure 4 . Its empirical composition, corresponding to an ash of 6.07%, was Al OH.Str_2.0.82 HStr. Hence to produce the di-soap Al OH. Str_2, a total of 0.82 moles HStr has to be extracted per mole of original soap. When acetone nearly saturated with stearic acid is used, only 0.24 moles H Str is extracted, as is seen in Figure 10 ; that is, the sample loses only 6.7% of its original weight. This is only 0.24/0.82 or less than one-third of the stearic acid above that combined as di-soap. This places an upper limit to the amount of free stearic acid that pre-existed as such in the original soap. The remaining 70% of the amount of stearic acid in excess of that required for di-soap is not free, but must be bound, either as acid di-soap mixed with di-soap, or sorbed by di-soap.

On the other hand the flat portion of the curve in Figure 10 at 100% saturation of the acetone with stearic acid reveals that at least 5.7% of the original soap is completely free stearic acid since it was capable of dissolving in nearly saturated acetone and bringing it up to 100% saturation.

The successive extraction shown by the arrows in Figure 10 show that as the extraction proceeds the acid becomes less and less available, as if the acid were being progressively desorbed. This makes the interpretation as sorption of acid by di-soap highly probable even though it has been shown that fineness of subdivision and degree of crystallinity may markedly affect the reactivity of aluminum soaps and somewhat distort the evidence for chemical combination based upon theoretical considerations. For a crucial test for Al OH Str_2.H Str the specimen would have to be fully crystallized.

Sample No. 2 is the same as used in experiments of p. 56 - 61 of the Yearly Report. The present results are shown in Figure 11 and are believed to be more reliable than the previous ones (Yearly p. 58 - 60). They are essentially similar to those of sample No. 11.

The results with sample No. 45 are shown in Figure 12. Comparison of this figure with the preceding one shows that the behavior of these two samples differs appreciably. In sample No. 45 the amount of free acid appears to be smaller, of the order of only 2%.

Figure 10

Concentration of HSt in Acetone and Isooctane in Equilibrium with "AlSt" (13-F284-11) at 30°C.

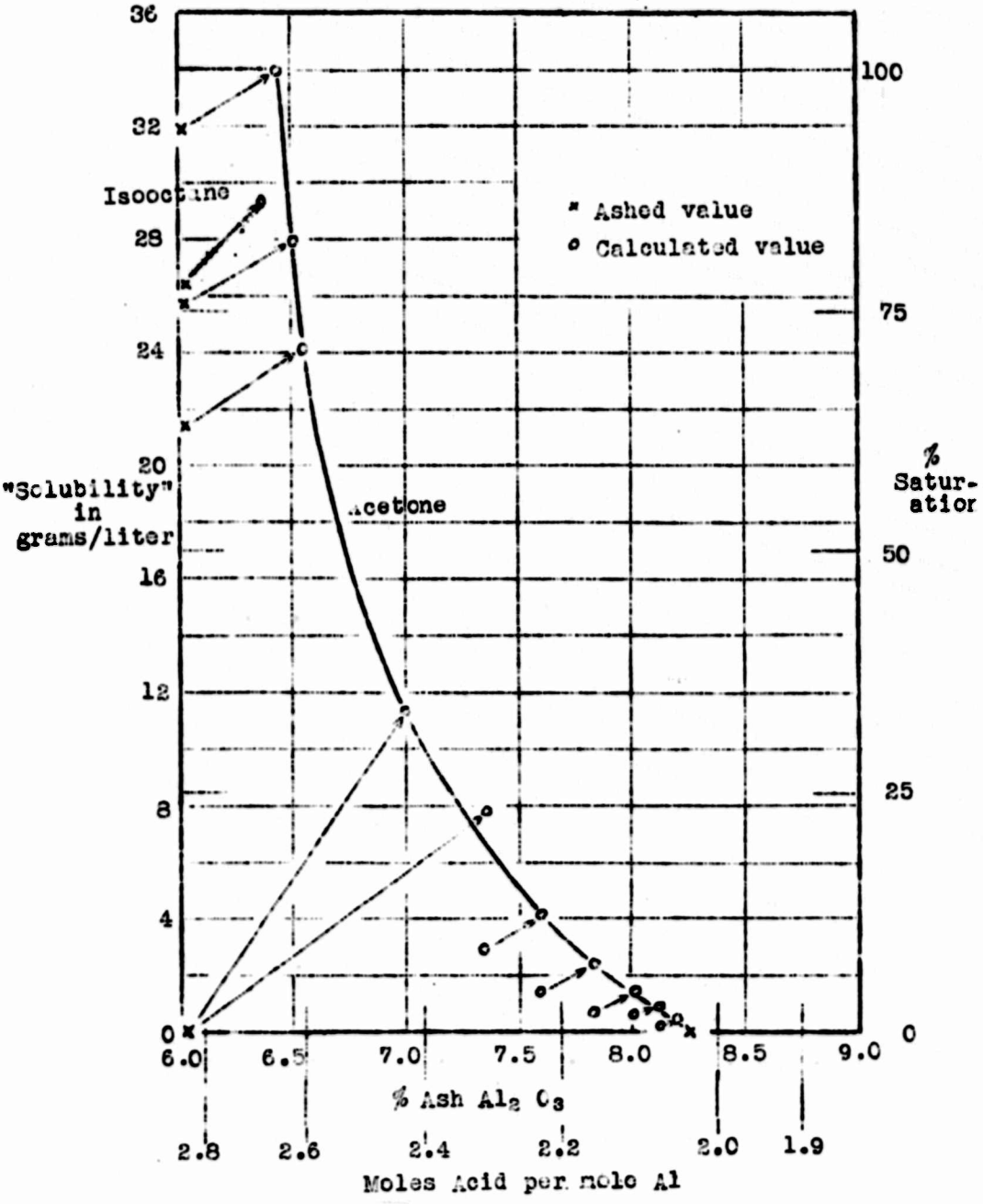
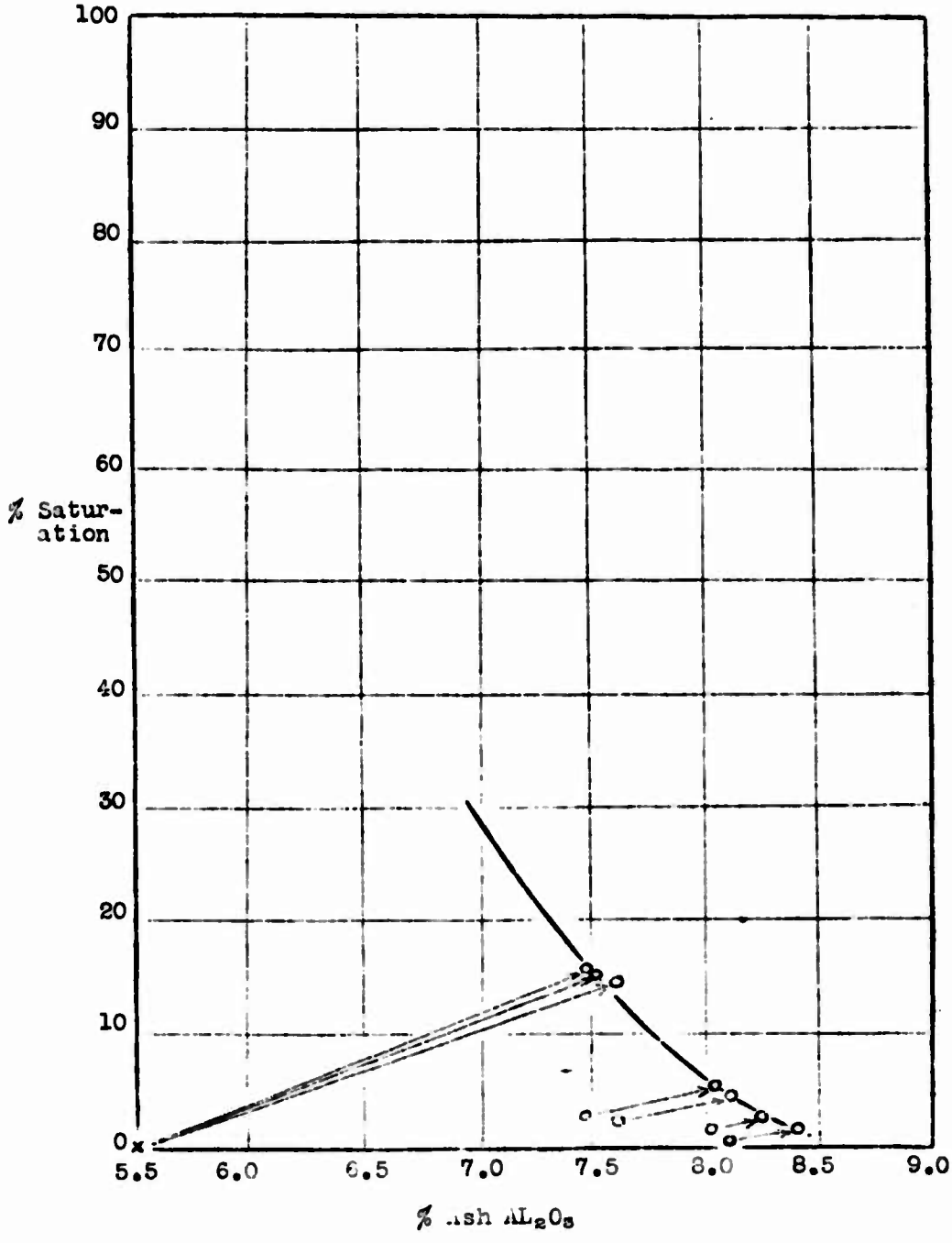


Figure 11

Concentration of stearic acid in acetone in "equilibrium" with aluminum stearate Sample No. 2 at 30°C.



However, in particular, the solubility values for sample No. 45 instead of falling upon a single line, seem to lie on two lines, one of which (like that in Sample No. 11) points towards the composition of distearate, and the other lies a little on the side towards the mono-soap.

This discrepancy of solubilities from sample No. 45 seems to be beyond experimental error. The only apparent explanation is that this sample No. 45 contained originally some mono-soap (absent from sample No. 11) and that when the soap is placed first in contact with a concentrated solution of stearic acid, part of this acid combines with the mono-soaps and forms di-soap. The possibility of this reaction under similar conditions is suggested in Figure 13 below. If the sample has been in contact only with dilute solutions of stearic acid this reaction apparently does not proceed to completion.

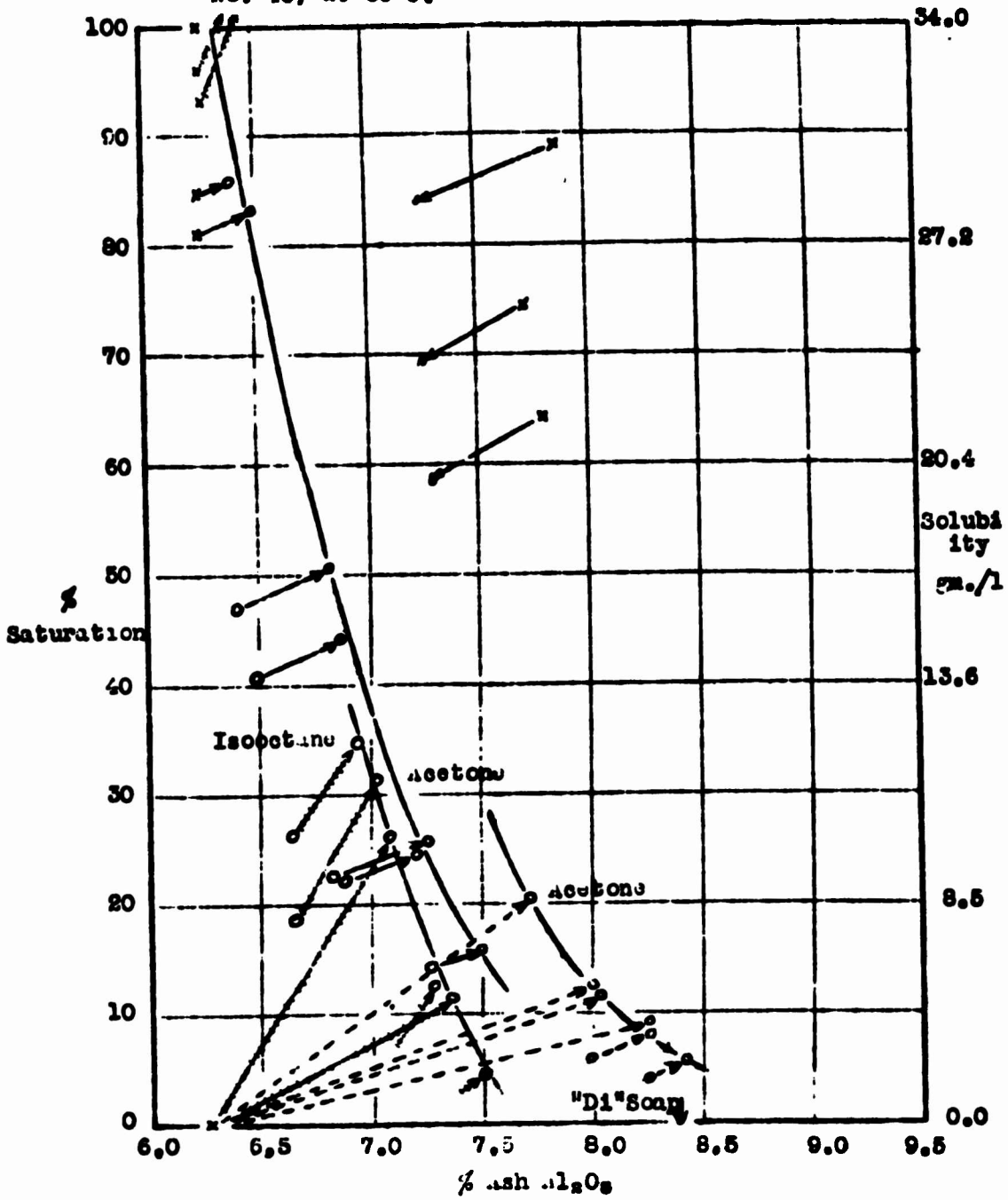
(ii) Extraction with isooctane. The separation of soap from supernatant liquid by centrifugation is not as clear-cut as with acetone because small slightly swollen soap particles have a tendency to remain suspended giving a slight opalescence. This may cause some of the solubility values to appear somewhat higher but is not believed to cause significant errors. Occasional checks on the supernatant liquid showed that it contained from 0 - 1% of the soap present.

With soap No. 11 only one experiment was performed and it fell on the acetone line.

With sample No. 45 the issoctane results appear to be

Figure 12

Concentration of Stearic Acid in Acetone and Isooctane in Equilibrium with Aluminum Stearate (Sample No. 46) at 30°C.



more consistent than the acetone ones and show a definitely lower relative solubility for a given composition.(Figure 12)

As the saturation value is also much lower in isooctane (Nov. p.66) it is obvious that the absolute solubility of fatty acid from this soap is much lower in isooctane than in acetone.

(iii) Effect of moisture. The effect of moisture is shown in Figure 13 for sample 11 and in Figure 14 for sample 45. Here the percentage of water present is indicated by the notation on the arrows. For comparison, the equilibrium line for extraction with dried solvent is dotted in.

The surprising result is the lack of effect of the presence of water even up to rather large quantities (4%). This may at first appear to be in complete contradiction to the well-established fact that aluminum di-soaps are markedly hydrolyzed by acetone containing even small amounts of moisture. (Cf. eg. British P.W.B. Memo 151, our Yearly p. 26, this report p. 46). Closer examination of the data reveals however that the present results are the only ones obtained using moist solvent containing a substantial amount of stearic acid in solution. This suggests that in the presence of sufficient acid the hydrolysis of di-soap by moist acetone may be prevented.

(iv) Reaction of "mono" stearate with stearic acid. The arrows pointing downward and to the left in

Figure 13

The Composition of Acetone Solutions of Stearic Acid in Equilibrium with Aluminum Stearate at 30°C

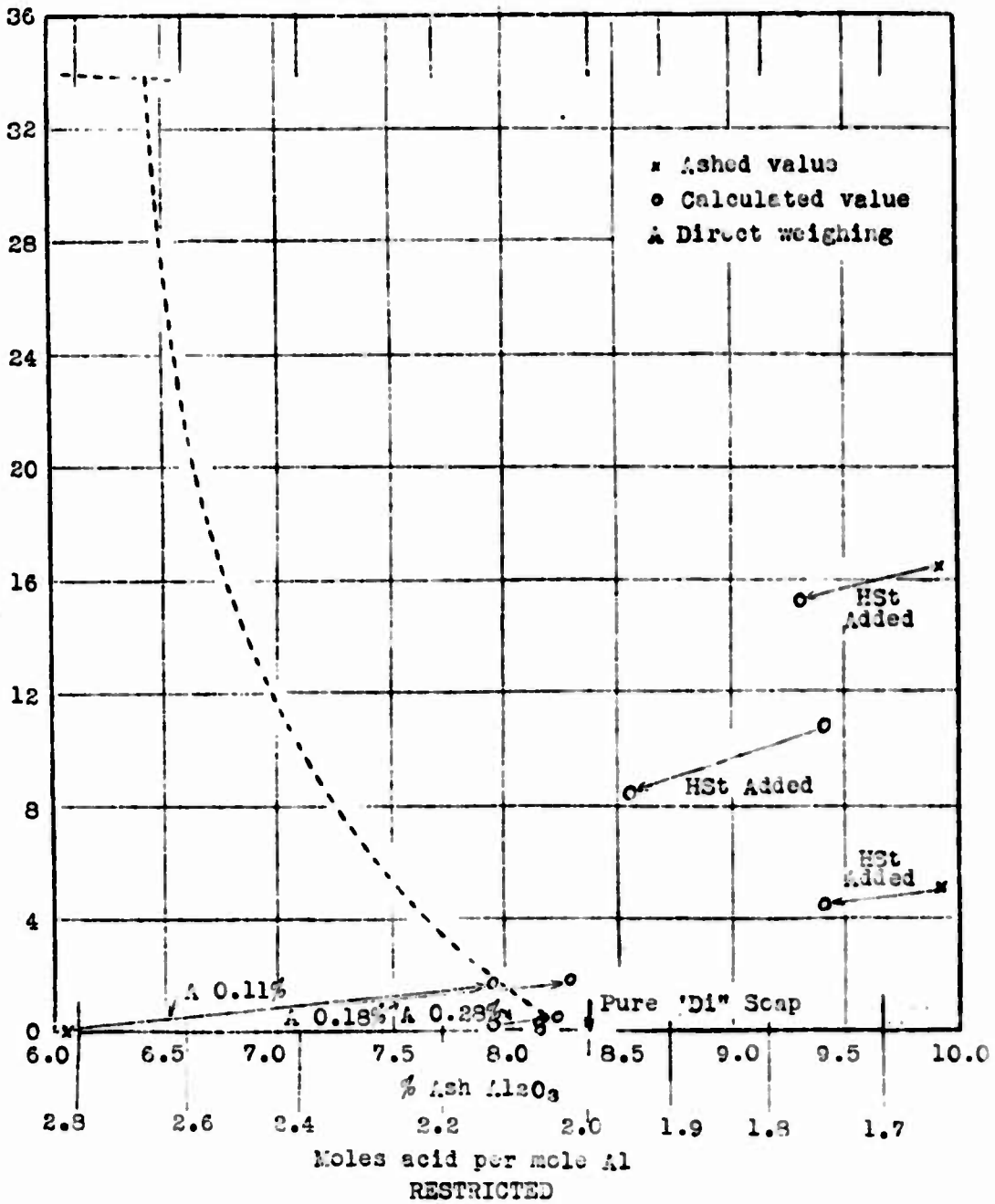


Figure 14

Concentration of Stearic Acid In Moist Acetone and Isooctane in Equilibrium with Aluminum Stearate No. 25 at 30°C Compared to the Concentration in Dry Solvents.
(The figures indicate the added percentage of moisture in the acetone)

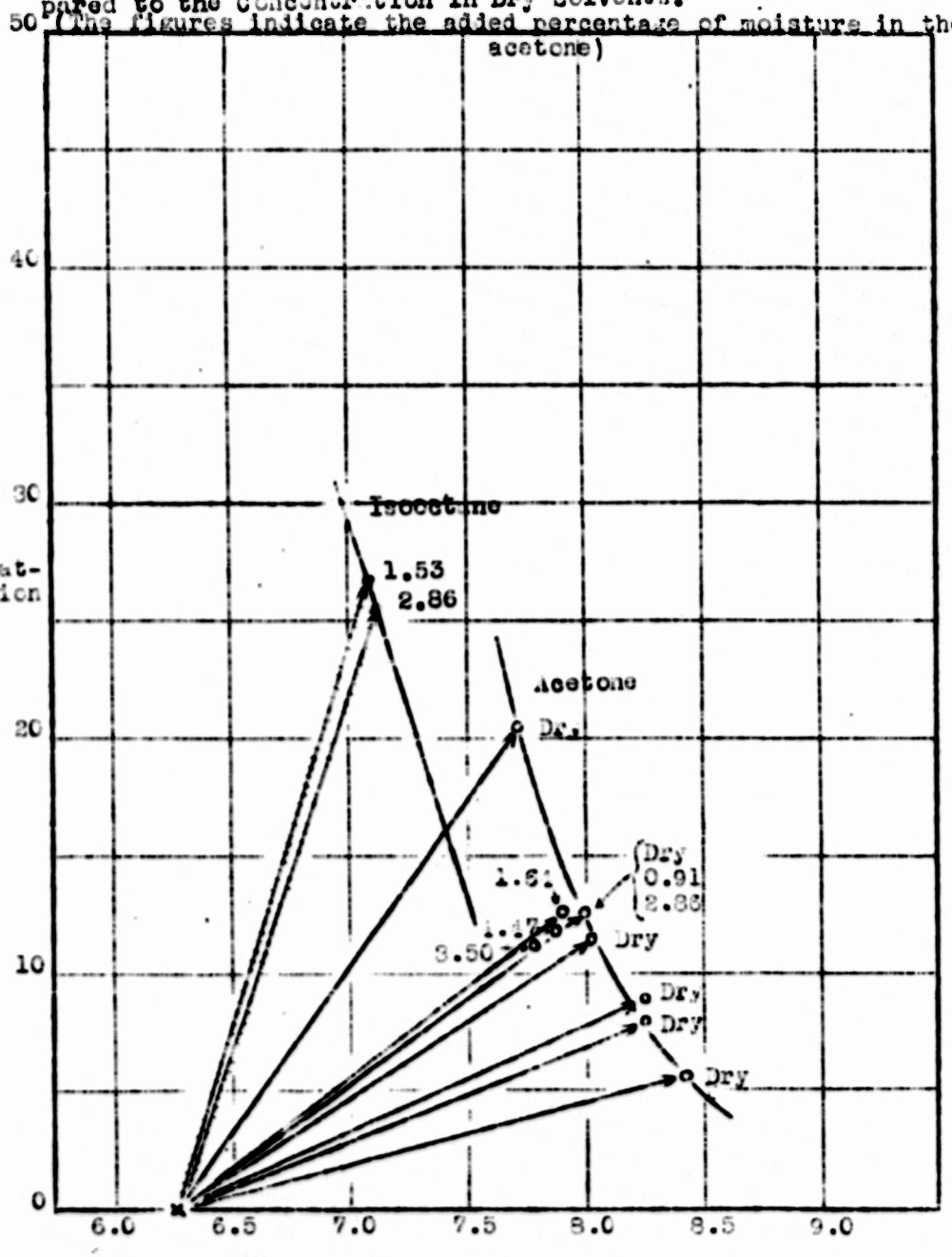


Figure 13 were obtained by placing samples of the same soap (No. 11) but extracted and partially hydrolyzed by Soxhlet extraction to an ash of 9.92% in acetone containing stearic acid. In all cases the amount of stearic acid in solution was reduced. The most likely interpretation is that at least part of it reacted with the monostearate present to form distearate and water. The presence of the latter would prevent the reaction from proceeding further. There is however an alternative possibility, namely that the acid is simply sorbed by the solid soap.

Time was not yet available to distinguish between these hypotheses (cf. p.126 Benzene Distillation).

(v) Interpretation. The outstanding result of these experiments is the definite proof that fatty acid may be present in molecular form in a soap without being free; the soap having the capacity of fixing probably by surface sorption, about one-half a molecule of acid.

On the other hand molecular acid present above the amount sorbed may be proved to be completely free and its amount determined.

Finally the frequent occurrence of pure di-soap containing sorbed acid in aqueous precipitates and the difficulty of separating these two components without partial destruction of the soap is emphasized.

C. Extraction of Napalm.

As shown by the preceding experiments the problem of extraction of aluminum soap and the separation of soap from acid is far from being simple even in the case of pure soaps. In the case of Napalm it is further complicated by the presence of a variety of free and combined acids, the reactivity of the soap, the presence of unsaponifiable substances and of inorganic salts.

Soxhlet extraction of this soap at the boiling point of acetone either dried or in the presence of moisture, have been conducted by C.W.S. Columbia (B.B. 45) and showed a behavior similar to that found by us in case of pure soaps but with a less pronounced break between the rapid and slow portion of the extraction curve.

They developed a simple method for determining "free" acid in Napalm by batch extraction with a large amount of

acetone and obtained results of the order of 7% (B.B. 71/72).

We have used a similar but titrimetric method with a relatively large volume of acetone on small samples of pure soaps. (Yearly 25-, 27).

(a) Extraction with methanol ether and with acetone.

Harshaw treated Napalm with a mixture of methanol ether under conditions not specified and considered that the extract thus obtained represents free acid (their Sixteenth and Fourth Monthly Report).

This value is very high as compared with the C.W.S. value. In order to compare the two techniques we extracted two portions of a single sample of Napalm with acetone and 50-50 ether extract mixture and found that the latter gave a markedly higher result presumably through alcoholysis of the soap (October 16 - 20, also British P.W.B. Memo 451).

We have also found that unsaponifiables from Napalm have a high iodine number and are easily extracted so that an iodine number on a Napalm extract may give an erroneously high oleic acid content unless the unsaponifiables are first separated.

(b) Extraction with isooctane.

Both of the above solvents might have produced by hydrolysis (or alcoholysis) at least some of the acid they extracted. To eliminate this possibility we used isooctane.

Since Napalms disperse completely or swell markedly in isooctane (cf. p. 162), if sufficient contact time is allowed, it is necessary to conduct the extraction rapidly.

Contact for 5 minutes yields 3 - 5% of extract. This extract contained a small amount of soap since it had an ash of 1%, and had an acid number of 135. If the ash is AL_2O_3 there is approximately 10% of soap in the isooctane extract and even if one assumes that the aluminum can react with KOH in the titration the acid value necessitates the presence of uncombined acid in the extract.

(c) Interpretation.

Thus a minimum value of about 2 - 4% is placed on the amount of uncombined acid by the isooctane extraction and a maximum value of about 7 - 9% by acetone extraction.

Whether this acid is free or molecularly bound remains undecided because probably in neither case was the solvent saturated with acid at the end of the extraction.

D. X-ray Examination of Aluminum Soaps.

In the early part of this work all the x-ray diffraction patterns and microphotometer tracings were kindly made by Dr. Sydney Ross and his advice was received throughout this work- all without support of N.D.R.C. funds.

Powder (Debye - Scherer) diffraction patterns of aluminum soaps have thus far been obtained because these soaps have never been produced as single crystals or well formed fibers.

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 in the texture and sharpness 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 a few percent of a substance seldom gives a definite pattern unless it is very crystalline. The presence of a small amount of impurity seldom affects the pattern of another substance.

When but little information is obtained as to the crystal structure of a substance, but the phase rule criteria show that it is reasonably pure, the x-rays often give a characteristic fingerprint of it by which it may be traced thereafter.

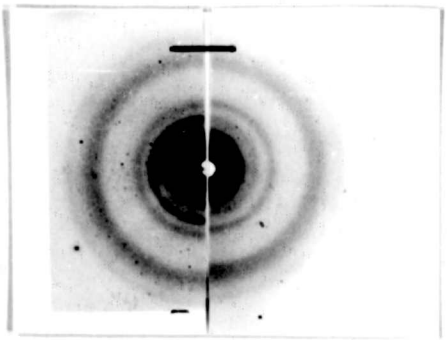
(a) General survey of x-ray diffraction diagrams.

Napalms give x-ray powder diagrams consisting of fairly sharp rings as shown in Figure 15 . They closely resemble those of aluminum dilaurate, likewise given for comparison in Figure 15 . This figuregives both a photographic replica of the actual diffraction patterns and microphotometer tracings along a diameter of these patterns. For ease of reproduction we show hereafter only the microphotometer tracings. Figures 16 and 17 give microphotometer tracings for the x-ray patterns of ten Napalms as received by us. They show definite differences between various manufacturers but have not been correlated with any other properties.

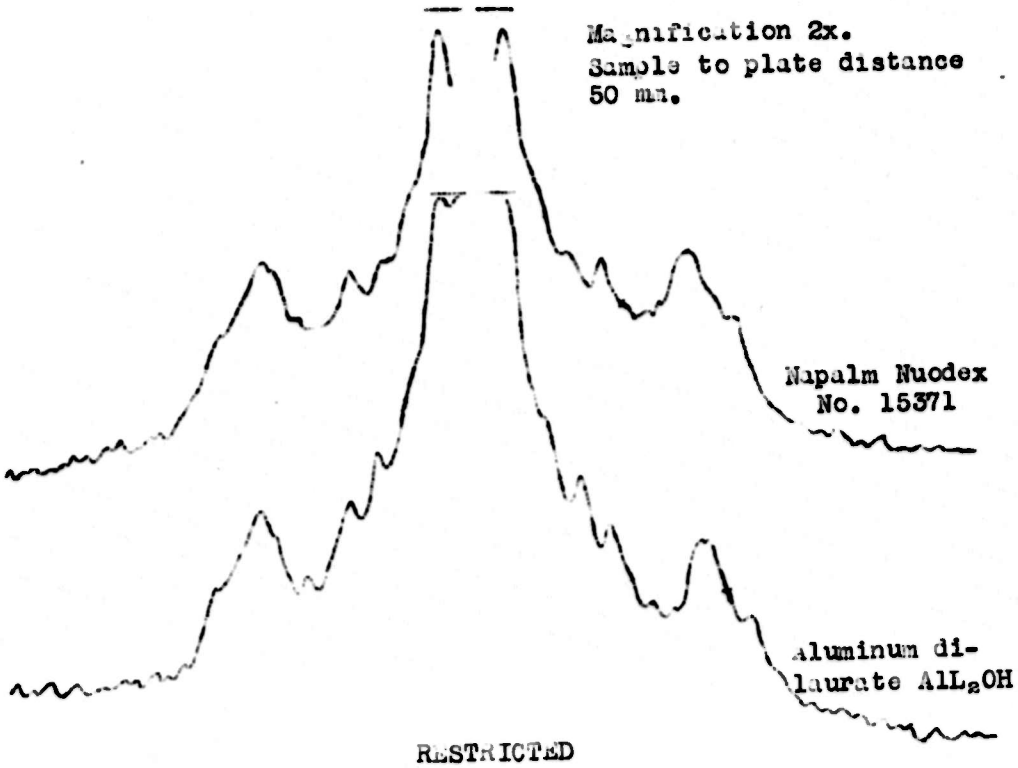
The effect of variation in the physical state (crystallinity) of a single soap upon its diffraction pattern is illustrated by Figure 18 . The samples tested range from a highly crystalline to an almost amorphous substance, yet

Photographic reproduction x-ray diffraction patterns of Napalm and aluminum dilaurate.

Figure 15



Reproduction of microphotometer tracings of the above x-ray Patterns.



all were of the same chemical composition corresponding to the dilaurate Al (OH) L_2 but obtained by various physical treatments as described in Table IV below.

Similar results on Napalm will be discussed later (p. 139).

The effect of protective colloid during preparation of Napalm has already been discussed on p. 32 ,

Figure 19 is a schematic diagram of x-ray diffraction patterns of the known forms of alumina 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 peptizates of aluminum by fatty acid. The alumina pattern is absent from their x-ray diagram.

Characteristic tracings of aluminum laurates and stearates are discussed in detail below. Tracings of dioleate, di-cyclohexane carboxylate, and dinaphtenates are shown in connection with the individual soaps. Those of commercial stearates and oleates and naphthenates are discussed in the October report p. 31, 46 and 19.

X-ray diffraction patterns dealing with the systems aluminum soap-water and aluminum soap-hydrocarbon are discussed later in connection with the corresponding chapters. Those of a few more Napalms, aluminum laurates, and sodium laurates are shown in Figures 10 to 13 of the Yearly Report of June 1942.

(b) Polymorphism of aluminum stearate and laurate.

A large number of samples of aluminum stearate, both extracted and unextracted, have been examined and some correlations may be proposed.

Figure 16

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

Sample to plate distance 5 cm.

magnification 2x.

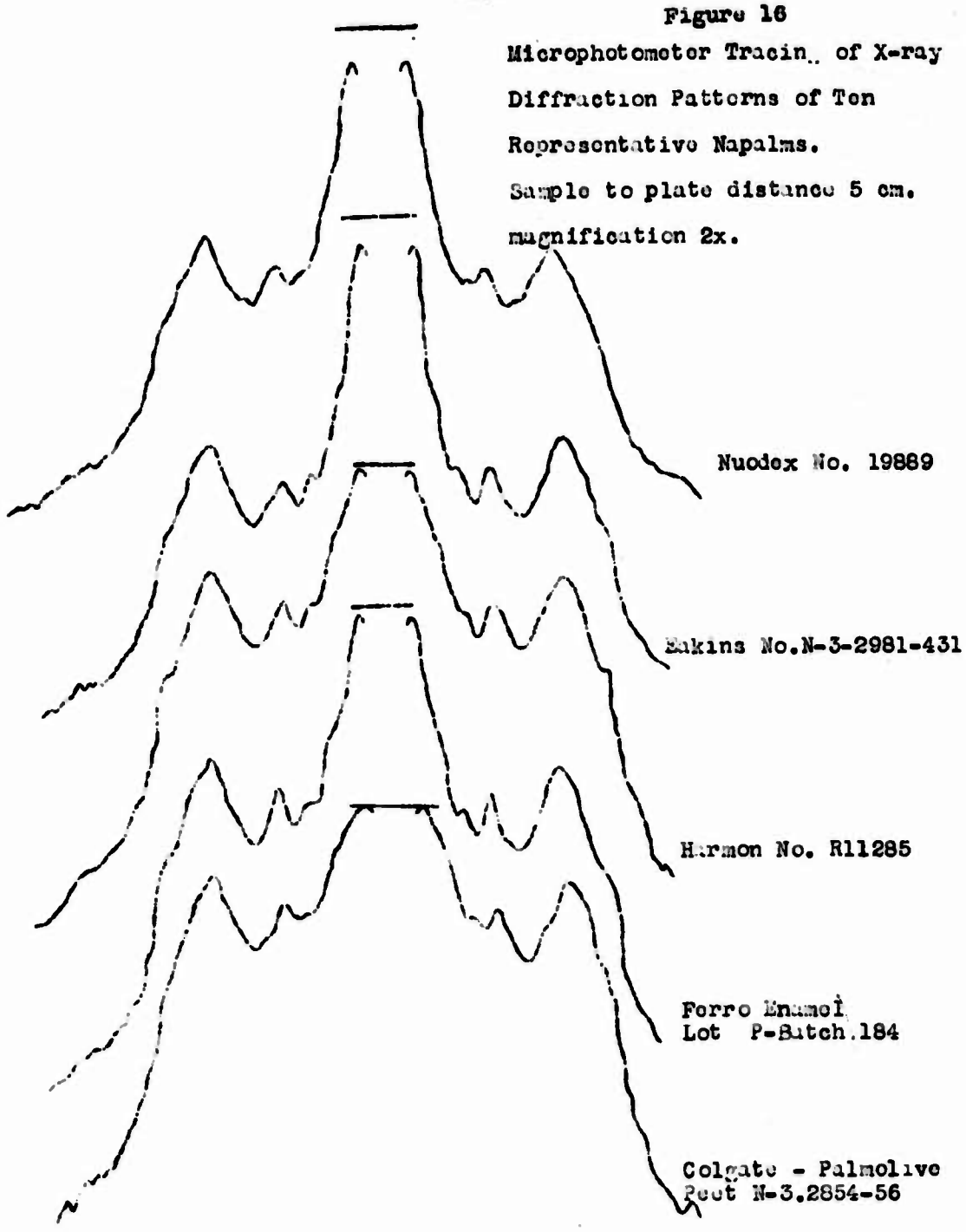
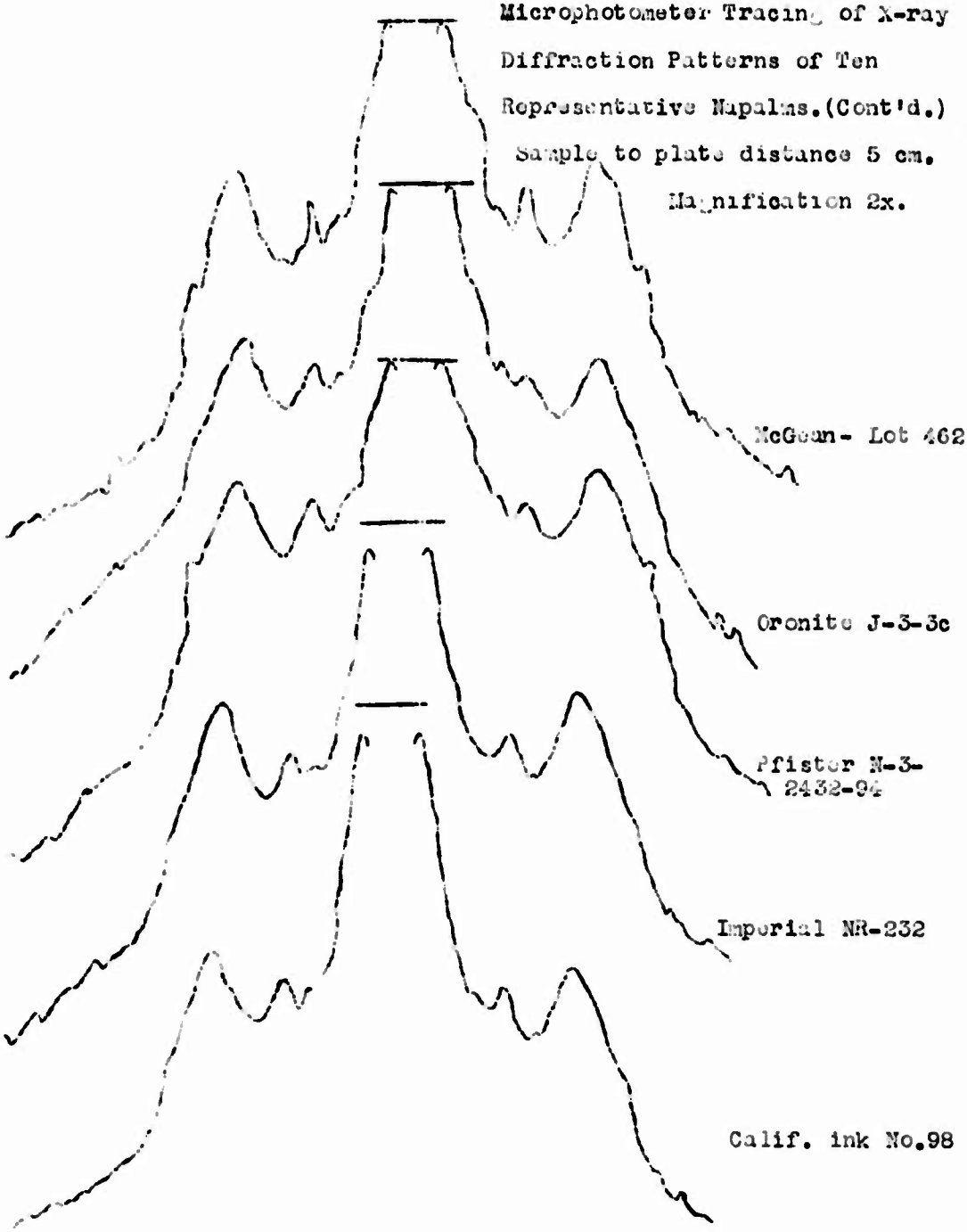


Figure 17

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

Sample to plate distance 5 cm.

Magnification 2x.



Microphotometer tracings of x-ray diffraction patterns of various forms of aluminum dilaurate.

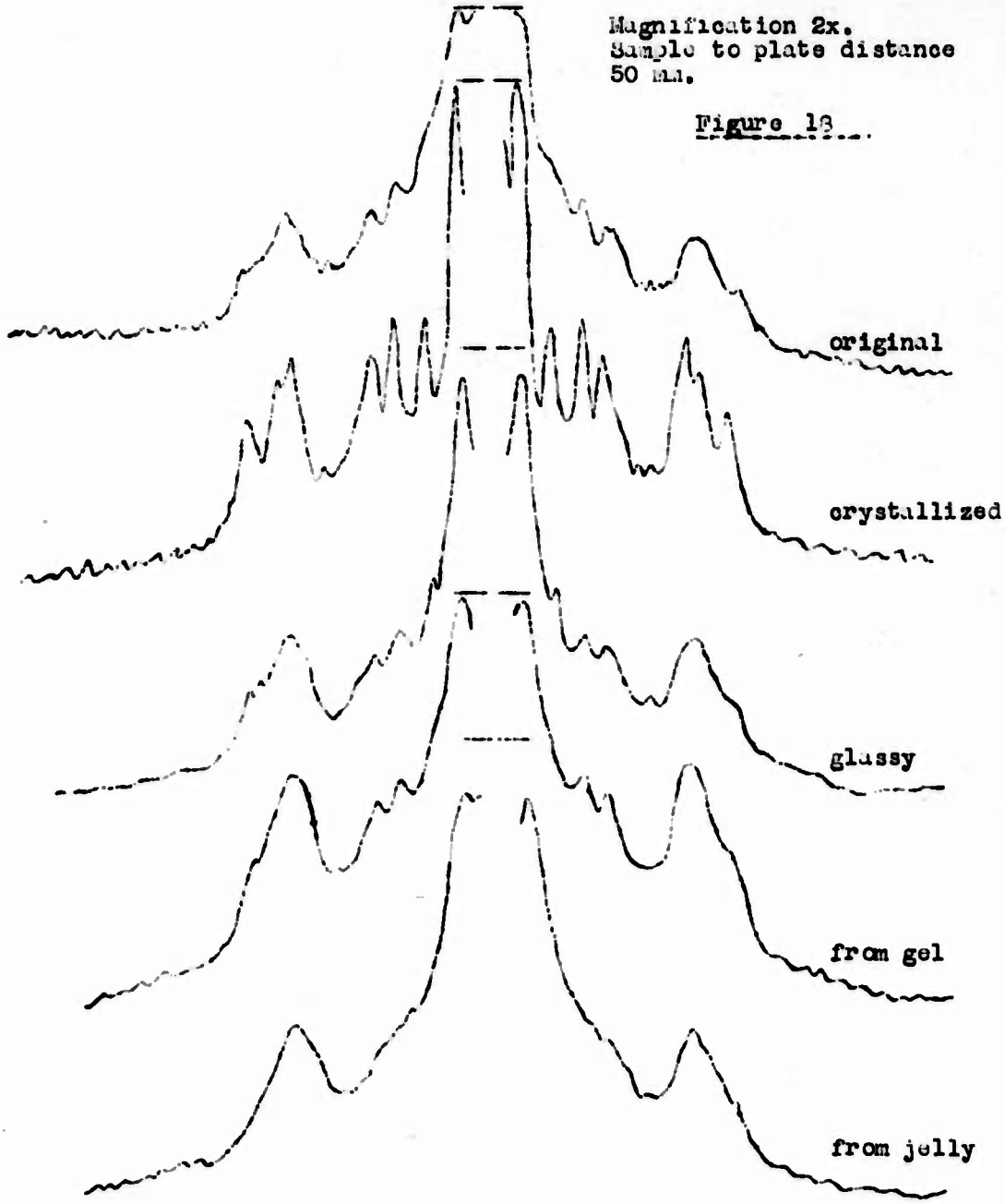
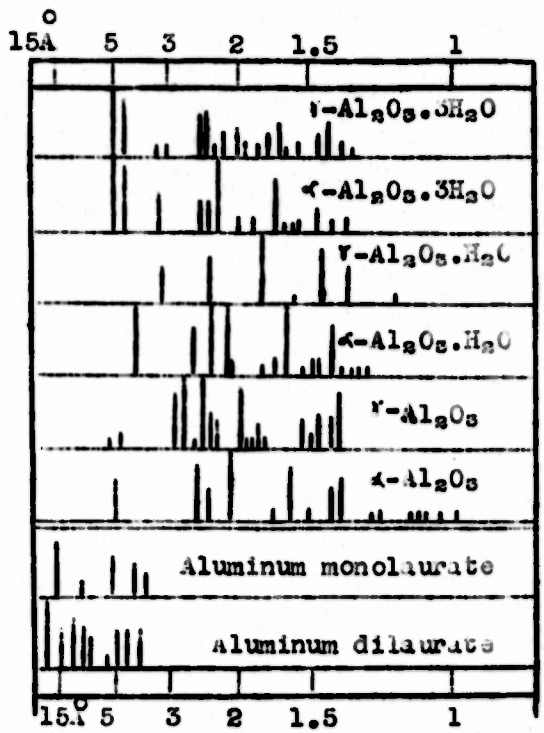


Figure 13

Figure 19

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



Only soaps obtained from Eastman Kodak stearic acid will be discussed because the structure of those obtained from the impure "Kahlbaum" potassium stearate are very ambiguous in their behavior.

The diffraction patterns seem to fall into five classes, and typical microphotometer tracings of each class are shown in Figure 20 . The corresponding Bragg spacings are reported in Table II ; some of the latter will be shown below to be attributable to free acid and are marked in brackets.

The class to which a sample belongs is determined by both the temperature at which it is prepared and that at which it is extracted.

Unextracted soap precipitated by our regular method at temperatures of 60°C and below all give diffraction patterns of the A_1 type characterized by a long spacing of 49.5 Å, short spacings of 4.60 (4.12) and a very weak one of (3.69°).

Those precipitated at 80°C and above (or heated in the mother liquor to that temperature) give diffraction patterns of type B_1 characterized by a long spacing of only 42.0 Å with three strong short spacings at 3.85 (4.11) and 4.60 Å (the last two merging into a band in the microphotometer tracing) and a weak one at (3.69 Å.)

Soaps of the B_1 type when extracted with boiling acetone give the B_2 type characterized by a long spacing of 40.0 Å. Their crystallinity is relatively high and three strong short spacings 4.15, 4.10 and 4.65 Å

Soap of the A_1 type when extracted with acetone at 30° C or below yield the A_2 type characterized by a long spacing of 47.4 Å and a single strong side spacing of 4.26 Å.

Figure 20

Typical microphotometer tracings of five types of X-ray diffraction patterns of aluminum stearates

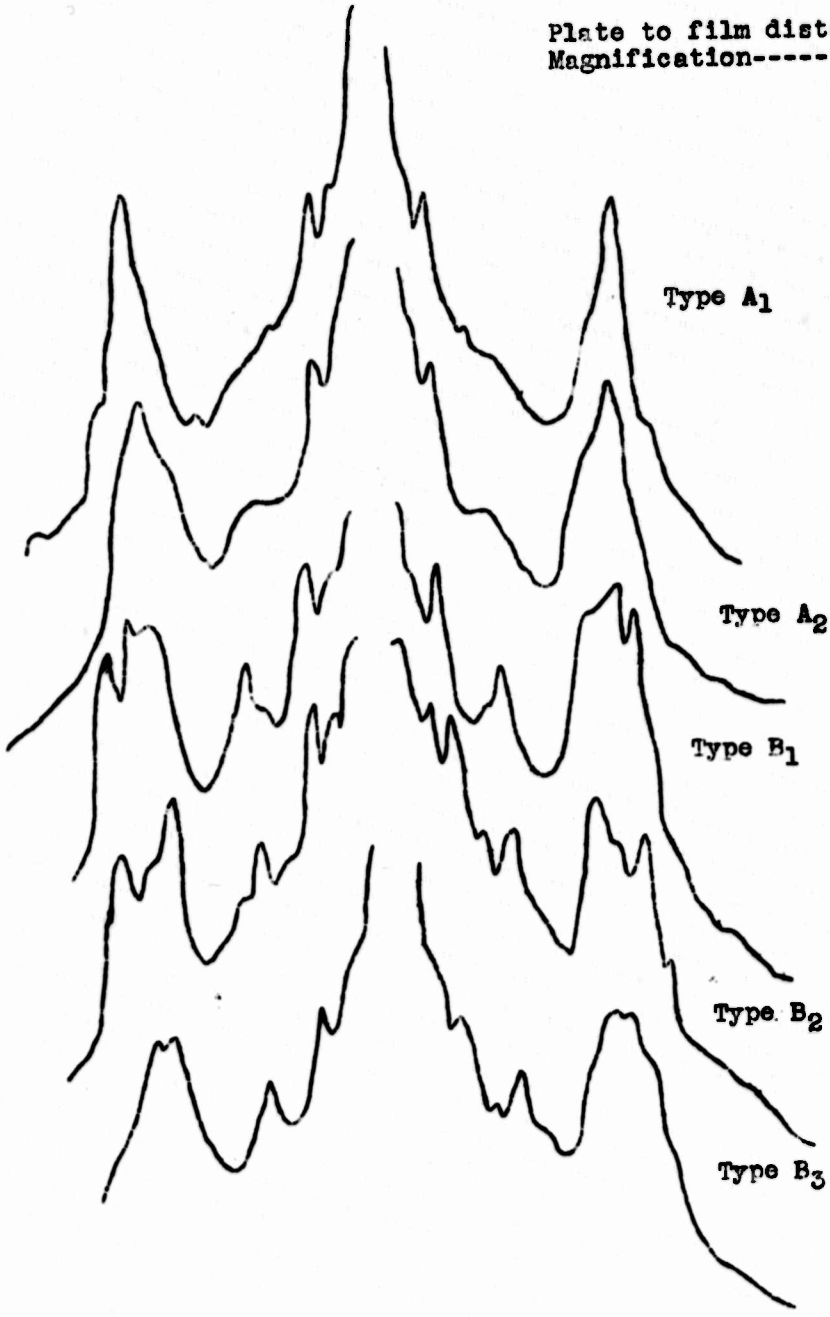


Table II

Spacing of Five Types of X-ray Diffraction Patterns of Eastman Kodak Stearic Acid and Aluminum Stearate Prepared by Our Method Therefrom

Type:	Conditions of Preparation	: Long Spacing	: Short Spacings :
A_3	Cold precipitation, unextracted	49.5 ± 0.5	4.60 ± 0.05, (4.12 ± 0.03) (3.69 ± 0.03)
A_2	Cold precipitation, cold extraction	47.4 ± 0.8	7.8 + 0.1, 4.7 ± 0.1, 4.26 ± 0.1
B_1	Hot precipitation, unextracted	42.0 ± 0.5	4.60 ± 0.03, (4.11 ± 0.03) 3.85 ± 0.03, (3.69 ± 0.03)
B_2	Hot precipitation, hot extraction	40.0 ± 0.5	7.44 ± 0.05, 4.65 ± 0.03, 4.20 ± 0.03, 3.85 ± 0.03, 3.60 ± 0.03
B_3	Cold precipitation, hot extraction	42.0 ± 0.5	7.75 ± 0.05, 4.68 ± 0.05, 4.26 ± 0.03, 3.85 ± 0.03
Eastman Kodak Steric Acid		38.1 ± 0.5	4.30 ± 0.05, 4.05 ± 0.03, 3.65 ± 0.05, 2.46 ± 0.03

It will be noted that the A_1 and B_1 types are very similar to the A_2 and B_2 types respectively, although the difference in the length of long spacing, and of at least one side spacing, seems to be beyond experimental error.

When the unextracted soap of the A_1 type (precipitated at low temperature) is extracted at the boiling point of acetone its diffraction pattern changes to B_3 characterized by a long spacing of about 42 Å and two strong but broad side spacings at 4.68 and 4.26 Å (which merge in the microphotometer tracing into a halo) and a weaker one at 3.87 Å.

Here extraction has changed the long spacing by about 8 Å and caused the appearance of a strong side spacing at 4.68 Å.

In case of aluminum laurate the large amount of free acid distorted the x-ray diffraction picture of the unextracted soap sufficiently to lead to the conclusion that the unextracted soap had a definitely different structure from the extracted one. More careful examination appears to show that diffraction pictures of the laurates are no more different (once the presence of free acid is taken into account) than the B_1 and B_2 types for the stearate. In other words, the crystal structure of the unextracted laurate, precipitated at any temperature from 25° to 100°C., is analogous to that of the B_1 type stearate precipitated above 60°C.

The extracted laurate is very similar to the B_2 type of stearate.

Figures 21 and 20 show the pertinent tracings and Table III the spacings found for the laurates and lauric acid.

Table III

Spacings of X-ray Diffusion Patterns of Aluminum Laurates and Lauric Acid.

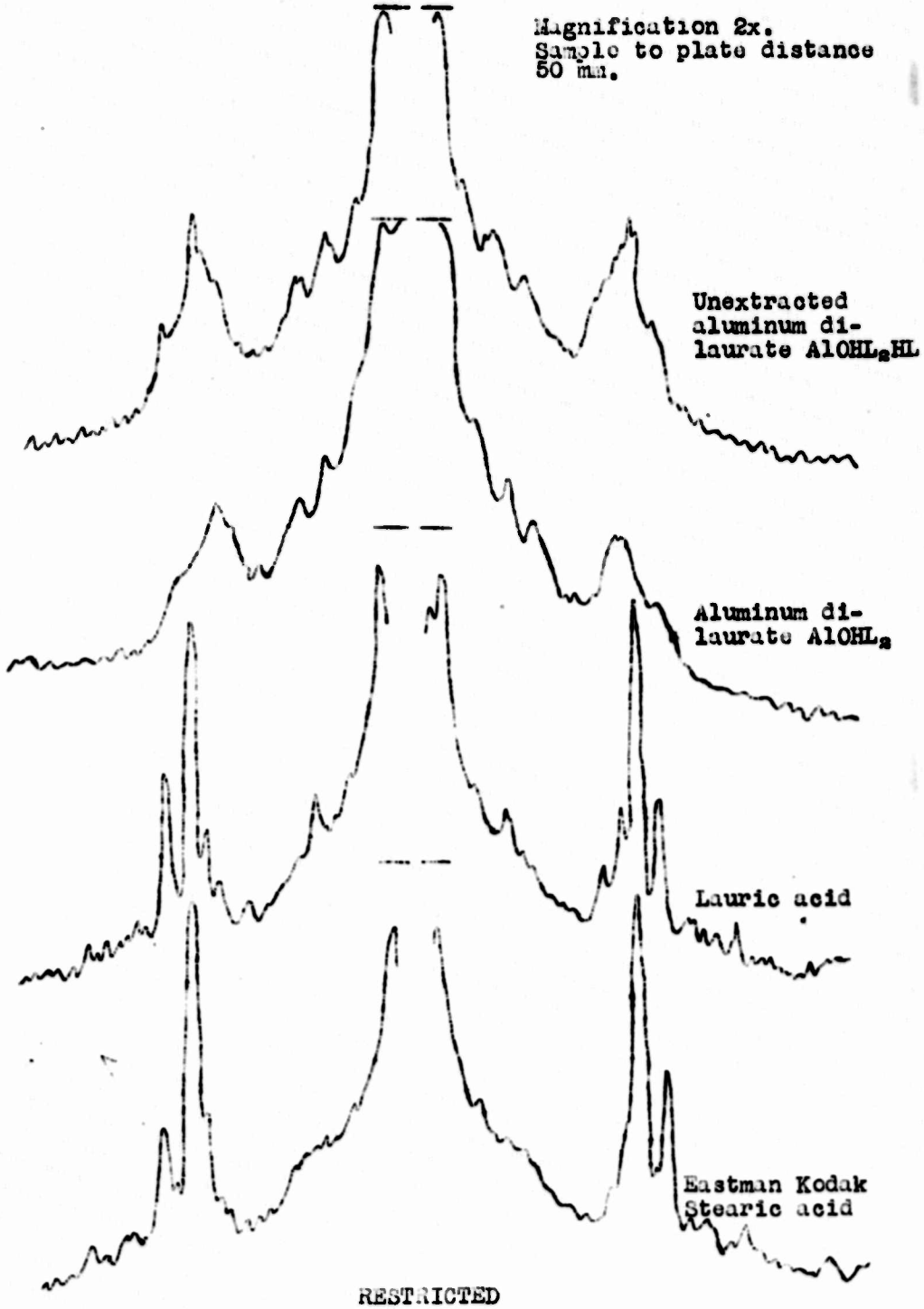
Conditions of Preparation	Long spacings	Short Spacings
Unextracted	30 ± 0.5	7.8 ± 0.1, 4.58 ± 0.05, (4.13 ± 0.05), (3.75 ± 0.05)
Extracted	28.1 ± 0.5	7.6 ± 0.1, 4.59 ± 0.05, 4.30 ± 0.05, 3.85 ± 0.05.
Eastman Kodak Lauric Acid	27.4 ± 0.5	4.58 ± 0.05, 4.37 ± 0.05, 4.13 ± 0.05, 3.76 ± 0.05

(c) X-ray evidence for the presence of some free acid. When a fatty acid is present completely free in an aluminum soap, its activity undimished by solid solution, sorption or other molecular attachment, it should form separate crystals and such crystals, if present in sufficient amounts, could be detected by x-ray diffraction, provided that it is possible to determine which lines belong to the fatty acid and which to the aluminum soap.

All the aluminum soaps we have obtained thus far have particle sizes so small that a powder diffraction picture shows smooth continuous lines indicating that the number of particles, each giving a point on the line, is enormous. One sample, however, of unextracted aluminum stearate prepared at

Figure 31

Microphotometer tracings of x-ray diffraction patterns of aluminum laurate, unextracted and extracted, lauric acid and stearic acid.



zero degrees showed a definite graininess and unevenness of some of the larger rings. Closer examination showed that these lines corresponded to lines of stearic acid alone while the smooth lines were those found in the extracted di-soap and not found in the acid. This accident allowed us to attribute some of the lines in the unextracted soap to the free acid and some to the di-soap containing bound acid. Synthetic mixtures of extracted di-soap and finely powdered acid confirmed the results.

It is quite fortunate that at least two lines belonging to the acid are different from any line of the soap, (See Tables II and III). so that the presence of these lines may be taken as evidence of the presence of free crystalline acid in the soap. Most of the other lines of the acid are either superimposed or so close to lines of soap that their presence or absence cannot be judged unless the acid is present in large quantities and the increase in intensity is very marked.

These characteristic short-spacings, shown only by fatty acid lie (a) At 4.13 Å, which may be distinguished, although with some difficulty, from the 4.70 Å line of the aluminum soap and is different from any short spacing of sodium and potassium soap. (b) At 3.67 Å for the stearic acid and 3.75 Å for the lauric acid. These are far enough from any line of the aluminum soap proper to be easily visible but lie close to some strong lines of sodium and potassium soaps so that traces of the latter might cause a mistake.

The presence of both these lines may be considered as good evidence of the presence of crystals of free acid.

Examination of our x-ray diffraction patterns shows that all the soaps precipitated by one regular procedure, and containing about three quarters of an equivalent more acid than corresponds to the di-soap, have these lines while they are absent from the extracted soaps.

From a comparison of the intensity of the lines in the soaps and in synthetic mixtures containing known amounts of acid, it is estimated that the amount of free acid present is of the order of 5 to 10% in case of the unextracted stearate. This is the same order of magnitude as obtained by the batch extraction method reported above. In case of the laurate the amount of free acid appears to be much larger, of the order of 25%.

(d) X-ray evidence for molecularly bound acid.

It is quite obvious that between A_1 and B_8 there is a rearrangement of the crystal structure as shown by the large (7% change in the long spacing, (p.76).

It is not yet possible to determine however whether the two A and the three B types are all completely different or correspond each to a single crystalline structure somewhat distorted by the presence of stearic acid to give somewhat different diffraction patterns. If this were true it would form a strong additional argument for sorption of the molecular acid by the soap.

An argument for the identity of B_1 and B_2 is the high crystallinity of all B_2 samples. If a recrystallization occurred during extraction, it would hardly be expected that the new crystals would be well formed. When the A_1 type is transformed into B_2 under some conditions of extraction the crystallinity is low and the lines broad.

Transformation from A_1 to A_2 type during extraction seems to correspond to a slight but definite lowering of crystallinity.

The conclusion that can be drawn safely is that the removal of molecules of stearic acid may cause deep change in crystal structure (A_1 to B_2) but may also occur, under favorable conditions, without evidence of any radical alteration (A_1 to A_2, B_1 to B_2).

(e) <u>The Crystal structure of aluminum soaps.</u>

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 of the order of 40-50Å for tristearates.

The B_2 types of 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 22 . 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 5Å 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).

All the lines corresponding to long spacings are due to successive orders of diffraction (001) 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 = Δ c sin β . Since the distance between alternate carbon atoms in a hydrocarbon chain is 2.54 Å the corresponding value for Δ c for double molecules is 6 x 2.54 Å = 15.24 Å. The ratio of these values is sin β = 0.741. Hence β , the monoclinic angle for both soaps, is 48°. The same value of β =48° was

Microphotometer Tracings of X-ray Diffraction Patterns
Distance - sample to plate .. 5 cm
Magnification ..... 2 x
Bragg spacings in Angstrom units.

Figure 22

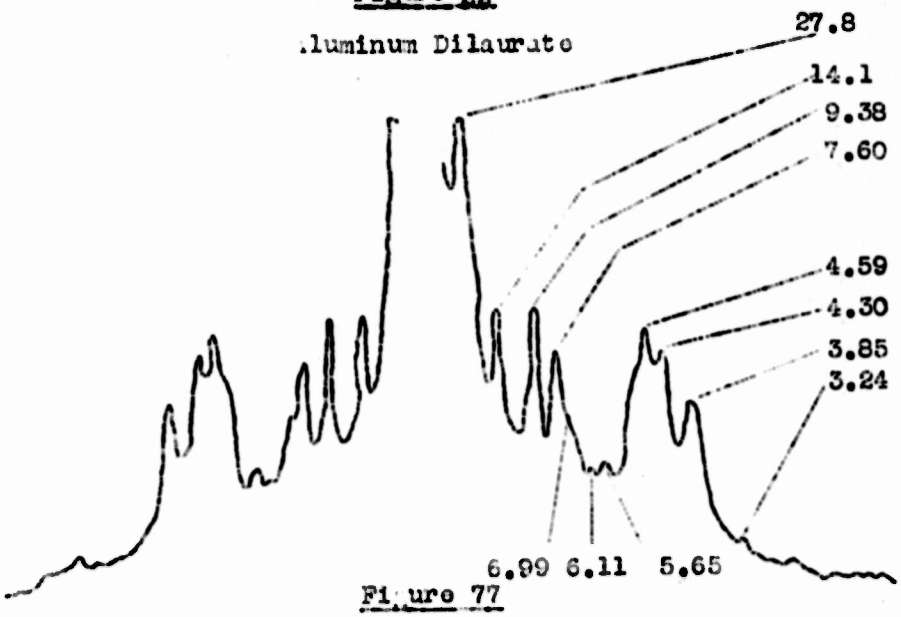
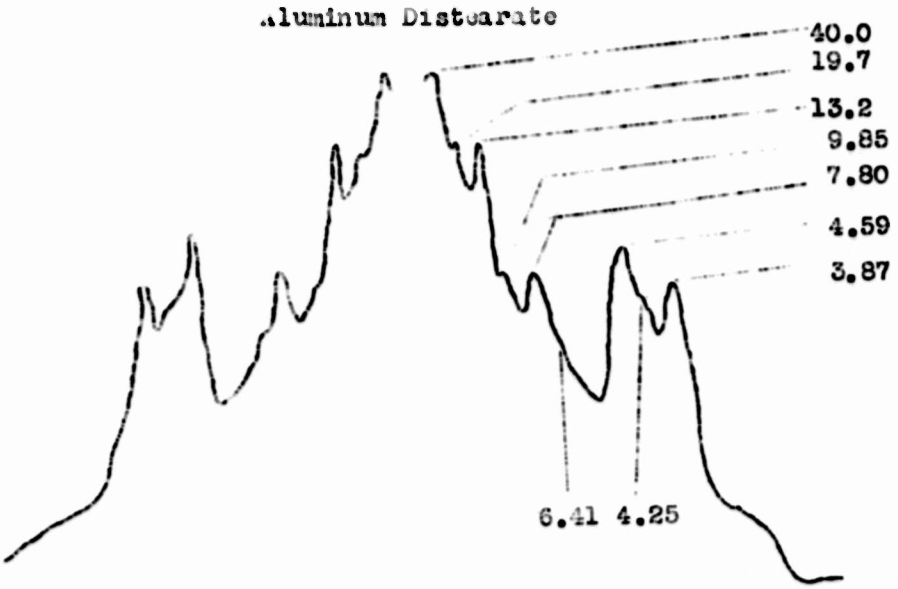


Figure 77



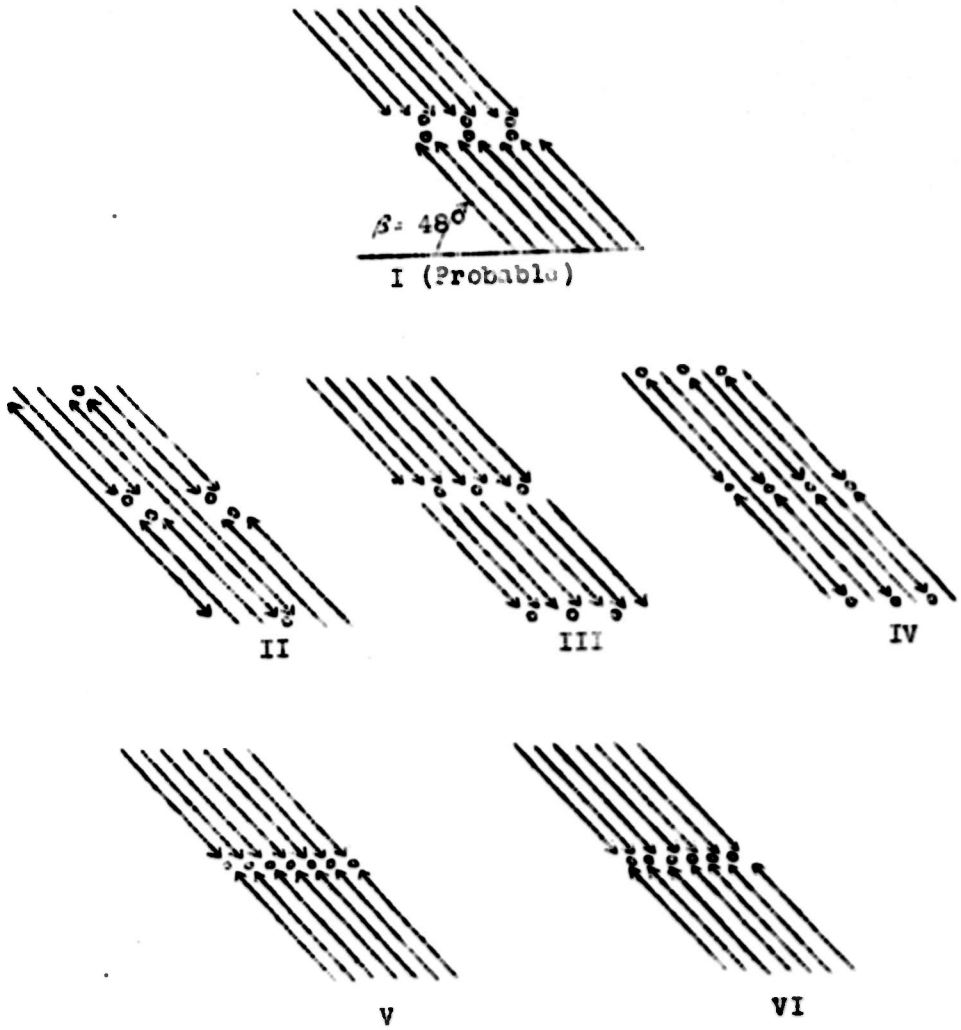
experimentally obtained by Brill and Meyer for lauric acid.

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 23 .

Comparison of the long spacings of the A_2 type of stearate with those of the B_2 type whose structure is thus determined leads to an angle β of about 60° assuming unchanged chain length.

Figure 23

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



E. The Individual Aluminum Soaps.

The two most important properties of aluminum soaps, their behavior toward water and toward 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, dioleate, three di-naphtenates, and dicyclohexane carboxylate; and finally aluminum monolaurate. Finally Napalm is discussed. The problem of existence of tri- and acid di-soaps has been discussed in the first chapter. The tri-soaps almost certainly do not exist as no preparation withstands the tests for a chemical compound.

(a) Aluminum dilaurate, $Al(OH)L_2$.

(i) Preparation and properties. Aluminum dilaurate was best prepared by adding a neutral aqueous solution of potassium laurate to a large excess of an aqueous solution of hydrated aluminum chloride 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 acid.

This was either extracted rapidly in a fritted glass funnel with dried, cold acetone using 80 ml. of solvent per gram of soap (Yearly p. 28) or in a Soxhlet extractor with isooctane at room temperature (See p.51) or with acetone at 0°C. (See p.43).

The ash value was 11.56 - 11.62% Al_2O_3, theory 11.49%. The lauric acid content 89.3%, theory 90.5%. Thus the lauric acid and alumina account for over 99% of the substance.

The soap obtained is a fine white powder which is caked by pressure. It is slightly hygroscopic and 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 (Our April 1944 Report p. 8 - 10). The x-ray diffraction pattern shows a series of relatively sharp lines and a halo (Fig. 15)

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 decomposition. (Annual Report p. 29).

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.

(ii) 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.

Table IV summarizes the properties and preparation of these various forms. (See also Annual Report p. 30 - 31).

TABLE IV

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

	1	2	3	4	5	6
Name	Original	Crystalline	Glassy	Recovered from gel	Recovered from jelly	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
ml 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 18	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 any other form in sealed tube, cooling to 160-170°C until crystallized and slow cooling.	Melting of 1 or probably any other form 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.

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 temperatures; (see p. 158) but all of these forms can be converted into the same sharply melting 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. (See p. 160).

(iii) The molecular weight of aluminum dilaurate. Aluminum soaps are not high polymers. At finite concentrations the osmotic pressure of typical high polymers is low and increases faster than the concentration.

Aluminum dilaurate in benzene on the other hand has a rather high osmotic pressure which increases much more slowly than the concentration. There is a great change of apparent molecular weight (change in degree of association) throughout the measured range corresponding to $(Al(OH)L_2)_6$ in 0.001% and $(Al(OH)L_2)_{500}$ in 1.0% 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 $Al(OH)L_2$.

(b) Aluminum distearate ($Al(OH)Str_2$). Aluminum distearate resembles the dilaurate. Its preparation and crystal structure have been discussed in detail in previous sections, also (Yearly 50-51). 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 opalescent.

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 portions 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.

(c) Aluminum oleates. In general, the preparation of the aluminum oleate followed a similar technique to that employed for aluminum laurate and stearate. However, there were complications resulting from the fact that oleic acid is liquid at room temperature and is readily oxidized. To remedy the difficulties arising from the liquid oleic acid, the sample was handled as close to 0°C as possible. This facilitated filtration and grinding, since the oleic acid, melting at 14°C was solid at the lower temperatures. The soap at 0-5°C was found to be of the same general nature as aluminum laurate at 25 - 30°C in respect to gumminess and friability. (Oct. Report p. 40).

The final product prepared from kahlbaum potassium oleate was an orange -tan, granular powder at 0°- 5°C, becoming gummy when the free oleic acid was allowed to melt.

Extraction at 0°C with dried acetone yielded a product having an ash content slightly higher than corresponded to

the dioleate Al $OH.Ol_2$. The deviation from the theoretical value was however relatively small (Fig. 7) and was further reduced by the use of isooctane (p. 52).

Another preparation precipitated at 80°C (and washed free of chloride with ice water like the preceding one) behaved, during extraction with dried acetone at 0°C, exactly in the same way as the one precipitated at 25°C. (November p. 48).

The extracted soap is in the form of small, quite friable granules not coalescing at room temperature. This is quite different from commercial aluminum oleates or those described in the British Reports or by Ostwald and Riedel (Koll. Z. 69, 115, (1934)) which are gummy or waxlike.

X-ray diffraction patterns of both extracted and unextracted oleate show only halos and only in one case very faint lines which might possibly be due to some other soap. They are shown in Figure .

The particles of extracted soap are translucent. When thin, they are transparent but show no birefringence. Upon heating no sharp change could be noted but only a very gradual softening of the whole product.

This behavior must be contrasted with the behavior of aluminum distearate and dilaurate which show very distinct x-ray diffraction patterns, a sharp change at the melting temperature, and when transparent below the melting point are strongly birefringent unless supercooled. On the other hand the stearate and laurate even above the melting point are extremely viscous. Their flow is hardly visible at 200°C.

This contrast of properties suggests that our aluminum dioleate may not be crystallized, but may be a liquid of extremely high viscosity. Whether the liquid state is a stable condition of the soap or a metastable state of a substance which should be crystalline and solid at room temperature cannot be answered at present.

In the absence of a melting point and of an x-ray pattern it is also difficult to make a statement as to the probable purity of the product.

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

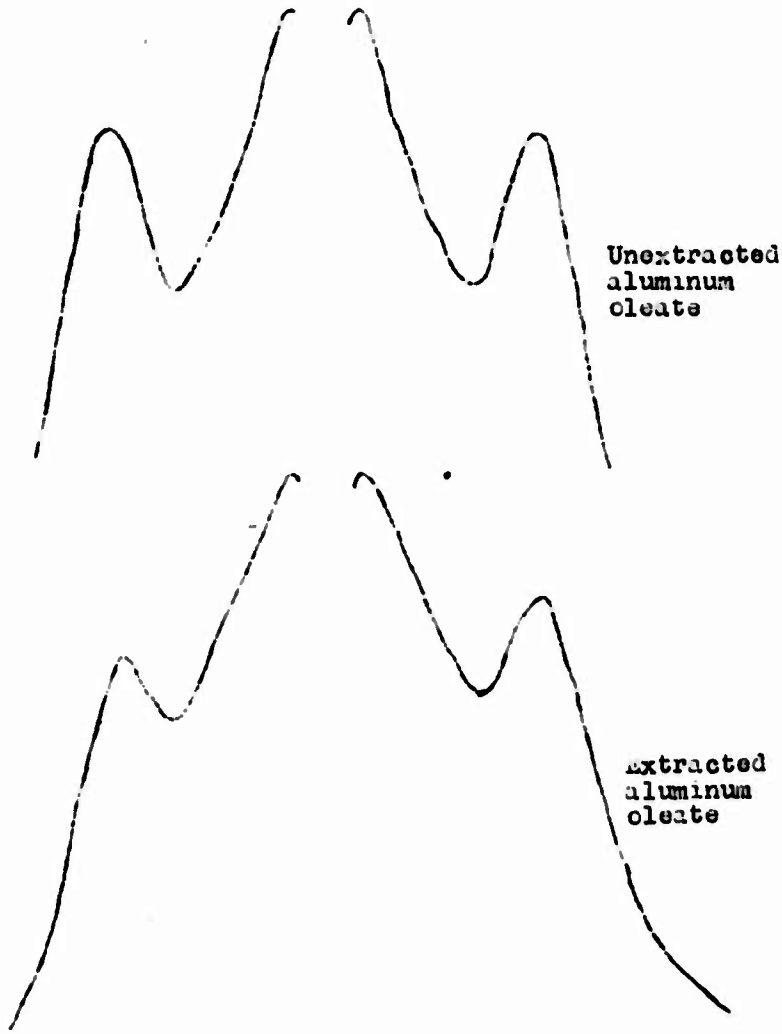
The preparation was similar to that of the fatty acid soaps (Yearly p. 63) but cyclohexane carboxylic acid differs from the latter acid by being somewhat soluble in water, as are some lower naphthenic acids. Washing of the precipitate with water to remove soluble salts removes therefore also a large 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 toward

Figure 24

Microphotometer tracings of x-ray diffraction patterns comparing samples of unextracted and extracted aluminum oleate.

Sample to plate distance-5 cm.
Magnification - - - - - -2 x



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 is included in Figure 25 .

(c) Aluminum naphthenates. Several samples of aluminum naphthenates have been prepared from samples of commercial naphthenic acids, which were kindly supplied by the Standard Oil Company of California. The sodium soaps were first made and washed exhaustively with acetone to remove color bodies and traces of residual oils. The aluminum soaps were then prepared by metathesis in water with aluminum chloride in the manner employed for the preparation of aluminum soaps of fatty acids. The aluminum naphthenates were washed with water until free of chloride ion, dried and then extracted with acetone.

Analysis of these aluminum naphthenates showed that some fractionation of the naphthenic acids had occurred as a result of the drastic acetone extractions. The formulae were found to correspond roughly to 65-70% of dinaphthenate + 30 - 35% of mononaphthenate as determined from the extracted ash value (extracted with boiling acetone over Drierite) and the neutralization value of the acids freed from the finished soap by hydration.

The aluminum napthenates were x-rayed and the micro-photometer tracings shown in Figure 25 .

The aluminum dicyclohexane carboxylate is markedly less amorphous than the three samples of aluminum naphthenates, which are all of comparable crystallinity. The halos produced by the aluminum dicarboxylate are narrow, whereas those from the other naphthenate samples are wide and diffuse.

(f) Aluminum monolaurate $Al(OH)_2L$. 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 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 (Figure 26). 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 (Figure 26) by storing the product for several weeks under methyl alcohol at 90°C. Figures 18 and 19 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.

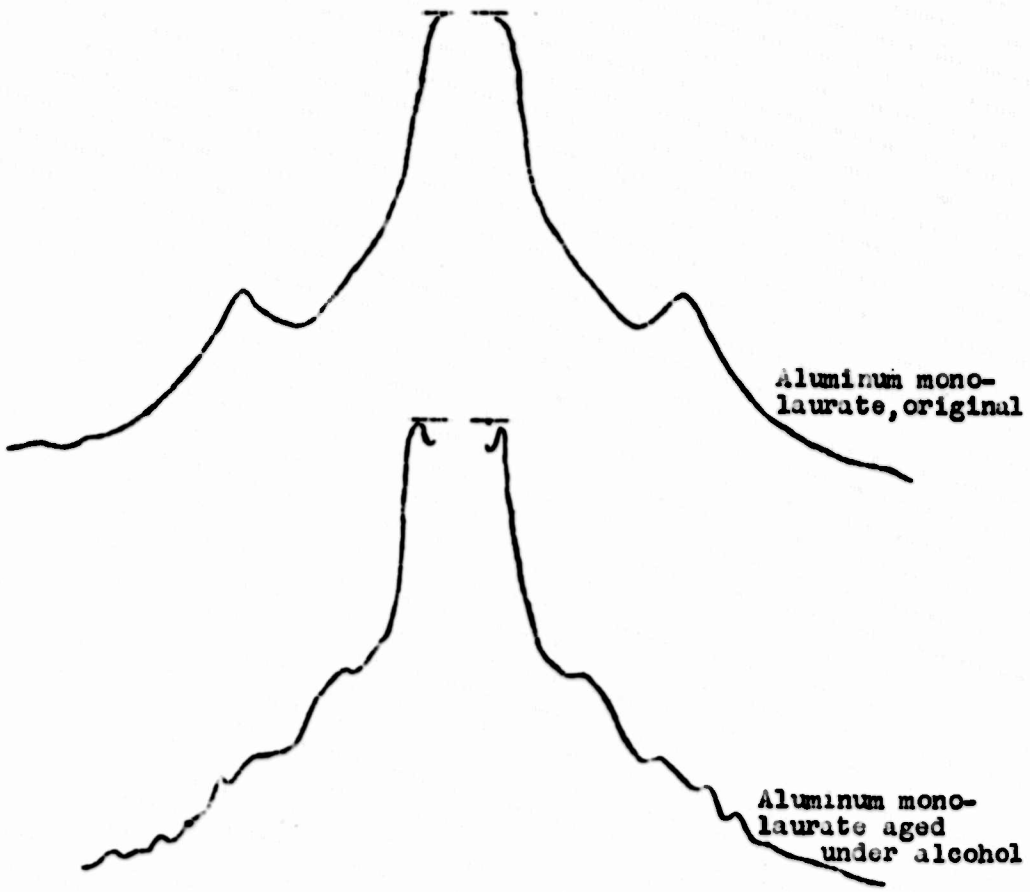
(g) Napalm. Compared with the pure soaps Napalms are very complex mixtures. They contain moisture which is very difficult, if not impossible, to separate from the remainder of the soap (p. 119). They also contain volatile oil and acids whose recovery is possible only to a limited extent (p. 114). The fixed nonvolatile Napalm contains free or loosely bound uncombined acids and unsaponifiables extractible with dry acetone etc. (p. 63), and inorganic salts sedimenting from liquefied jellies whose content varies widely with various manufacturers. (p. 103).

The above substances represent probably altogether about 10% of the Napalm. The remainder is aluminum soap. Even this remainder, however, need not be homogeneous. In two Napalms among those tested; namely, Pfister and particularly Imperial,

Figure 26.

Microphotometer tracings of x-ray diffraction patterns of two forms of aluminum monolaurate.

Magnification 2x
Sample to plate distance 50 mm.



we found that part of the soap was relatively very inert to hydrocarbons. While all other Napalms, and the bulk of these two also, dispersed completely in cyclohexane and benzene, this inert soap remained as an almost unswollen residue in cyclohexane and swelled but did not disperse in benzene. Upon heating in isooctane it swelled slightly while the other soaps dispersed at temperatures below 70°C.

In order to learn something more about this inert substance, a larger amount of it was isolated from Imperial Napalm by separating the sediment insoluble in gasoline and washing it with benzene and isooctane. It was then dried thoroughly. The yield of the dried inert substance was about 10%. Due to unavoidable losses during the separation we estimate that the actual content was about 25% in the original Imperial Napalm.

Its most striking difference from Napalm seems to be the inertness to the hydrocarbons. In this respect it resembles aluminum monolaurate. However, its x-ray pattern is very similar to that of the original Napalm. Its ash is higher, 13.4%, but this may be due to a large extent at least to the concentration of inorganic impurities in the soap, and the acids split therefrom have an acid number of 261 which is only about 7% higher than for the original Napalm. Thus the composition suggests that this inert material is not far from a di-soap and gives no clue to its inertness.

It may be noted that this inert soap has in itself no deleterious influence upon the gelling and dispersion of the remainder of the soap, but of course when present in large amounts reduces the effectiveness of the Napalm as a whole.

CHAPTER III

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 (Broughton and A. Byfield p. 45).

Our work on this subject was concerned mainly with the role of inorganic impurities in Napalm upon its water sorption with the application and significance of x-ray diffraction, with the sorption balance, and with benzene distillation and Karl Fisher results as compared with the volatile material lost on vacuum drying.

A. The Role of Inorganic Impurities in the Water Sorption of Napalm.

Moisture might be held in Napalm either by the aluminum soap itself or by the inorganic impurities present therein. The Harshaw group has shown that Napalms of various manufactures differ greatly in their content of inorganic impurities. This was done by determining the $SO_4^{=}$ and M^{+} content and calculating therefrom the Na_2SO_4 and $Al_2(SO_4)_3$ contents. The values ranged between 0.51 and 3.42% (Harshaw's fifteenth monthly report).

We have isolated 2% of inorganic impurities from McGean 462 Napalm by centrifuging a liquefied jelly and thoroughly washing the sediment. (Yearly 93). It contained no organic matter and was partially insoluble in dilute HCl (Yearly 93 - 94).

An x-ray diffraction picture of these impurities has also been obtained. Upon very long exposure (6 hrs. instead of the usual two) faint lines could be detected. Some of these lines correspond with known lines of sodium sulfate heated and hydrated, and of aluminum sulfate, while others could not be accounted for. The bulk of the material however failed to diffract x-rays appreciably. (Nov. 18).

These facts indicate that the inorganic impurities present in Napalm (Yearly p. 93) are a very heterogeneous mixture predominating in mixed and basic aluminum salts with a small proportion of normal sulfate of aluminum and sodium. This suggests also that Harshaw's estimate is conservative

and that Napalm may contain even larger proportions of inorganic impurities.

Sodium sulphate, aluminum sulphate, alumina and presumably the basic salts are capable of forming hydrates with large proportions of water. Thus, if the impurities behave in Napalm in the same way as when isolated, the amount of moisture sorbed by them at equilibrium, at higher humidity, may be sufficient markedly to affect the gel forming ability of a Napalm containing a larger proportion thereof. (August 9 -10)

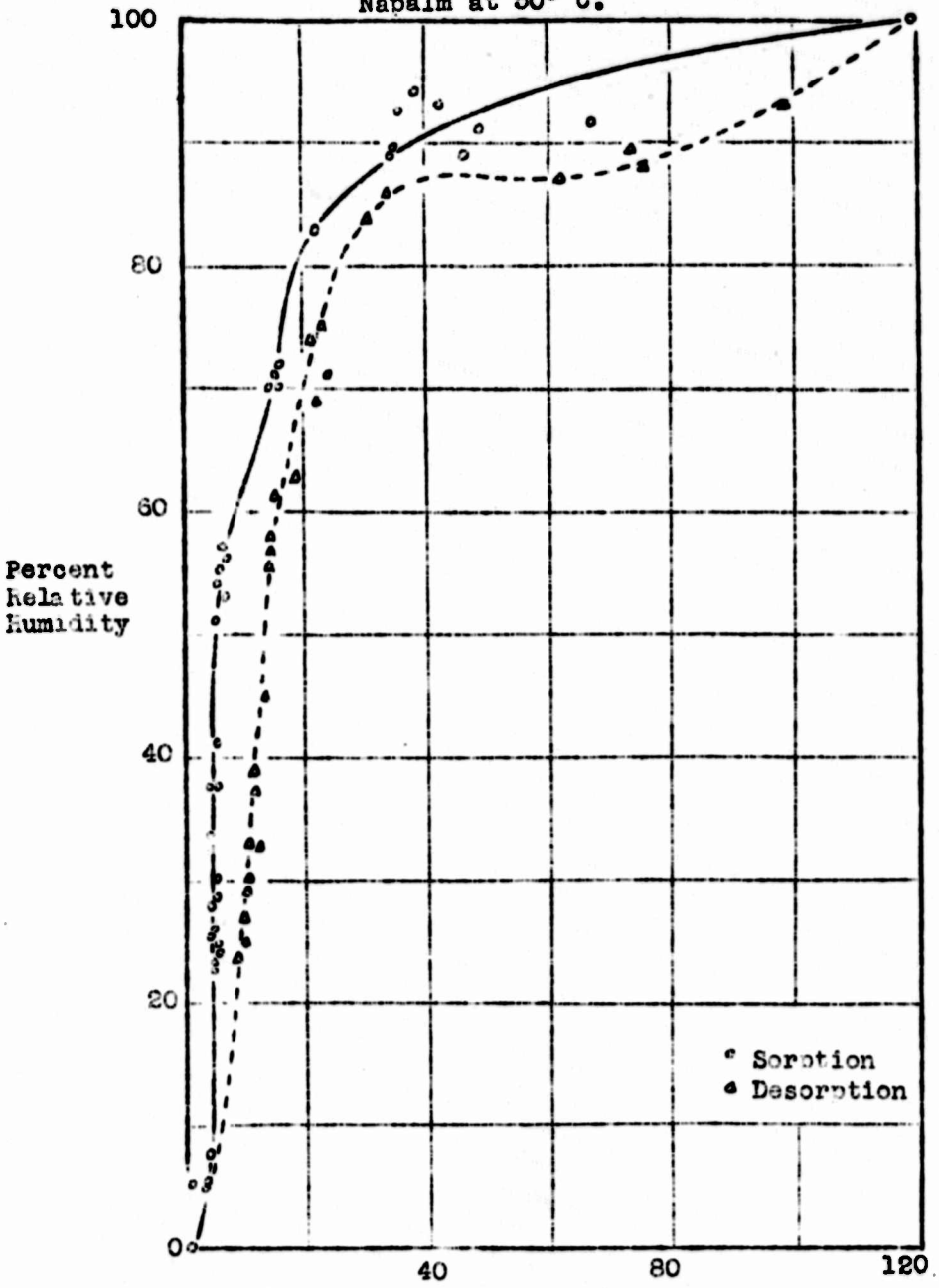
Exploratory measurements in a sorption balance at room temperature showed that these impurities sorbed about 4% by weight of moisture at 20% R.H., 7% at 50% and 105% at 90%. A complete isotherm at 50°C is shown in Figure 27 . The shape of this isotherm suggests the existence of a few steps consisting of vertical and horizontal sections, indicative of definite hydrates, but these are almost lost in the overall picture. It also shows that the sorption of moisture is not completely reversible, the sorption and desorption points being distinctly different for each set of conditions.

Thus the pre-eminent characteristic of these impurities is their tremendous hygroscopicity at higher humidities contrasted with only moderate sorption of water at low relative humidities

This suggests that these inorganic impurities (present to the extent of 0.5 to 3.5% in various Napalms) may fix up to their own weight of water and play an important part in the deterioration of Napalm exposed to very moist air, and that the moisture thus sorbed by the impurities is readily given off, and is effective as a peptizer. Their action as a drying agent is negligible (August 10-11).

Figure 27.

Sorption isotherm of water by inorganic impurities from McGean 462 Napalm at 50° C.



B. X-ray Diffraction by Dry and Moist Aluminum Soaps.

Both pure aluminum soap and Napalms show some hygroscopicity. The question naturally presents itself as to whether the water enters the crystal structure of soap or whether it is fixed only upon the surface. In the former case it should affect the x-ray diffraction pattern, in the latter it should not.

To study this point we developed the technique of placing the soap in one end of a long, thin walled glass capillary (diameter 1.0 mm., wall thickness 0.04 mm.). A small amount of water was added to it. The end of the capillary containing water and soap was stored in dry ice and the capillary evacuated and sealed. It was then placed in a fixed position on the x-ray collimating system and allowed to come to equilibrium. Since the capillary was evacuated and

its temperature uniform, the soap was exposed to saturated water vapor and therefore sorbed a maximum amount of water. An x-ray diffraction picture was then taken.

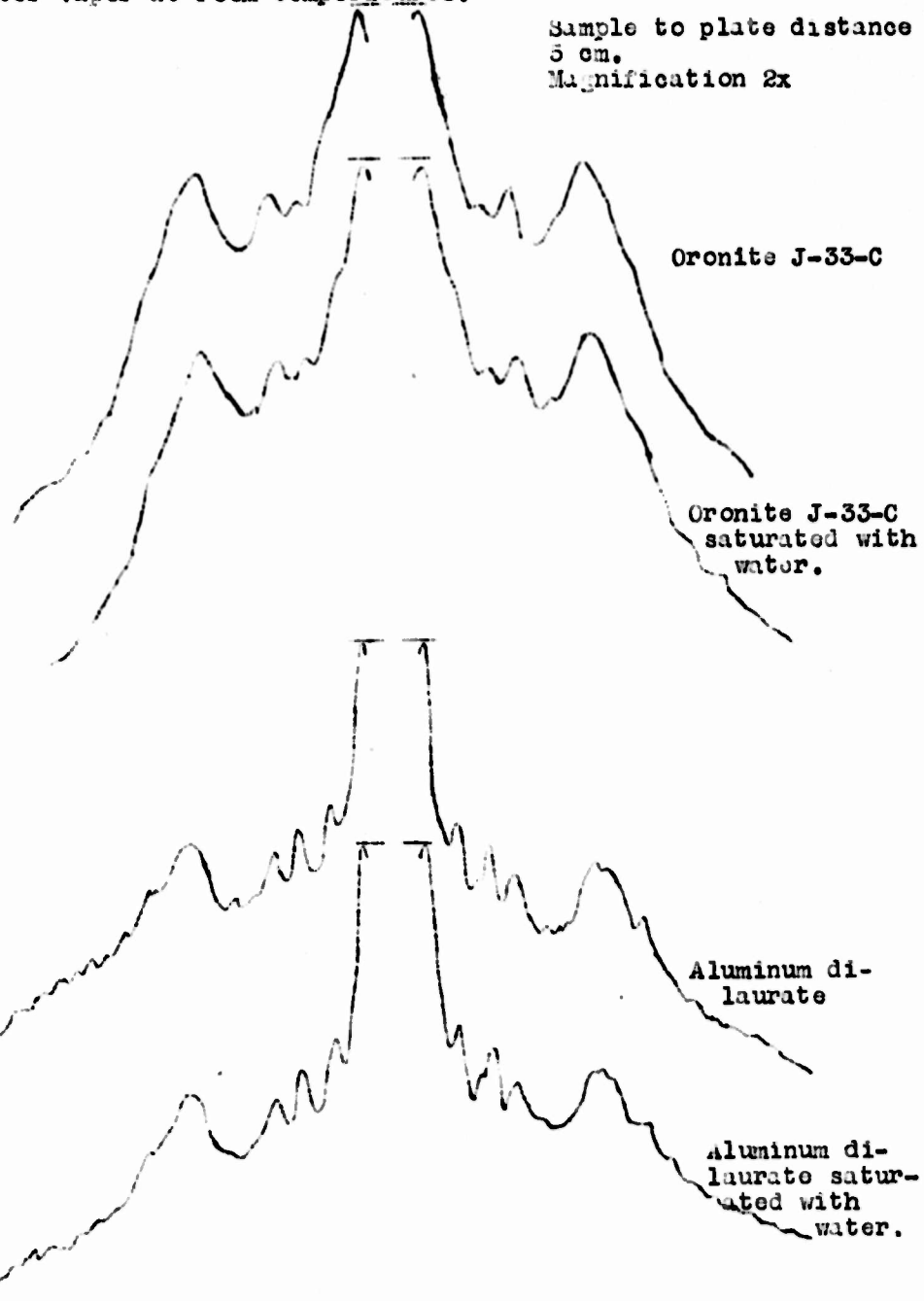
The end of the capillary which did not contain the soap was then immersed in dry ice-cellosolve mixture without changing the position of the capillary. After equilibrium was again established, the soap being thus completely dried, a second picture was taken.

Figure 28 shows microphotometer tracings of the two diffraction patterns, dry and moist for both the aluminum dilaurate and for Napalm. For the latter one week was allowed for equilibrium to be established.

The tracings and measurements show that there is no perceptible change in crystal structure in either case upon sorption of water. This suggests that it is fixed only upon the surface of the soap, or by noncrystalline materials.

Figure 20

Microphotometer tracings of x-ray diffraction patterns of aluminum soaps dried and equilibrated with saturated water vapor at room temperatures.



C. Application of the Sorption Balance to Aluminum Soaps.

The sorption balance is shown in Figure 29. It 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 liquid, 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.

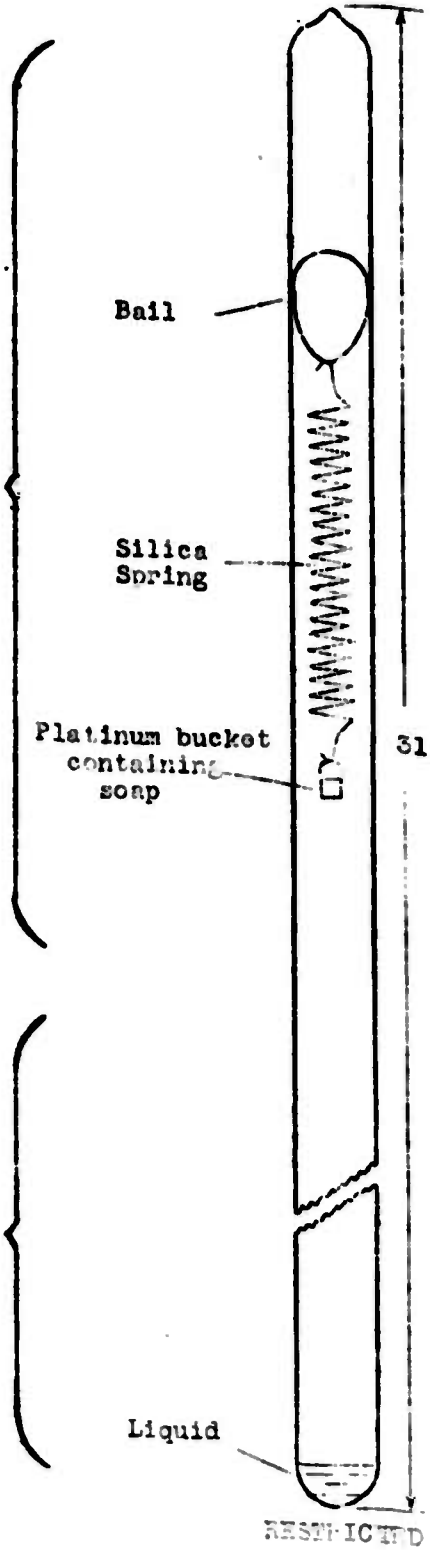


Figure 29

McBain-Bakr Sorption Balance

Reduced to one-half size

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. Using it, it is possible to follow the change in weight of 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.

It proved its worth in systems where only one volatile and one fixed component were present, such as water-inorganic impurities of Napalm (alone), or water-dilaurate but gave only approximate results when slightly volatile components of the soap entered the picture as in case of the system water-Napalm.

(a) Pure aluminum dilaurate AlOH L_2.

The isotherm obtained at 50°C for this soap is shown in Figure 30 . 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

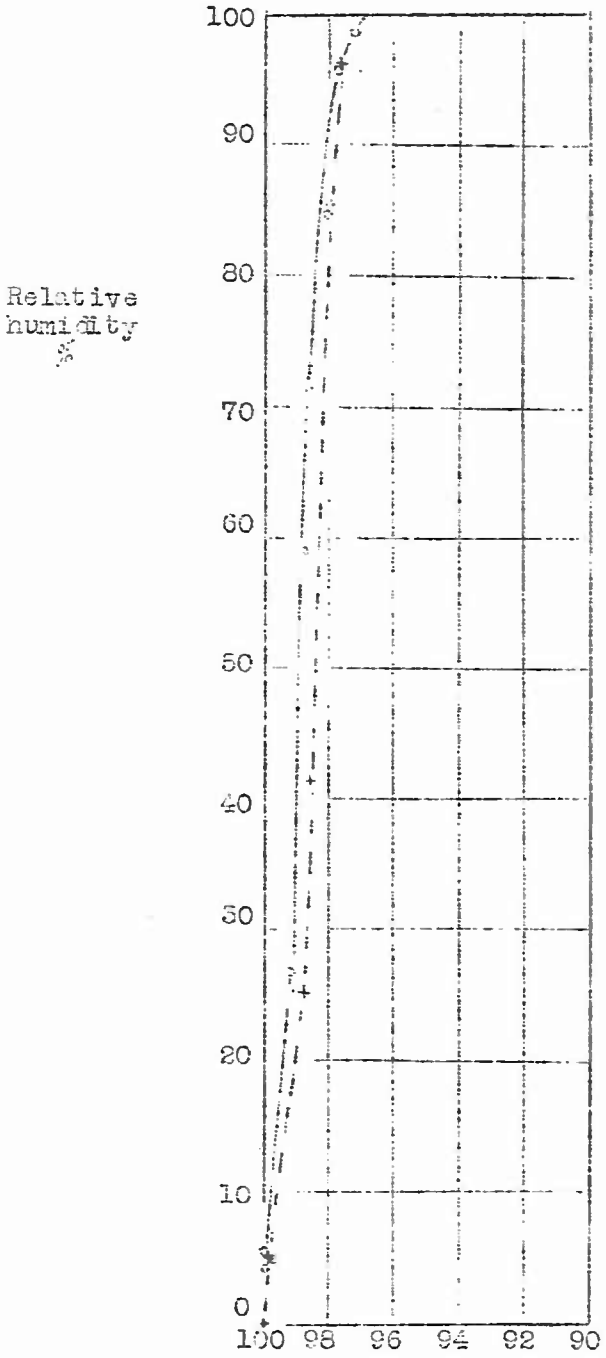


Figure 30

Sorption of Water by Aluminum Dilaurate at 50°C.

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 (Yearly p. 9) took place, the sample losing 14.2% by weight in 4 days.

The 50°C isotherm shown in Figure 30 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.

Thus a dry state of the soaps is readily obtained in case of pure aluminum dilaurate and is independent of temperature over the range 25 - 60°C and practically independent of relative humidity below about 5 - 10%. (Yearly p. 68).

(b) Aluminum dilaurate with bound or sorbed lauric acid.

While attempting to determine the moisture content of unextracted aluminum laurate (containing excess of lauric acid), we found that this soap, when exposed at room temperature to the very low pressure of water vapor at dry ice temperature, continued to lose weight over a very long period of time. At the writing of this report the experiment has been going on for 70 days and the soap has lost over 24% of its original weight. The loss was initially relatively rapid (1.5 % per day) but is still continuing at the rate of about 1/4 % per day.

It is quite obvious that such a loss cannot correspond to moisture present in the original soap, and as reported above, the weight of pure aluminum dilaurate (obtained by solvent extraction of the soap presently studied) remained constant within 0.1% for several weeks under the same conditions (and also after its temperature had been raised to 50°C).

The only possible conclusion is that molecularly bound lauric acid is distilling off the soap. In a check experiment we found that lauric acid at room temperature in a sorption balance whose lower end is at dry ice temperature loses 6 % by weight per day by sublimation.

This suggests that under properly controlled conditions the sorption balance may serve as a tool for the determination of the activity of acids in aluminum soaps. Such a method, while more cumbersome in some respects, would have the great advantage over the acetone or iso-octane extraction method which we have been using in that the danger of interaction

between solvent and soap would be completely eliminated. This method would be limited probably to lauric acid and lower acids. For stearic acid the distillation rate would seem to be prohibitively slow, except at elevated temperature.

This experiment further confirms the nonexistence of aluminum trilaurate in aqueous precipitates since lauric acid so bound would obviously not be able to distill under these conditions, and it is apparent that all the acid present above that corresponding to the dilaurate is distilling. This acid must be present in molecular form, partly free but mostly bound (sorbed).

In aluminum dilaurate on the other hand the lauric acid was all combined (since none of it distilled under even more drastic conditions).

(c) Napalm.

(i) Volatile components. The most important conclusion of the above clear-cut experiments on pure soap is that under conditions prevailing in a sorption balance uncombined acids even as heavy as lauric acid (corresponding to the average molecular weight of acids in Napalm) behave as somewhat volatile substances.

We have previously found direct evidence for the presence of small amounts of volatile oil and acid in Napalm. These experiments were made in especially designed all glass apparatus which allowed the collection of the distillate from 20 - 30 g. of Napalm in a calibrated capillary held at -78°C. Here the conditions of diffusion were much less favorable

than in a sorption balance and only about 0.1% of non-aqueous distillate was collected (Nov. p. 19-23).

(ii) Thermal hysteresis. In sorption balance experiments it was never possible to obtain a true dry weight of a sample of Napalm independent of time and constant over a range of temperatures analogous to that obtained for aluminum dilaurate.

Part of the difficulty has been traced to the great thermal sensitivity of Napalm which is similar to that of un-extracted aluminum soaps. It is well illustrated by the following experiment (See also Yearly p. 78-79 and Aug. p. 8-10).

A sample of Oronite Napalm batch J-33-C was kept in the sorption balance over water at dry ice cellosolve temperature, that is exposed to water vapor having the negligible but constant pressure of 0.00056 mm. Hg. The soap was allowed to come to constant weight first at room temperature, then at temperatures increasing stepwise to 55°. Then the temperature of the soap was lowered stepwise back to room temperature.

Figure 31 shows the results of these experiments and indicates that the further loss of weight of Napalm under these drastic conditions is approximately linear between 25 and 55°C and is completely irreversible, the soap recovering none of the weight lost when the initial conditions are restored. The total loss of weight over the range studied amounts to about 0.7%.

This thermal susceptibility was so great that it required development of special precautions to be taken during the sealing of the sorption balance; namely, the introduction of a heat guard into the tube. The description of this device and of tests proving its usefulness may be found on pages 24 to 31 of the November report.

(iii) Rate of loss of weight. After introduction of the heat guard, reasonably regular and reproducible rates of loss of weight by Napalm were obtained as shown in Figure 32 for samples conditioned at 20% R.H. and then exposed to 0.002% R.H. (Soap at room temperature, lower end first at 0°C then at -78°C). Both samples show the same rapid loss of the first percent of moisture and a regular and slow loss of weight during the following 8 or 10 hours until a long plateau is reached; the weight remaining constant for 12 hours. We are inclined to think that the rapid initial loss of weight corresponds mainly to loss of moisture while the latter shows loss due mainly to other volatile components.

However even the plateau thus reached is not a permanent zero point for Napalm over dry ice at room temperature. After the plateau has been reached during the first desorption the weight may remain constant for 24 hours and then change suddenly by 0.3% within six hours. Upon a second and third desorption the successive plateaus become lower and lower.

(iii) Sorption isotherm. Early in this work sorption patterns of Napalm were obtained at 50°C in tubes

Figure 31 .

Variation of the equilibrium weight of Cronite Napalm (J-33-C) upon stepwise heating and cooling.

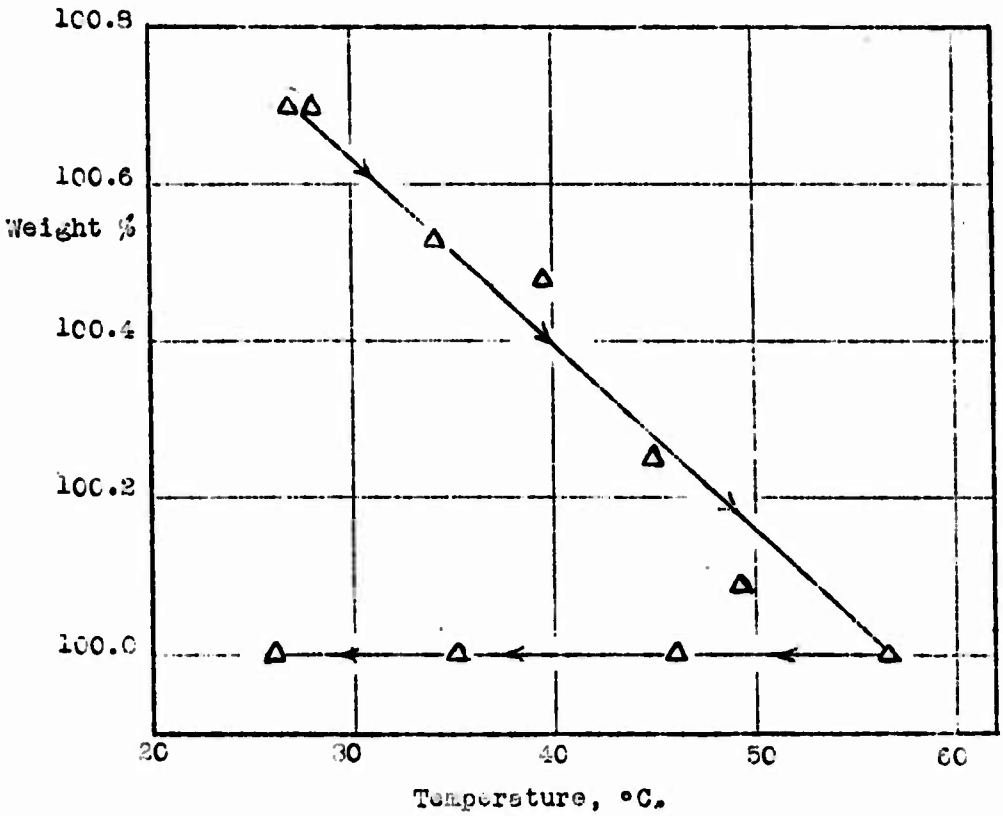
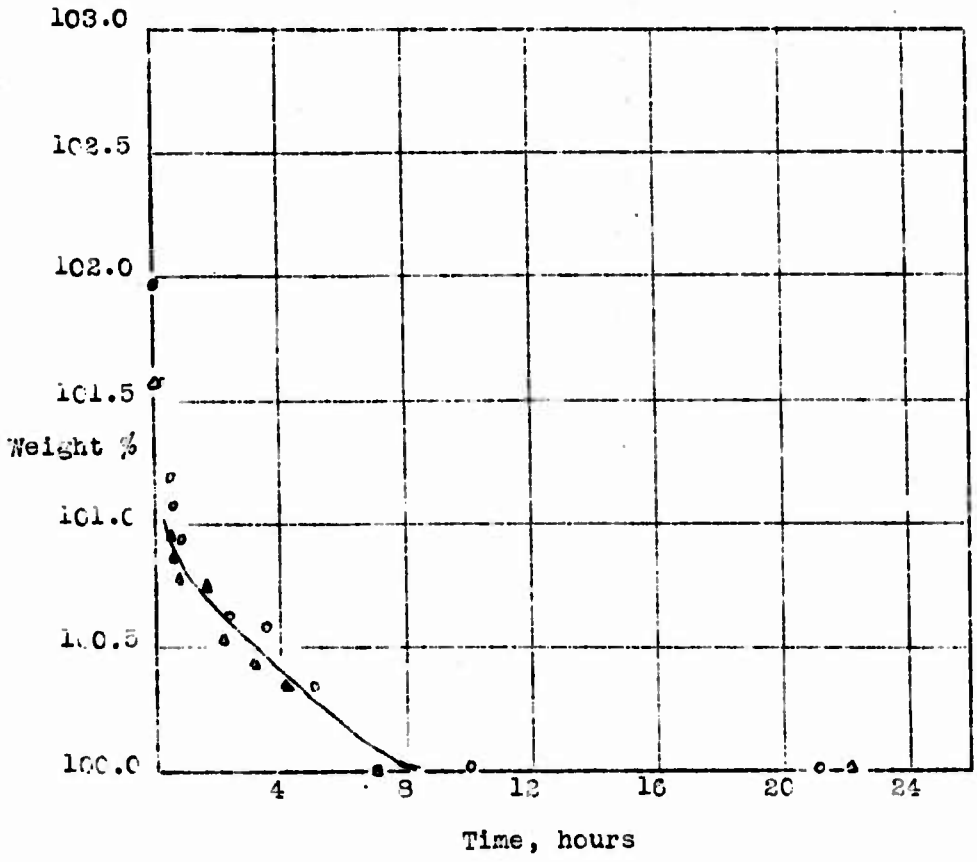


Figure 32

Loss of weight of Cronite Napalm (J-33-C) at room temperture over dry ice in sorption balance with a heat guard.



prepared without heat guards. No attempt was made to obtain a zero point before the isotherm was run but the lowest weight obtained after the desorption part was completed. Figures 33 and 34 show the results.

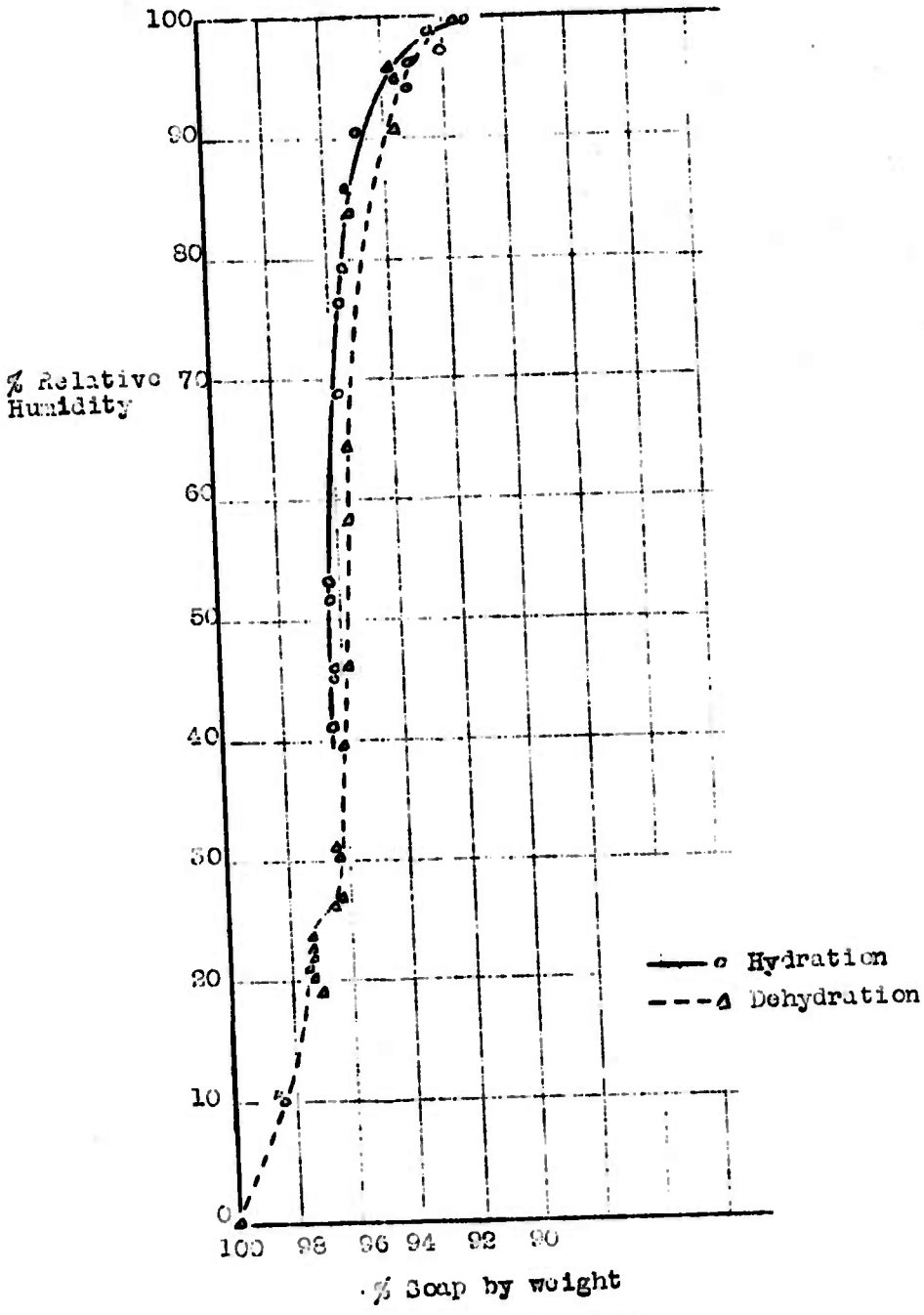
The curves show the same general character as those of aluminum dilaurate. There are no flats which would indicate formation of definite compounds or hydrates and the sorption and desorption lines are significantly different as often happens among powdered or porous solids. (Yearly 77 - 78).

(iv) Conclusion. The sorption balance is but a perfected gravimetric tool for moisture determination analogous in many ways to a vacuum oven or a desiccator (depending on the temperature at which used) and limitations of its usefulness are limitations on all gravimetric methods. Our study has shown that these gravimetric methods are satisfactory on pure aluminum soaps but are a priori unable to yield precise and completely significant results with Napalm.

This in no way diminishes their usefulness as useful tools in approximate, comparative or control work.

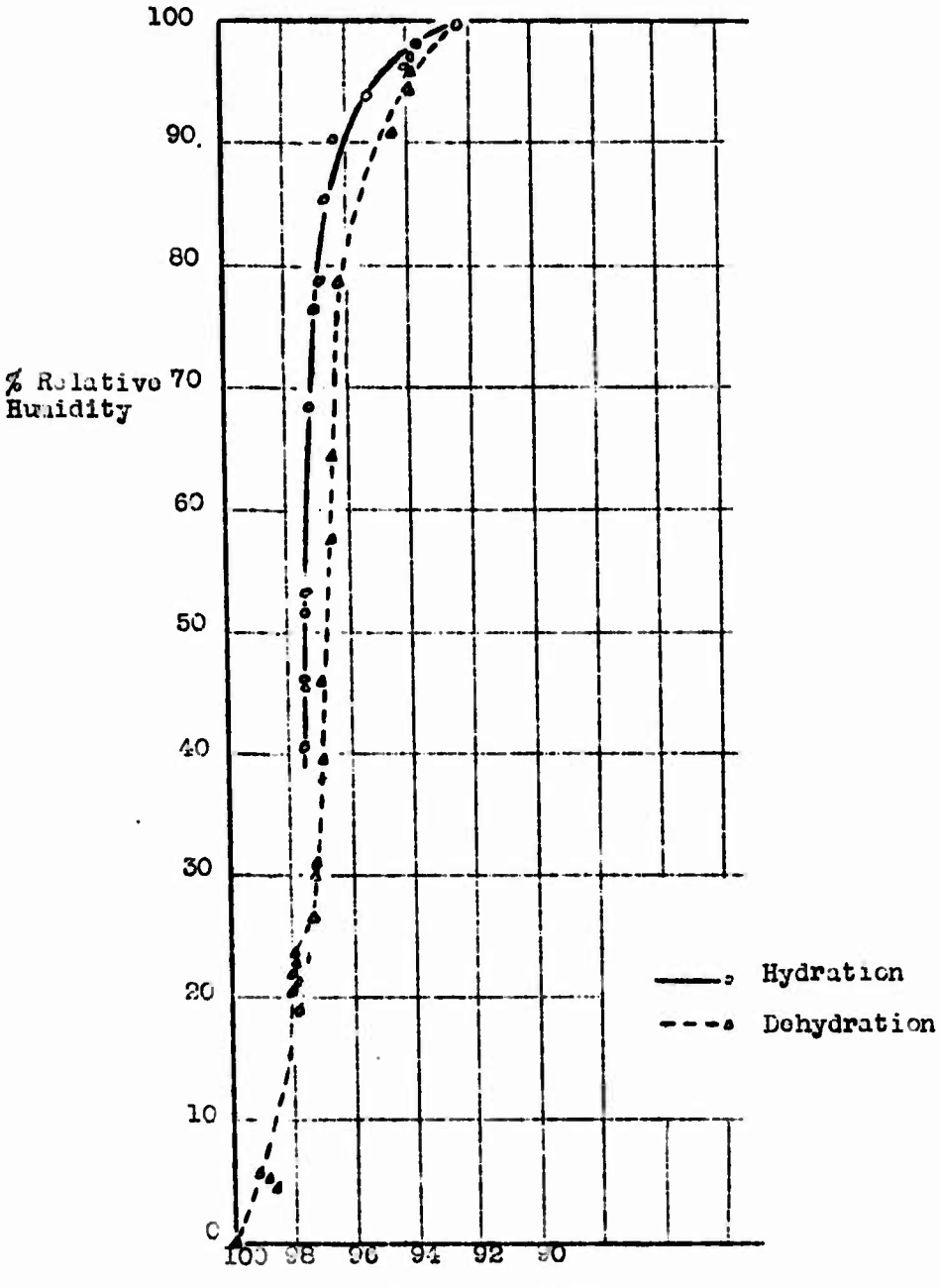
Figure 33

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



- Figure 34

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



D. The Karl Fischer Method.

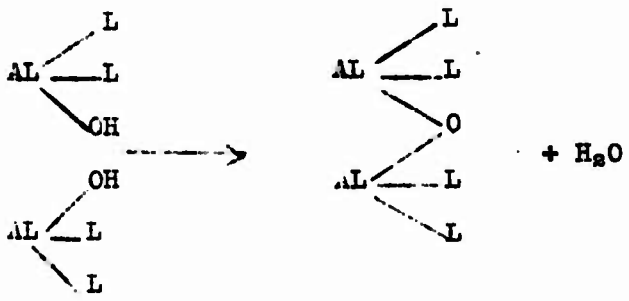
The Karl Fischer moisture determination method was applied to two samples of aluminum soaps through the kindness of the Shell Development Company. These samples were prepared and dried thoroughly by evacuation at room temperature at Stanford University and forwarded, sealed, to the Shell Development Company at Emeryville.

(a) Aluminum dilaurate $Al(OH)L_2$.

As mentioned previously this soap readily reaches a definite constant weight (p112) and by analysis corresponds within about 1% to the above formula (p. 87). The Fischer method gave a moisture content of 2.5± .4% 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 according to the reaction 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.

In case of our sorption or drying experiment we have never observed anything suggesting such a reaction.

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 does form during the Karl Fischer 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.

(b) <u>Aluminum distearate with molecular stearic acid; the nonexistence of tristearate.</u> In all our work as well as in our survey of the literature we have found no definite indication of existence of aluminum tri-soaps:

$Al(OOCR)_3$. The following presents further positive evidence for their nonexistence under conditions of aqueous precipitation which should be favorable to their production.

An aluminum stearate having an ash of only 3.50% was produced by our usual method of preparation in the presence of 0.75 equivalent of hydrochloric acid added to the aluminum chloride solution. Its ash corresponded to the presence of about 4.7 molecules of stearic acid per molecule of aluminum. Thus the soap was precipitated together with much more stearic acid than corresponds to a tri-soap in order to favor its formation.

This soap could therefore contain either 41% of aluminum distearate containing two molecules of ionically bound acid and 59% of stearic acid (part of which might be bound molecularly to the soap) or 64% of aluminum tristearate containing three molecules of ionically bound stearic acid and 25% of stearic acid (free or bound molecularly).

We used the Karl Fischer moisture determination to distinguish between these two possibilities. Aluminum tristearate and stearic acid obviously cannot form any moisture determinable by this method. We have shown however above that hydroxyl groups in aluminum dilaurate ($Al\ OH.L_2$) are capable of reacting so as to produce "moisture" as determined by the Fischer method. The pure di-soap produces one-half molecule of H_2O. In the presence of acid it may produce one molecule since additional H^+ ions are available. Our soap therefore should contain either zero or 0.6% or 1.2% of moisture by the Fischer method, depending on which hypothesis

of its constitution is true, i.e. whether hydroxyl is present or not and whether one-half or one molecule of water is formed by reaction of the hydroxyls.

The results of the moisture determination were 0.75% or 0.91% moisture by repeated titration to a slowly fading endpoint (reaction occurring) and 0.99% by titration to a stable endpoint after an hour and twenty minutes.

This water content corresponds well with that calculated on the assumption that only aluminum distearate is present and disagrees by much more than the possible experimental error with the assumption that aluminum tristearate and not distearate is present.

E. Benzene Distillation.

The benzene distillation method is reported to give results either very close to the vacuum oven method (B.B. p.57) or quite different and in general higher ones (B.B. p. 55 and 45). Its precision is low, especially on small samples of soap and the result depends largely on experimental conditions. (B.B. p. 47). Our technique has not yet reached the point where it can be relied upon to less than 0.5%.

We were especially interested in the question whether any reaction between hydroxyls themselves or between hydroxyls and fatty acid occurred during this method. Thus the soaps and acids studied were first dried thoroughly by evaporation. (However it is probable that appreciable amounts of moisture were picked up during transfer and this part of the operation should be improved before reaching final conclusions).

Aluminum dilaurate $AL(OH)L_2$ might undergoe condensation of hydroxyls such as occurs during the Karl Fischer method according to the reaction.

$$2\ Al(OH)L_2 \longrightarrow Al\ OL_4 + H_2O$$

This would yield 2.03% of moisture. Actually we found less than 0.9%.

Adding over 1 equivalent of lauric acid to the dilaurate might lead to the formation of moisture by reaction between hydroxyls and the acid according to

$$Al(OH)L_2 + HL \longrightarrow AlL_3 + H_2O$$

This would yield 4.06% moisture. Actually we found only .04%.

Aluminum monolaurate has probably (p. 98) 2 hydroxyl groups. If one of these was interacting according to

$$2Al(OH)_2L \longrightarrow Al_2OH_2OL_2 + H_2O$$

it would produce 3.46% of moisture; actually we found 0.9%.

Adding over 1 equivalent of lauric to the monolaurate might also produce water according to

$$Al(OH)_2L + HL \longrightarrow Al(OH)L_2 + H_2O$$

and the amount produced should be 6.92%. Actually we find 0.5%.

These results lead to the definite conclusion that none of these reactions proceeds to completion or occurs even to a substantial extent. Before concluding however that they do not proceed at all, more accurate experiments are needed.

CHAPTER IV

THE SYSTEM ALUMINUM SOAP-HYDROCARBONS.

Introduction.

When an aluminum soap is placed in a liquid 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 it 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

CHAPTER IV

THE SYSTEM ALUMINUM SOAP-HYDROCARBONS.

Introduction.

When an aluminum soap is placed in a liquid 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 it 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, and 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 additives (including "peptizers") is discussed in the next chapter.

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

(1) 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" extracted 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 flock 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.

(b) Definitions and Background. To distinguish these forms we use the terms gel for the opalescent noncoherent lump form("apple sauce"), sol for the clear and freely flowing liquid form, and jelly for the clear, rigid and elastic form.

This usage conforms to the historical development of these terms (Yearly p. 86) and we observe it strictly when describing pure soaps. In the case of Napalm-gasoline mixtures, the term gel is often used generically to include both gels and jellies.

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 sometimes use the term jelly-sol to denote both.

On the other hand, many colloidal systems, called gels, consist of semi-opaque or turbid, noncohering 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 curd or gel consists of a mass of perfectly crystalline curd fibers enmeshing a liquid present amongst them.

(c) Experimental Criteria. We found four experimental methods for distinguishing between gel and jelly-sol.

(i) Their appearance. 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.

(ii) Their mechanical properties. The jelly-sol is continuous and either easily flowing or stringy (or both). The gel is crumbly ("applesauce") 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.

(iii) 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 18 (p. 71). 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.

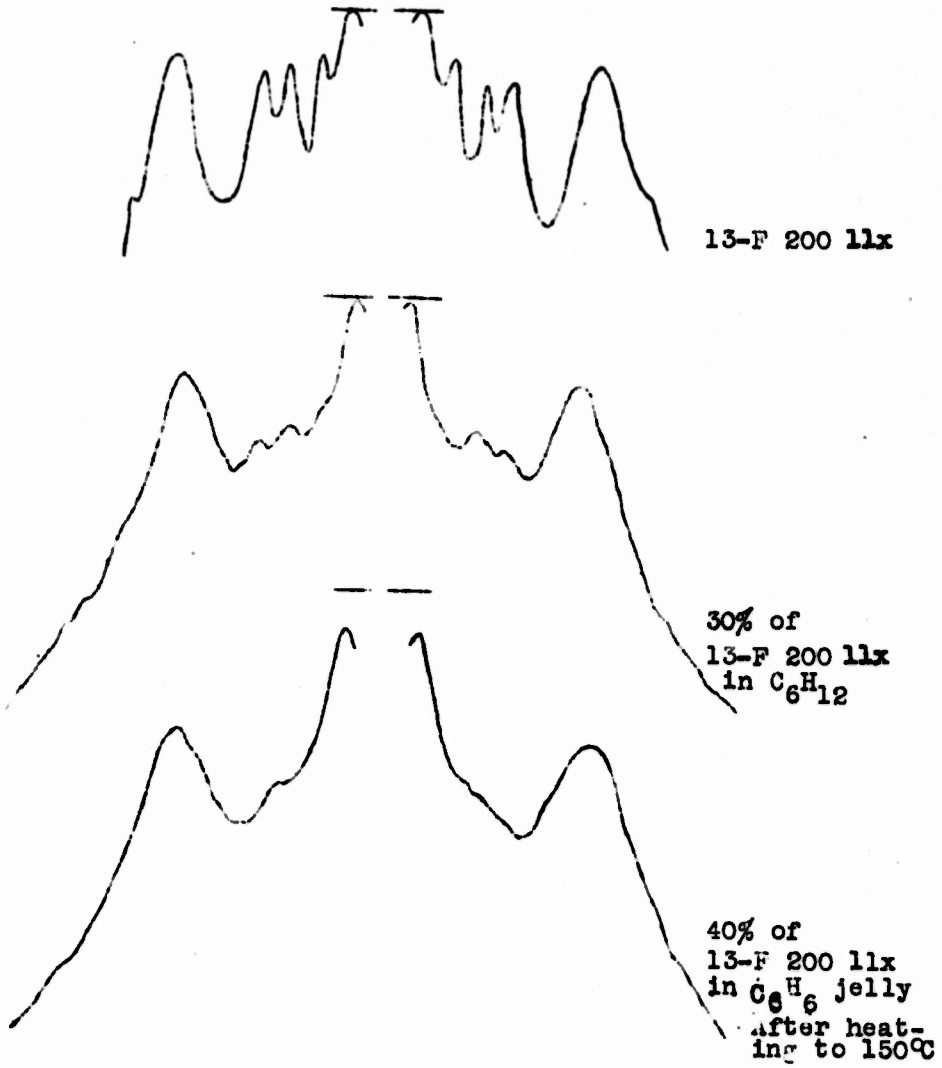
(iv) The x-ray diffraction of the system itself. This method is insensitive and could be applied only to concentrated systems. From preliminary experiments it appears that the gel shows all the lines of the soap, while in the

jelly these become blurred or disappear completely, or exhibit faintly a long spacing and some side spacings and halos.

Figure 35

Microphotometer tracings of x-ray diffraction patterns of dry aluminum dilaurate, the gel in cyclohexane and the jelly in benzene.

Sample to plate distance 5 cm.
Magnification 2x.



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.

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 R11285 and Ferro Enamel Lot P Batch 184. Commercial 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 (Figure 36) shows these systems one week after preparation.

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 liquefied i.e. changed to sol without a marked change in turbidity by adding small amounts of liquefiers (peptizers). Presence of 10% by volume of nitrobenzene in cyclohexane and isooctane caused liquefaction of mixtures containing 4% Napalm. When compared with the series of mixtures of toluene and isooctane shown in Figure 36 the addition of 10% of nitrobenzene had the same effect on turbidity as addition of some 10% of the toluene which caused no liquefaction. Furthermore upon prolonged standing or centrifugation of the more liquid systems a white sediment appeared, leaving a clear jelly or sol.

This led to the separation and investigation of this turbidity agent which turned out to be inorganic impurities of Napalm (p.104 and Yearly p. 92-94).

(b) <u>The existence of gel and jelly forms of Napalm in gasoline</u>. 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

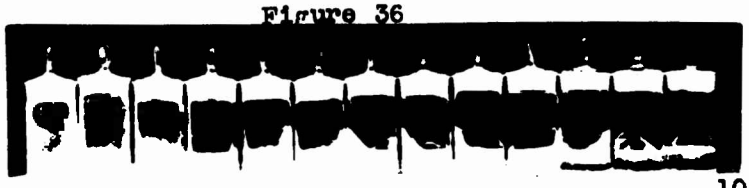
Mixtures of the two extremes, isooctane and toluene, give a progressive series passing from a two phase sol-gel system to a clear jelly. The attached photograph (Figure 36) shows these systems one week after preparation.

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 liquefied i.e. changed to sol without a marked change in turbidity by adding small amounts of liquefiers (peptizers). Presence of 10% by volume of nitrobenzene in cyclohexane and isooctane caused liquefaction of mixtures containing 4% Napalm. When compared with the series of mixtures of toluene and isooctane shown in Figure 36 the addition of 10% of nitrobenzene had the same effect on turbidity as addition of some 10% of the toluene which caused no liquefaction. Furthermore upon prolonged standing or centrifugation of the more liquid systems a white sediment appeared, leaving a clear jelly or sol.

This led to the separation and investigation of this turbidity agent which turned out to be inorganic impurities of Napalm (p.104 and Yearly p. 92-94).

(b) <u>The existence of gel and jelly forms of Napalm in gasoline</u>. 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

Figure 36



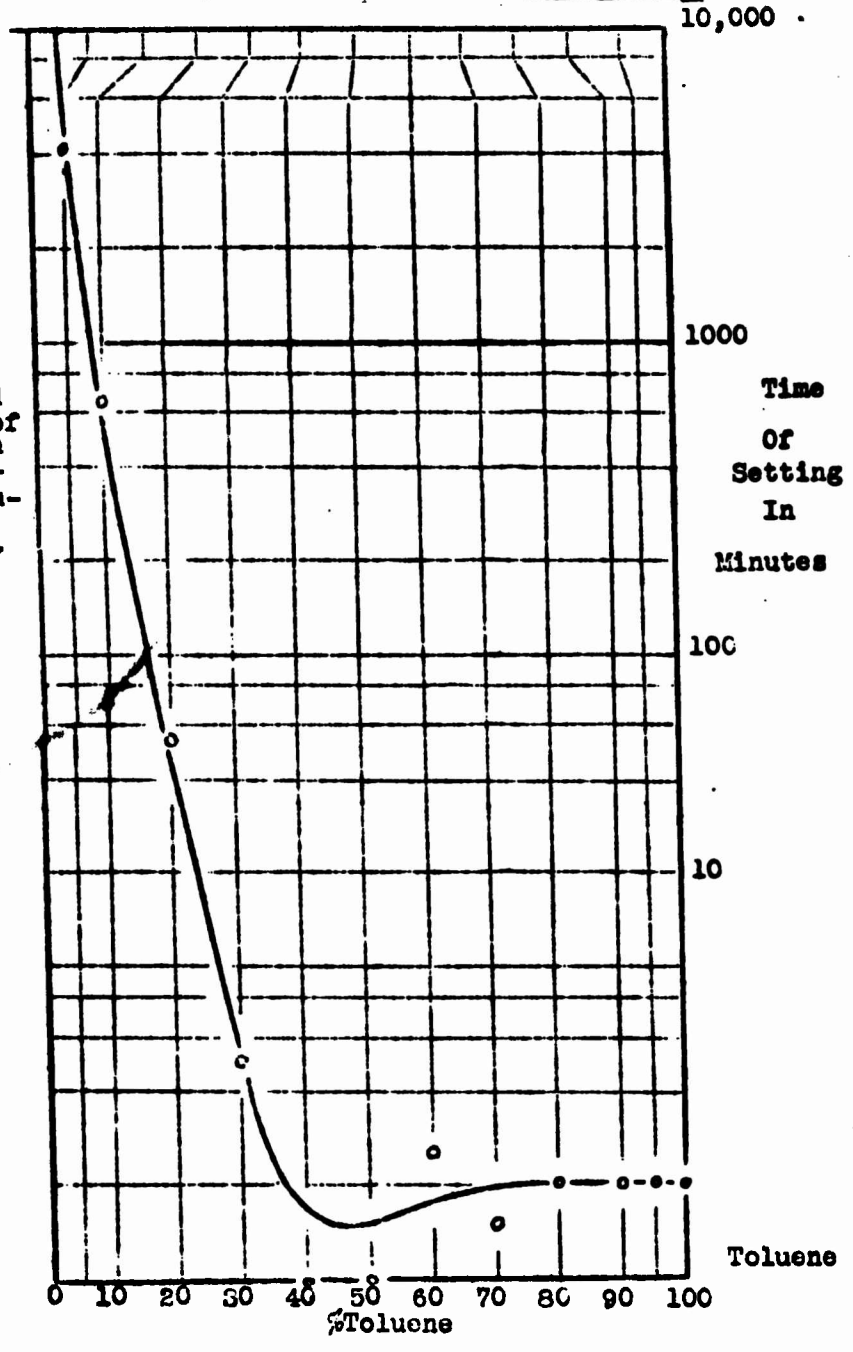


Figure 28

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

to show the distinction between gel and jelly in case of Napalm, x-ray diffraction patterns shown in Figure 37 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 presence of the gel form.

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

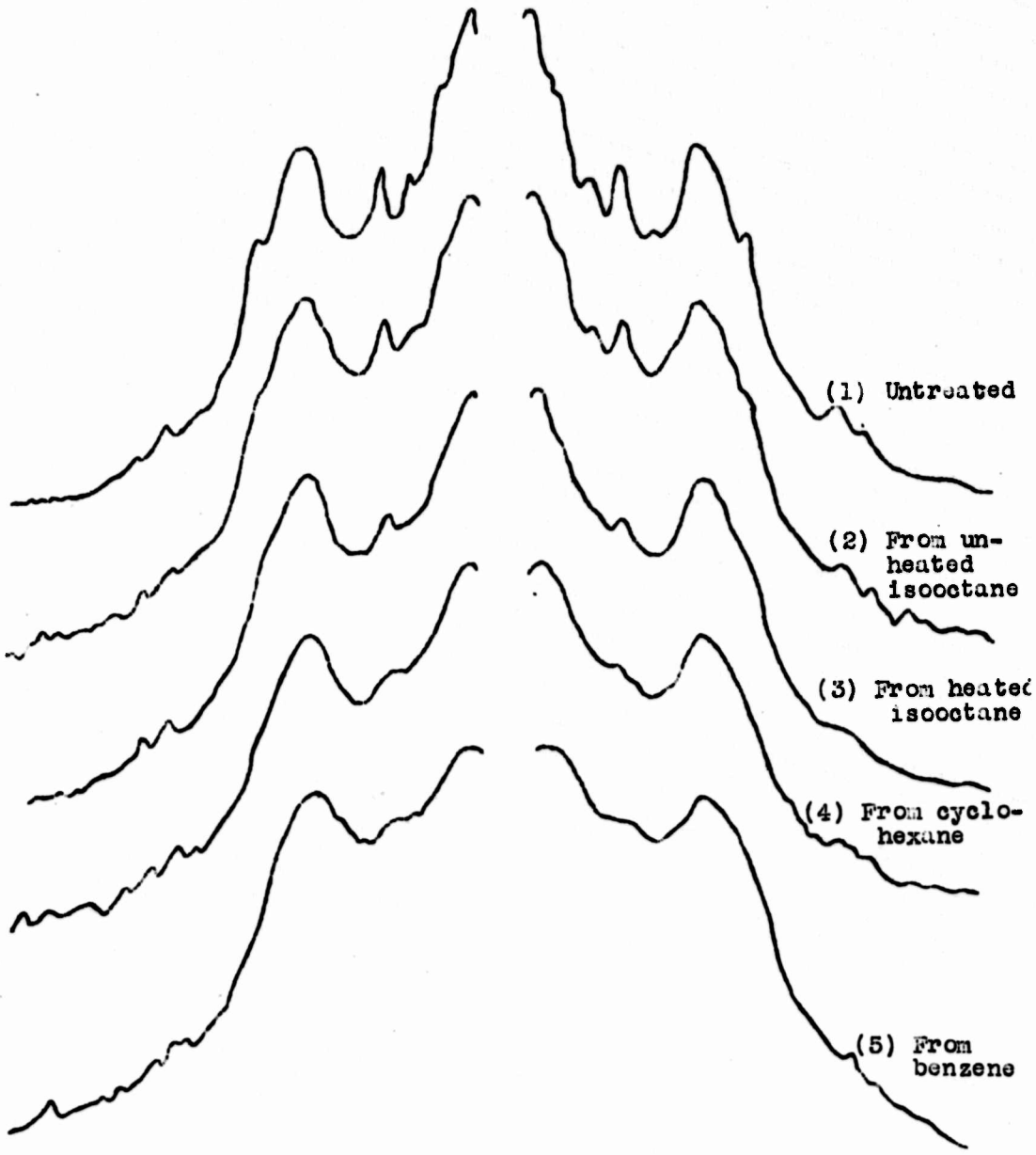
(4) Some Napalm placed in 11.5 parts of cyclohexane at room temperature formed a turbid mass. Frozen and dried by evacuation it shows a pattern of jelly, not gel.

(5) Same process as (4) but with benzene. An almost clear transparent mass was formed, and Figure 37 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 due to reversion during cooling and evaporation A very crystalline pattern was obtained from the residue of evaporation of a liquefied 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

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

Figure 37



difficult, the smell of nitrobenzene persisting after 24 hours of evacuation, and apparently a far-going reversion to gel took place in the meantime.

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

A. The Transitions from Dry Soap to Gel and Jelly.

We have observed these transitions visually by means of the McBain-Bakr sorption balance and by x-ray diffraction.

(a) Visual observation.

(1) 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, then remaining unchanged for months. (In one or two cases we may have observed slow decrease of swelling). 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 but remain discrete and easily dispersed. Centrifugation compresses them to a lower level and it required 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, 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, it cannot expand further; the same intimate contact between them results, 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.

When a very amorphous form of dilaurate "recovered from jelly" is observed at room temperature, or the "original" dilaurate is observed 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 decreases; the outer layers becoming fluid and finally resulting in a continuous transitio

from a firm jelly in the center to the thin surrounding sol without any visible boundary.

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

(ii) Napalms. Napalms of various manufacture differ markedly but essentially they resemble aluminum dilaurate, giving the same type of transition from dry soap to gel or jelly in various hydrocarbons; but the particles are larger and the clear transparent condition is approached only in aromatic solvents.

Effect of solvent: Aromatics (toluene) and paraffins (isooctane) show the typical extreme behaviors with McGean 462 Napalm.

In aromatics 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 flocculer outline which seems to disappear only very slowly.

In paraffins however the liquid between the 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 show their individuality by unevenness of surface, 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 accelerating effect of small amounts of toluene upon the time of setting (as measured by the appearance of rigidity at edges of the gel). Figure 36 (p.137) 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.

Effect of different Napalms. At the suggestion of Mr. Stevenson, the behavior of various commercial Napalms in pure solvents was examined, with the object of suggesting or developing a simple test of quality, and to see in how far they were alike or different.

Systems containing approximately 4% of the soap in benzene, cyclohexane and isooctane, were prepared in evacuated sealed tubes. (October p. 1). The detailed observations are collected in Tables XIIIa to XIIIc of the October Report.

In isooctane, only Colgate and Harmon Napalms finally filled the whole liquid volume. Colgate produced a jelly,

Pfister at 50 hours filled only 18% of the total volume. In general, isooctane produces partially swollen gels (discreet lumps, discontinuous blobs, not adhering to each other or to the tube wall, short even when packed close together, translucent to opaque blobs, applesauce to swollen granular). Only at sufficiently elevated temperatures do gels transform into clear elastic homogeneous jellies. (See p.162). The Napalms were found to be very different in this respect; some passing completely to a clear jelly, others consisting only predominantly of a fraction that passed to a jelly, while still others largely consisted of particles and lumps that swelled slightly or formed discontinuous short swollen gels.

In cyclohexane all but three Napalms filled the liquid after 24 hours. For Colgate Napalm this was due to the extremely rapid setting before complete admixture could be effected. Pfister and Nuodex were the two that remained partly in the state of gel, not filling the whole liquid. The others went largely to jelly, but differed in consistency. Oronite formed the most rigid jelly.

Benzene transformed all the Napalms into jellies with the possible exception of Nuodex where some liquid still remained free.

Cyclohexane gave the greatest spread between the individual soaps, while they all tended to remain gels in isooctane and go to jellies in benzene. This solvent was therefore selected for further tests in which approximately 0.1% Napalm was placed in 100 ml. of cyclohexane and observed with vigorous shaking every few minutes during the first 1/2 - 3/4 hour.

Within 10 minutes the sample containing the Oronite Napalm had become a homogeneous, stringy, elastic jelly. The samples containing Ferro, McGean, Colgate and California Ink Napalms all thickened the solvent but did not form jellies. The Nuodex, Pfister and Imperial Napalms did not show any noticeable thickening action and part of the soaps rapidly settled out as soon as the shaking had stopped. The rest of the Napalms exhibited an intermediate degree of thickening action. Table XIV of the October Report contains the most pertinent observations resulting from an examination of these systems and shows that:

(1) All the samples except Pfister, Nuodex and Imperial become stringy elastic jellies.

(2) All samples except Colgate and Eakins were hazy to some degree, the haziness often gathering at what appeared to be a jelly-sol interface. This hazy material was believed to be partially due to inorganic impurities.

(3) Oronite was the only completely uniform sample, passing from a homogeneous jelly to a sol.

(4) The differences between individual soaps appear more strikingly in the more dilute systems.

The opaque and gelled portions of Imperial and Pfister were washed with further addition of increments of fresh solvent. The residue from the Imperial acted like sand and remained opaque while that from the Pfister seemed to have a limited swelling to a semi-translucent state. These are the "inert soaps" discussed on p. 101 .

A different situation was observed when the 0.1% Nuodex was mixed. The gel had settled to a compact layer which seemed to have swelled to a limit, even after being broken up into small pieces. On addition of fresh solvent, part of this gel layer dissolved and after a total of 200 ml. of the cyclohexane had been used almost all of the gel had disappeared. It was noted that it dispersed from the gel directly to a sol form without appreciable thickening of the solvent surrounding the gel.

(b) Sorption of cyclohexane.

(i) Aluminum dilaurate. Figure 38 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 and it was observed that in the first run 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 corresponds to a change from gel to jelly in the state of the soap, the jelly sorbing incomparably more solvent and showing hysteresis (Annual Report p. 42-43).

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 jelly 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 throughout.

(ii) Napalm. The sorption isotherm for cyclohexane on Napalm Imperial NR202 at 50°C is shown in Figure 39. 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.

An almost identical curve was obtained for the sorption of benzene by Cronite 7-33-C Napalm. It is shown in detail in Figure 135 of our November Report.

These curves may be contrasted with the water sorption isotherm of Napalm given in Figures 30 and 33, which show that a few percent of moisture were enough to saturate the soap and produce nearly 100% relative humidity.

An isobar of Napalm over cyclohexane showing marked

Figure 38

Sorption of Cyclohexane by Aluminum Dilaurate at 50°C

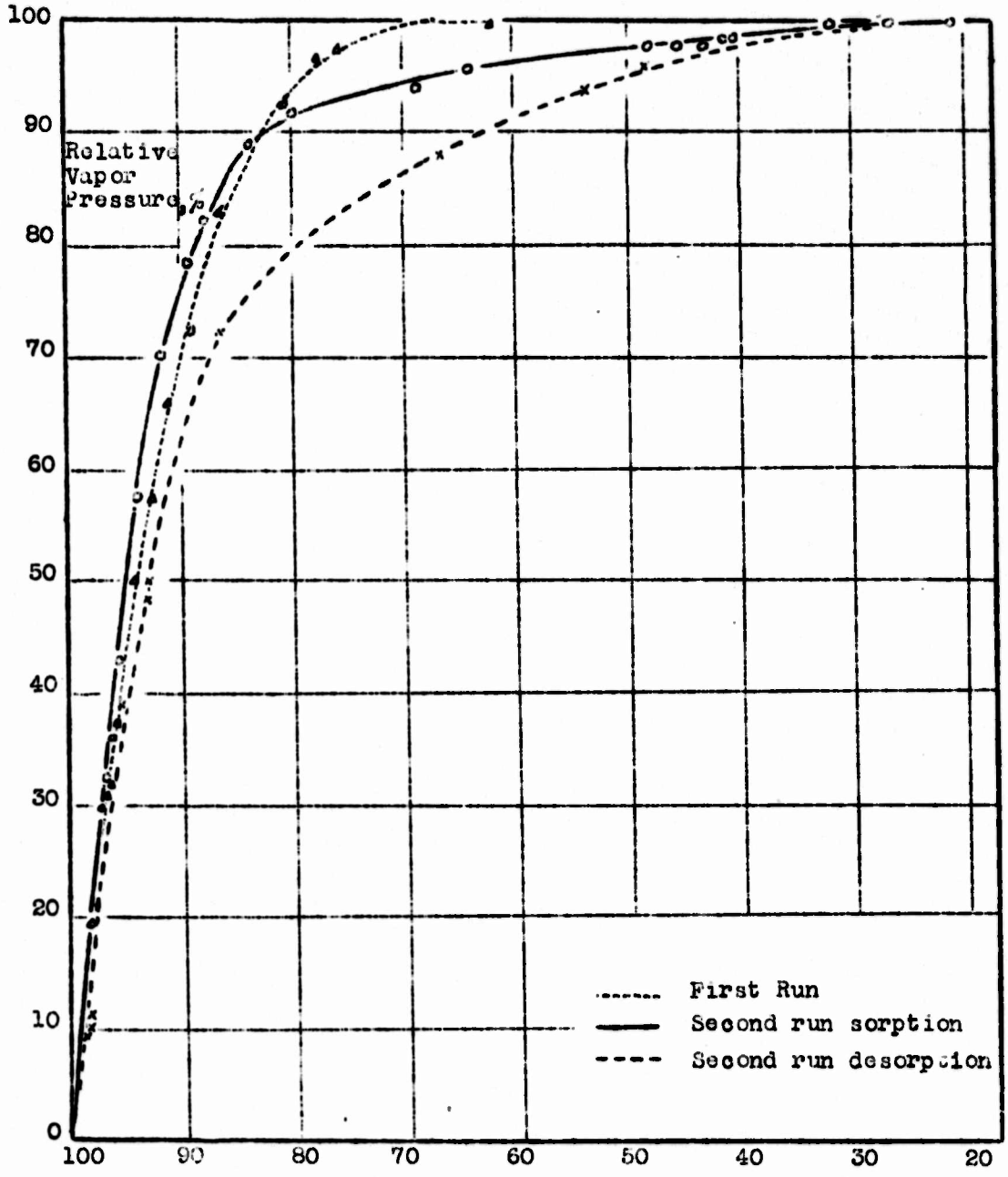
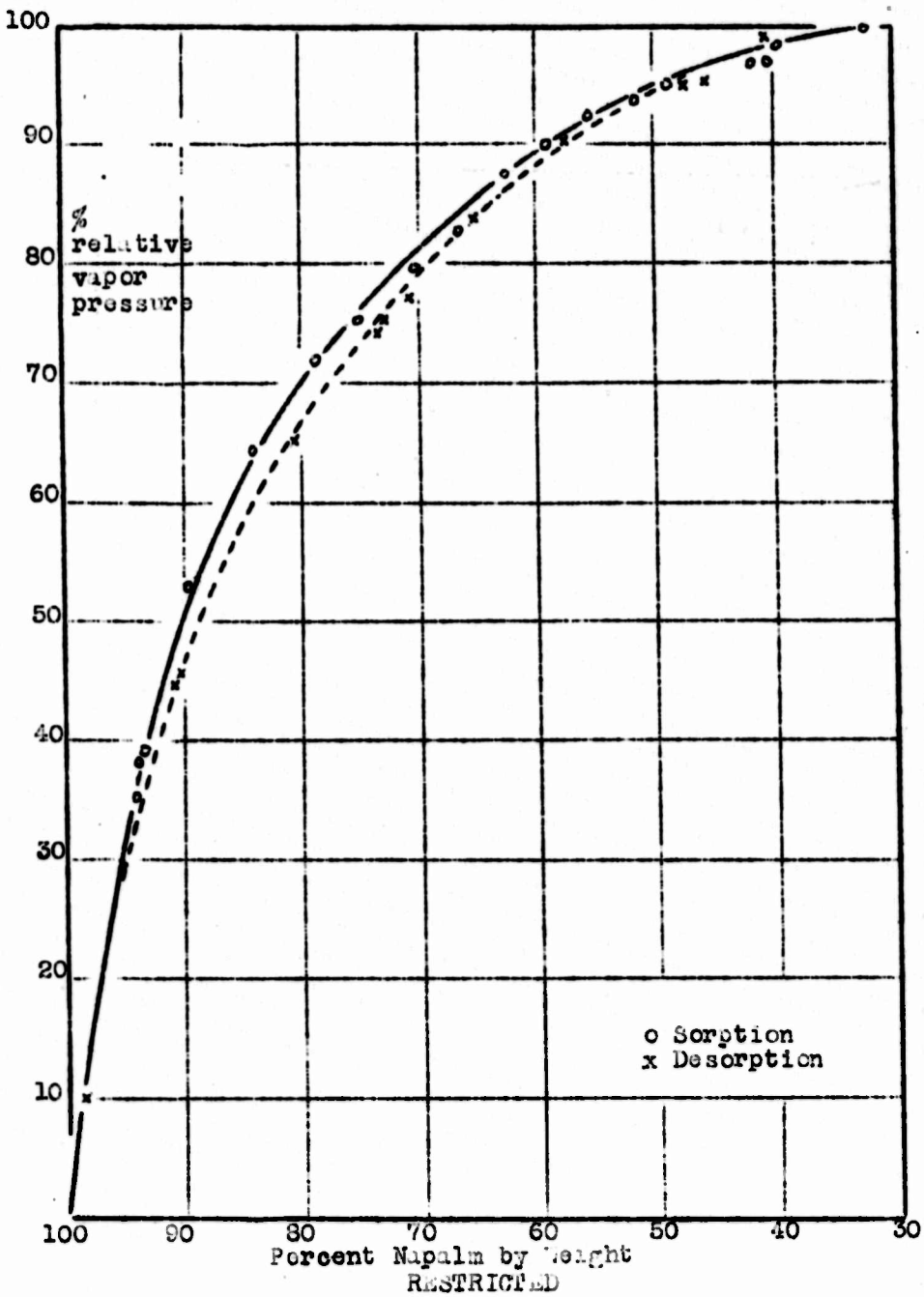


Figure 39

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



thermal hysteresis is reported and discussed in the Yearly Report p. 104-106.

(c) X-ray diffraction. The technique of obtaining x-ray diffraction pictures from systems enclosed in narrow and very thin walled capillaries is described in the January Report. The concentration of the systems observed is not known exactly, due to the difficulty of obtaining a homogeneous mixture. Due to the presence of both solvent and glass the diffraction picture is less clear than may be obtained from a soap alone.

Examination of the difiraction patterns shows that when the soap swells to a gel, there is little if any change in its diffraction pattern. Both the distances and sharpness of the original diffraction lines are maintained when aluminum dilaurate is placed in cyclohexane; and even after it has been heated therein to 45°C, which caused all available liquid to be completely imbibed, the gel examined had a concentration of about 20% of soap.

When the soap changes to jelly the difiraction pattern seems to change markedly most of the lines becoming indistinct or disappearing. Thus when aluminum dilaurate is placed in benzene and heated to 120°C and stirred to ensure transition from gel to jelly, the diffraction picture shows only the first long spacing and two halos in a 40% jelly.

This indicates that gel formation does not affect the structure of the bulk of the soap crystallites and is therefore either a surface phenomenon or one affecting mainly the most amorphous portions of the soap. The change to jelly on

the other hand must cause drastic changes or even disappearance of the original crystallites.

Figure 35 shows tracings of the pertinent diffraction patterns.

the other hand must cause drastic changes or even disappearance of the original crystallites.

Figure 35 shows tracings of the pertinent diffraction patterns.

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 is present. This transition has been studied by viewing sealed tubes during heating and cooling, by determining the solubility of the soap in the sol, and by x-ray diffraction.

(a) Visual observations. The technique of preparing sealed tubes and of observing the change from gel to jelly is described on pages 107-111 of the Yearly Report. In the concentration range of 1 - 10% it gives a determination of the final transition temperature within 1 or 2°C and the detection of less than 0.05% of soap in gel form. A typical log of such observation is also reported. By correlating many such observations the following conclusions are drawn and the phase diagrams of figures 50 to 53 (p.187-8) obtained.

(i) Effect of the physical form of the soap. The physical form of the soap has a marked effect upon its swelling (as noted in Table IV, p89) and upon the temperature of transition into the jelly or sol form. At room temperature, the crystallized form of aluminum dilaurate swells by less than 20%, whereas the "original" swells 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°.

(ii) Reversibility. The transition from gel to jelly is rather rapid, and if the soap is well dispersed throughout the liquid, may be readily determined within 1 or 2°C. The reversion from jelly to gel is in general slower but does occur if the tube has not been heated very high above the transition temperature. If, however, it has been heated to a high temperature (50 to 150°C above the transition temperature) the jelly may remain clear and stable for many months. Apparently seeds which promote the reversion may be present even in completely clear jellies but disappear upon further heating.

The gel formed upon reversion of the jelly often synerises. Upon heating it is again transformed into a jelly and this process may be repeated. Increases of 5 - 12°C have been observed between the first and subsequent gel-jelly transition temperatures in the same sealed tube. This suggests that a true recrystallization of the soap has taken place in the solvent (analogous to recrystallization previously observed in the absence of solvent at 160-200°C), the reverted soap being more crystalline than the original.

The above shows that the form of the soap has a great effect upon its swelling and transition temperature so that when comparing different solvents or peptizers, portions of the same sample of soap should be used and preferably the first transitions compared.

(iii) Effect of solvent. Aluminum dilaurate swells (or dissolves) in benzene, less in cyclohexane and still less in n-heptane and isooctane. Its transition temperture to jelly increases in the same order. Figure 40 is a plot of the volume to which the soap swells at 25°C (in cc per gram) versus the temperature of the gel-jelly transition. The points seem to fall on a smooth curve.

(b) X-ray diffraction. The results reported previously (p. 151) for the x-ray diffraction of gels and jellies of aluminum dilaurate in cyclohexane and benzene show that the two phases differ markedly in their diffraction pattern. We have not yet been able to observe a single system at different temperatures to follow the change from gel to jelly.

An interesting series of diffraction patterns was however obtained at room temperature on a dilaurate-cyclohexane mixture and is shown by the following Table V .

It may be noted that visual observation of faint opalescence is very difficult in such a thin capillary. Nevertheless the results suggest that tiny crystallites of soap may exist in apparently clear systems of jelly reverting to gel, and affect x-rays without markedly affecting the visual appearance.

(c) 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

Figure 40

Swelling and transition temperature of "original" aluminum dilaurate in hydrocarbons.

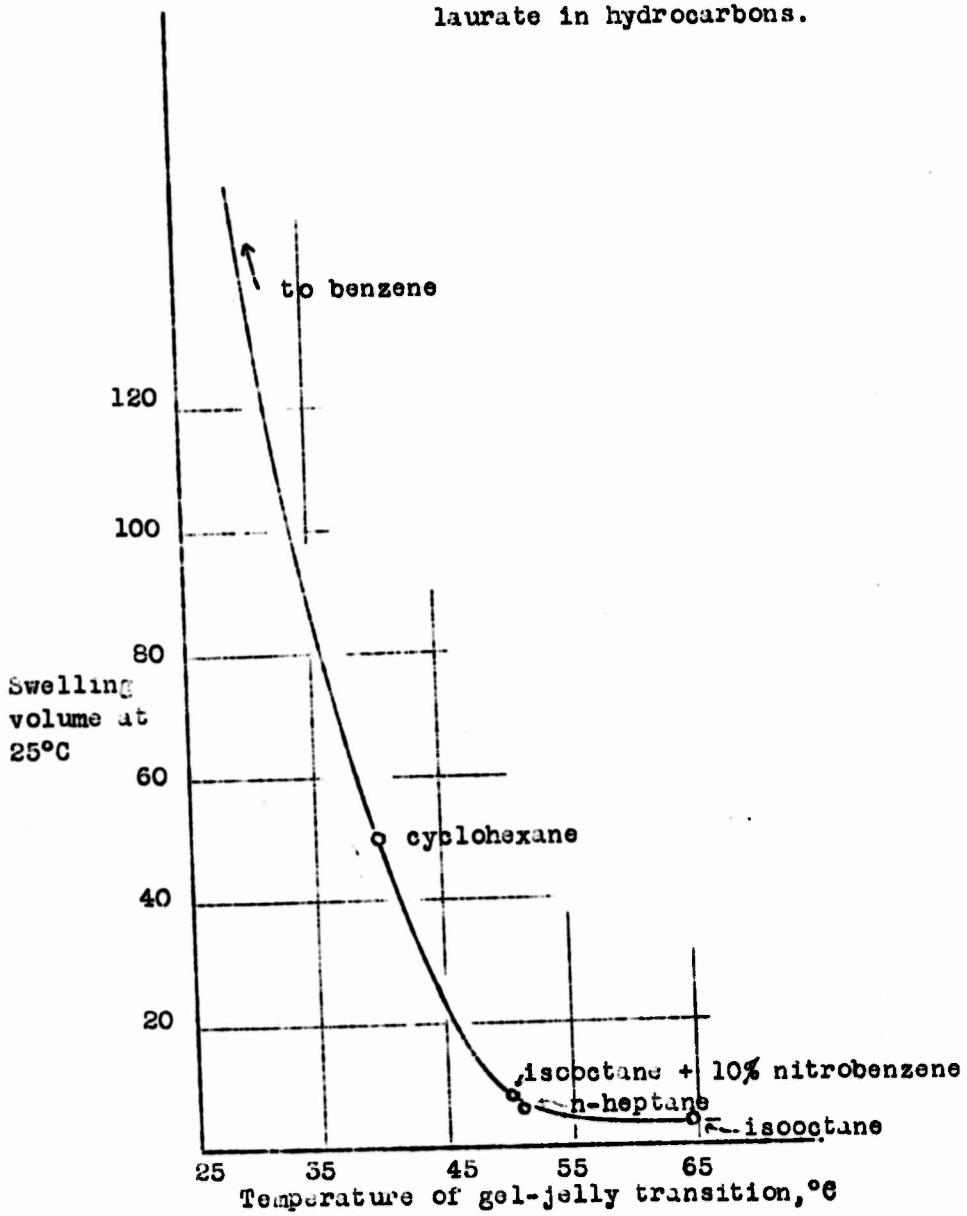


Table V

Successive X-ray Diffraction Patterns Obtained at Room Temperature on an Approximately 30% $Al(OH)L_2$ in Cyclohexane System Enclosed in a Thin-walled Capillary.

Previous Treatment:	Visual Aspect	: Diffraction Pattern
As prepared	Opaque white particles in a transparent or translucent medium. Inhomogeneous	Similar to that of original soap, only slightly weaker; both long and short spacings visible.
Heated to 38°C.	Stiff, turbid, more homogeneous.	Slightly weaker, both long and short spacings visible.
Heated to 80°C.	Clear.	Short spacings slightly weaker; long spacing weaker and much more hazy. Second order not visible.
Allowed to stand for 18 days.	Opalescent birefringent, visibly reverting.	Both long and side spacings visible - resembles second photograph above, but slightly weaker.
Reheated to 80°	Clear	Both long and side spacings are visible, but are weaker and hazier than in previous photograph.
Heated to 150°C	Clear	Both long and side spacings are much weaker than before - hardly discernible.

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 phosphorus 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.

The techniques of the measurements is described on p. 113 of the Yearly Report. The results are illustrated in Figure 41 to 43 .

Figure 41 shows the concentration of the solution as a function of the proportion of soap present. Over the ranges covered at both temperatures is a straight line passing through the origin. Figure 42 shows the same results expressing the proportion of soap dissolved as a function of proportion of soap present.

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

The presence of small amounts of lauric acid has little influence upon the solubility of $Al(OH)L_2$ in cyclohexane (Yearly p. 114) and could not account for the effects noted, Hence cyclohexane has separated the "original" dilaurate into a fraction readily soluble at 21.5°C amounting to about 8%, and one still insoluble at 25°C amounting to 75%.

Figure 41

Variation of Concentration of Cyclohexane Solution with Varying Amounts of $Al(OH)L_3$ Present. - 48 hrs. of contact.

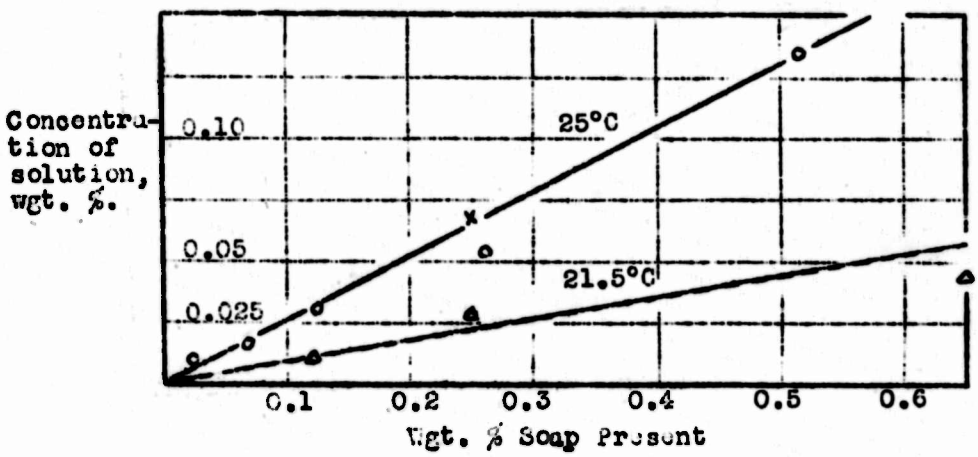
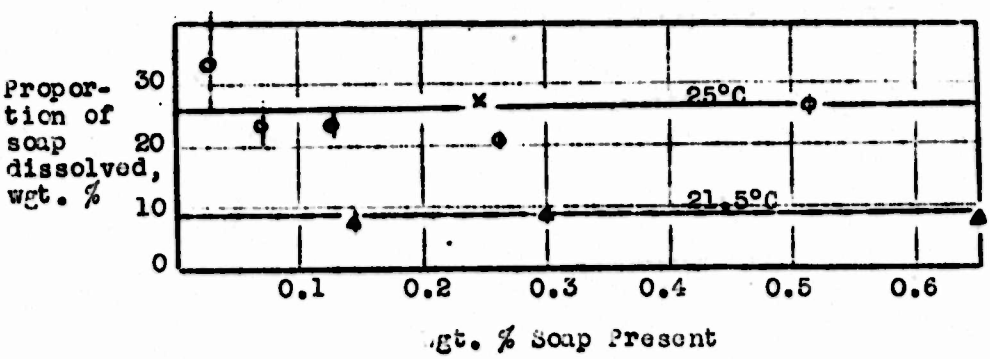


Figure 42

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



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 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 were indistinguishable. (Figures 13 and 14 of Yearly).

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 43 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.

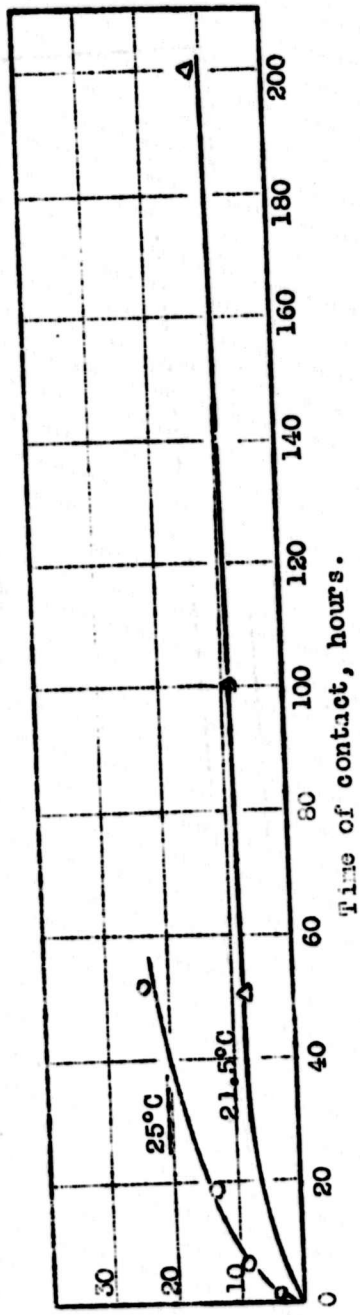
(d) Napalms. The gel-jelly transition temperatures in isooctane of the ten samples discussed previously were obtained by the method used on pure soaps. The observation of the gel-jelly transitions of Napalm samples was more difficult than with the pure soaps since the inorganic impurities

Figure 43

Proportion of Soap Dissolved as a Function of Time of Contact in the System

"Original" Aluminum Diaurate 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.)



and inert soaps present in Napalms appeared as opalescence or cloudiness in the jelly.

Eakins, Colgate and Harmon Napalms formed jellies with isooctane below room temperature (23 - 25°C). The transition did not occur far below this temperature since ca. 50 hours were required for the system to become a jelly. These samples had very little if any mono-soap and Colgate and Eakin Napalms had very little inorganic impurity as demonstrated by the clarity of the jellies.

The rest of the Napalms, except Pfister, swelled markedly at room temperature and passed to jellies when heated to higher temperatures. Nuodex formed a jelly at 25°C which was very cloudy but stable. The other Napalms in this group formed jellies between 46 and 53°C. The cloudiness of this group varied and was attributed to both inorganic impurities and mono-soaps. Imperial Napalm deposited a considerable amount of light tan sediment consisting of distinct particles of inert soaps. (See p. 101).

Pfister Napalm became a jelly at 65°C and contained a considerable amount of opaque material.

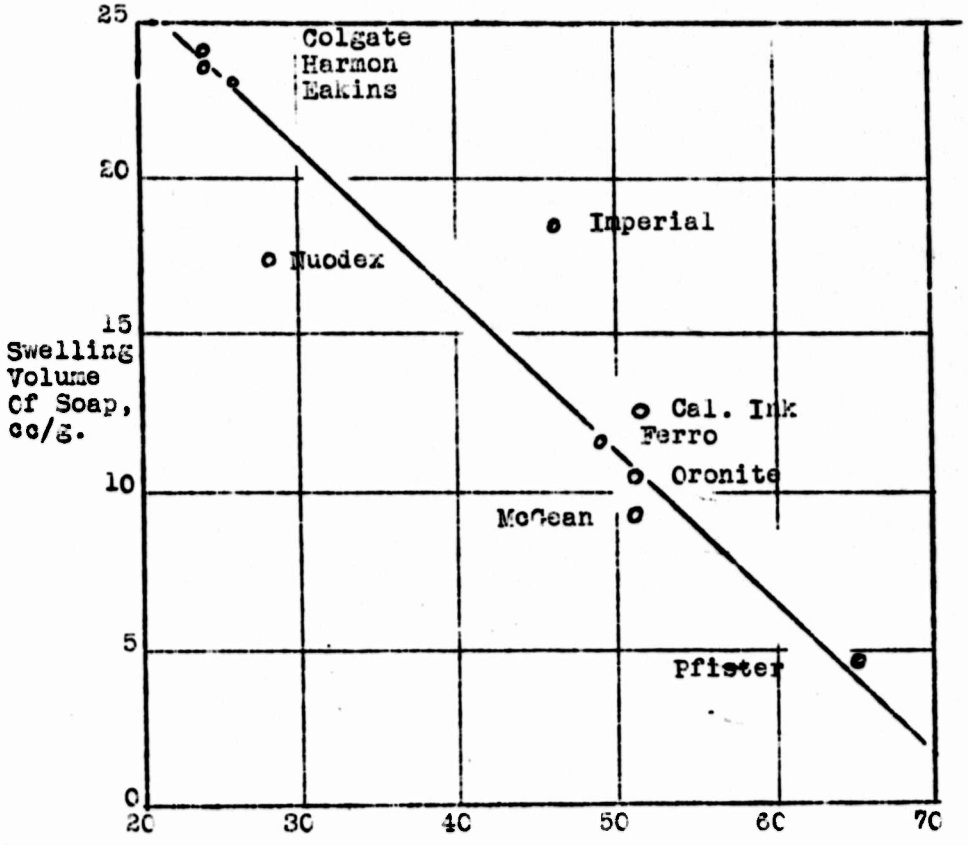
The increase of haziness or cloudiness roughly corresponds to the increase of organic impurities as found by Marshaw in their 15th Monthly Report.

The details of observations on these systems have been summarized in Table XXIII of the November Report.

The relationship between the volume to which the soaps swelled in 50 hours at 23 - 25°C and the temperature of the gel-jelly transition in isooctane appears to be linear as shown

Figure 44

Relationship between the gel-jelly transition temperature and the swelling volume, after 50 hours at ca. 25°C., of ten Napalms in Isooctane.



in Figure 44 . Imperial Napalm is the only marked deviation. A similar relationship for a pure soap in various solvents is shown in Figure 40 . The latter, however, is not linear.

(e) Reversion in thickened fuels etc. We have not observed any sign of reversion in our Napalm system but syneresis has been reported in a few cases under very drastic conditions with paraffin hydrocarbon and low temperature (B.B. p. 22) and suggests that such reversion is possible.

It is well known that pure substances crystallize in general more easily than mixtures and that the role of both seed formation and growth decreases as the complexity of the mixture increases.

In view of the slowness of reversion in pure soaps it is quite natural that the complex mixture of soaps which form Napalm should show reversion only in some instances.

In case of FRAS fuels which are prepared by heating, it is reported (British P.W.B. Memo 379) that there are cases of "structural instability" which result in opacity and precipitation especially at lower temperatures. This seems to correspond closely to a reversion or transformation from a jelly to a gel.

In case of aluminum soap base greases it appears that reversion from jelly to gel occurs regularly and is a necessary and desirable step in the manufacture. Thus U. S. Patent 2 343 736 is concerned with controlling the behavior of the soap at "a transition temperature of usually about 120° to 150°F" while the grease "changes from a stringy liquid to a solid gel" having an "unctuous gel or grease structure".

(f) Relation between transition temperature and consistency. The above experiments on the transition temperature between gel and jelly shows that it is an interesting characteristic of a given system depending both on the chemical and physical nature of the soap and on the solvent. It would be of interest if this characteristic could be correlated with the consistency of the system in its jelly form which is most important in a thickened fuel. It does not seem however possible to correlate them simply as we have evidence on the one hand that the transition temperature is reduced by additives (peptizers) which tend to liquefy the system and on the other hand protective colloids that reduce the crystallinity and thus the transition temperature, give stiffer gels. Further study may show however that limited relationships between these characteristics exist even though there is no general one.

C. The Transition Between Jelly and Sol.

We have found no characteristic sharply separating these two forms and the transition, as expected, is continuous 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.

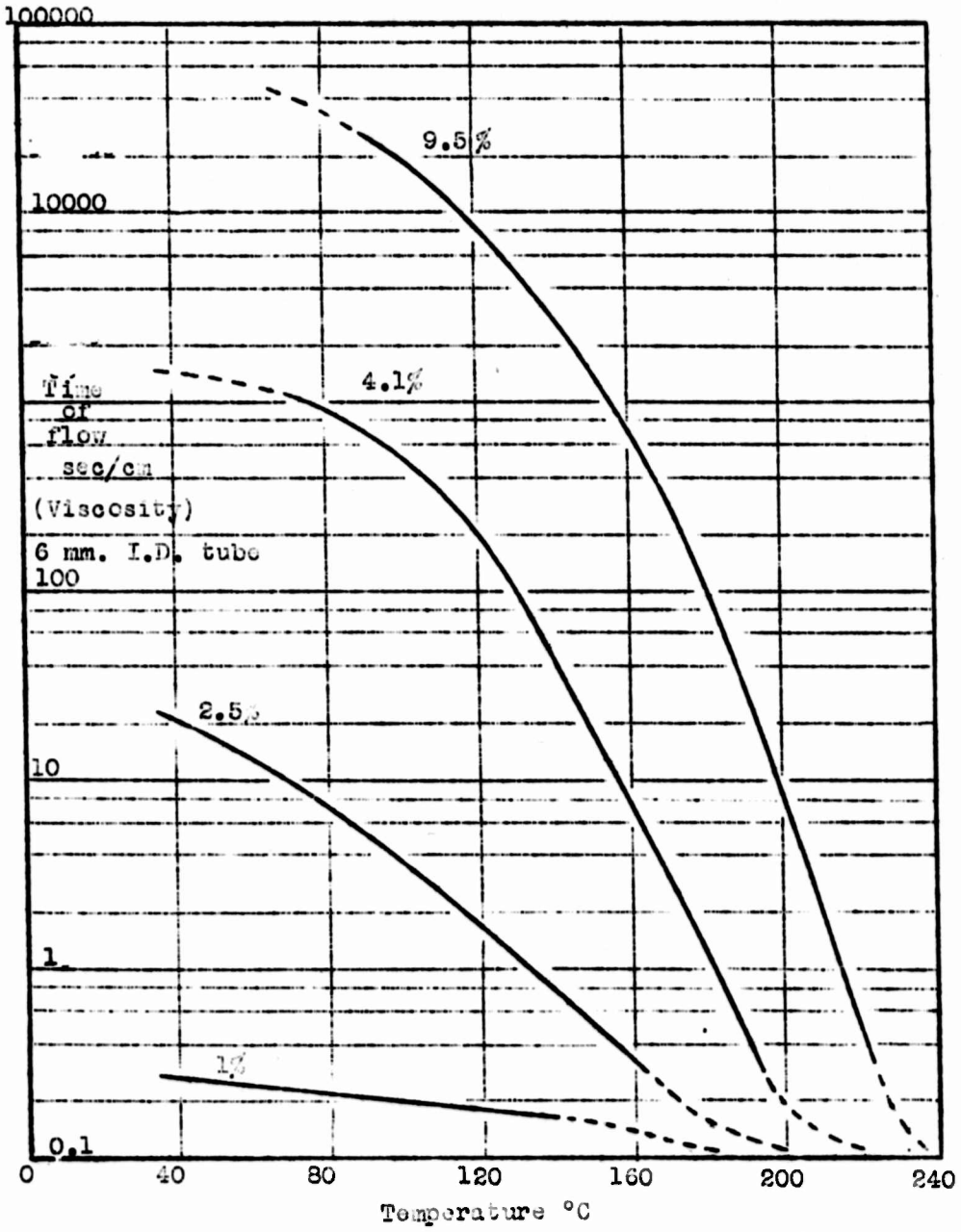
(a) Viscosity measurements in sealed tubes. In order to measure the viscosity of a system whose composition remained invariable over long times and wide ranges of temperature, we timed the rise, between two fixed points, of the vapor bubble in a sealed tube upon inversion. This method gave results of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

As expected, the viscosity is a function of the history of the system. The hysteresis effects are, however, of marked interest in themselves. The results are still exploratory and not completely definitive.

(i) Effect of temperature and concentration. Out of a rather large number of observations, which gave often widely varying results, it appears at present that the

Figure 45

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



effect of temperature may be represented approximately by the curves of Figure 45 . All systems at sufficiently high temperatures are typical sols and their viscosity is little more than that of the 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.

(iii) Hysteresis effects and kinetics of Sol to jelly transition. Two types of hysteresis were observed:- (1) thixotropy; that is, reduction of viscosity by prior flowing especially by rapid flowing, and (2) 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.

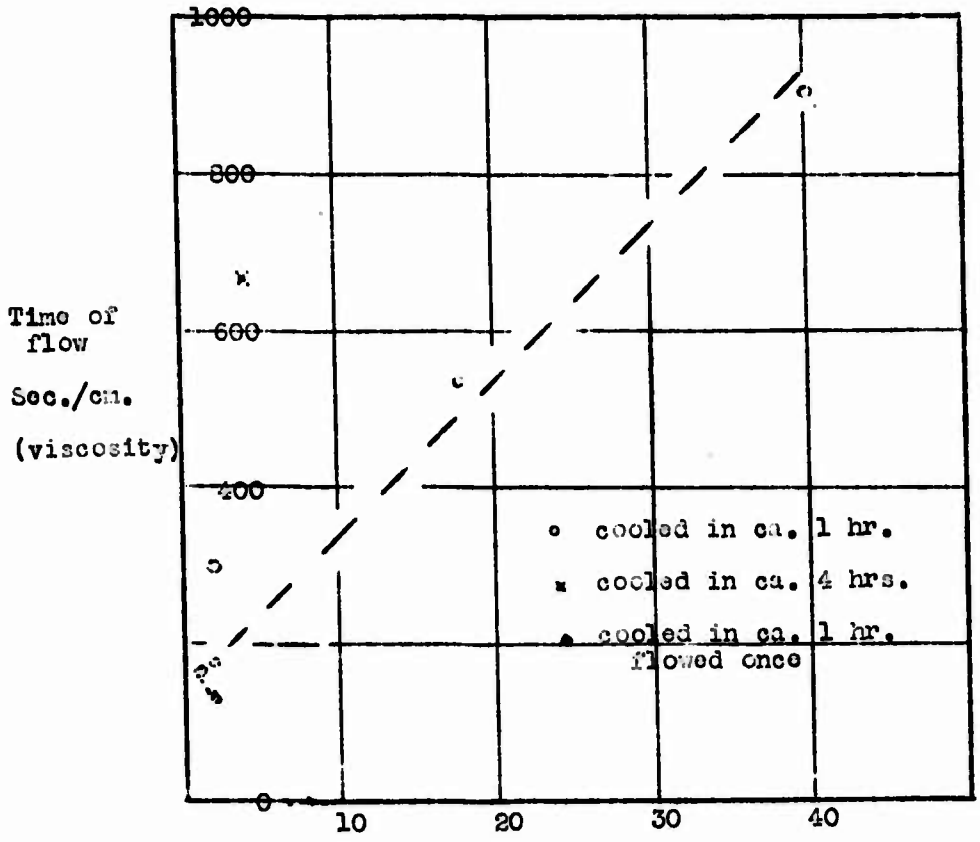
Thermotropy. It was observed that the viscosity is lowered by heating and recooling to the original temperature. Thereupon the viscosity slowly increases again. This rate of recovery seems to depend upon the temperatures at which it is occurring. The initial viscosity after cooling therefore depends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

Preliminary experiments (Yearly p. 121) shown in Figure 46 suggested that the structure of jelly causing

Figure 46

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 under exclusion of secondary hysteresis effects.



Time, in hours, since heating to 200°C.

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.

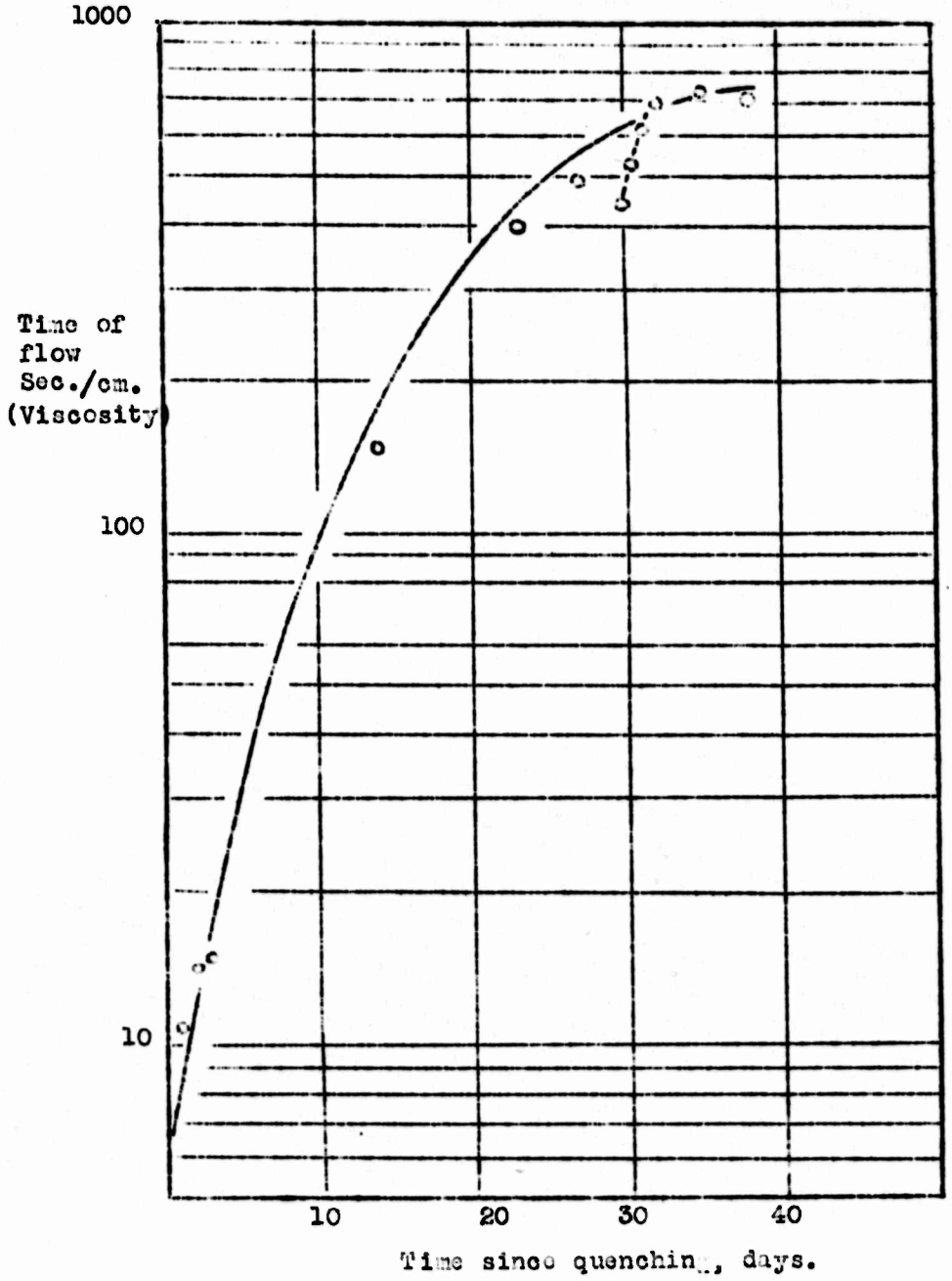
To test this hypothesis the tube was again heated above 200°C and then quenched by dropping it into cold water. This caused of course obvious inhomogeneity, but by the next day, this 4.1% $Al(OH)L_2$ in cyclohexane mixture became homogeneous; it was a slightly viscous liquid having a flow time of about 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 20 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 47 , suggesting that the structure being built up is proportional not to the viscosity but to its logarithm. The smooth line drawn is calculated on the hypothesis of a first order process and a first value of 1000 cm/secs.

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 47 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

Figure 47

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



the thermotropic effect, suggesting that the two may affect different elements of the structure.

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

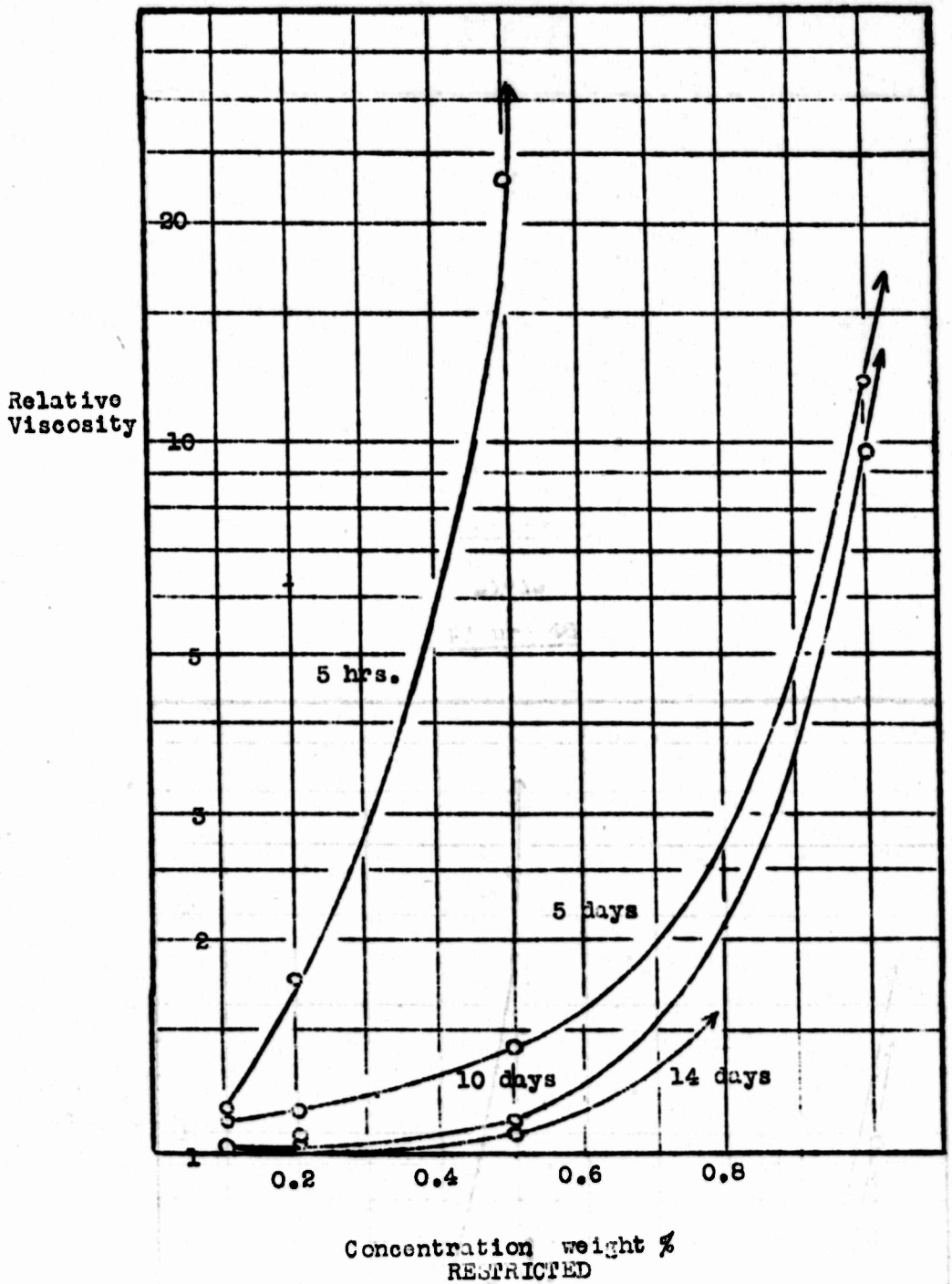
(b) Viscosity measurements in Ostwald viscosimeters. For more precise measurements over a limited range of time and temperature, the Ostwald viscometer is convenient (Yearly 126).

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 the solution to that of the 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.

(i) Time effect. The transition from jelly to sol. The viscosity of all freshly prepared solutions in benzene decreased with time as shown in Figure 48 . 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 solution is stored in the viscometer and frequently measured or stored undisturbed in a glass stoppered bottle. Heating seems to accelerate the ageing process. The comparative results were obtained over short periods of time during which this ageing effect is negligible.

Figure 48


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

(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 48 .

(iii) Effect of temperature. The remarkable effects of heating and cooling solutions of aluminum dilaurate are shown in graphs in Figure 49 . 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 ageing 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 decreased only slowly. This suggests that this more concentrated solution may have a different organization

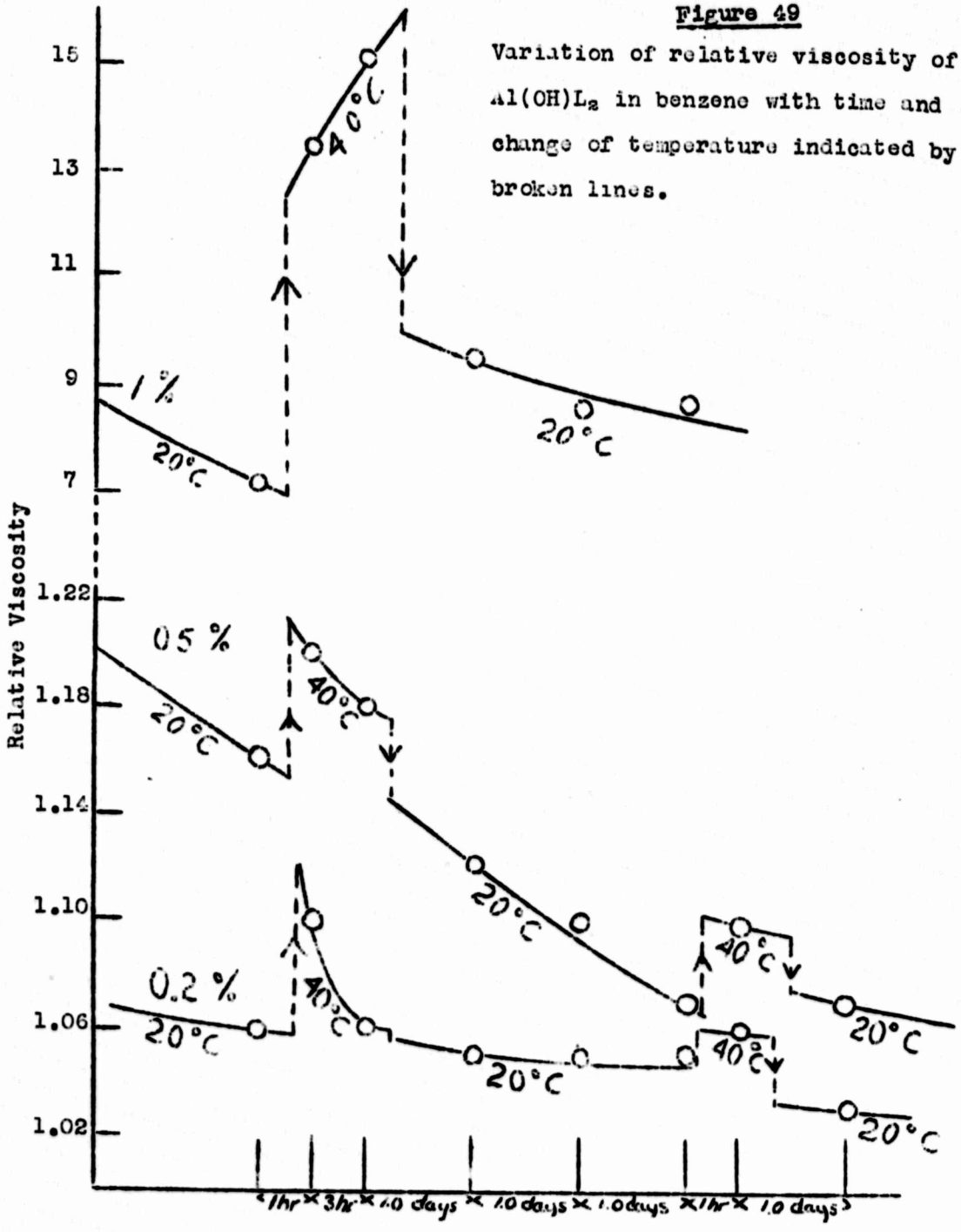


Figure 49

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

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, $Al(OH)_3$ 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 dioxone to pure benzene.

1% solutions of aluminum dilaurate in benzene are liquid at all temperatures; the osmotic pressure changes from less than 1 mm. at 18°C to 75 mm. at 25°C, and 190 mm. at 40°C. Hence the average degree of association changes from about 6000 molecules at 18°C to about 30 to 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 0.01 N 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.

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

Osmotic pressure of $Al(OH)L_2$ in benzene. The osmotic pressure divided by concentration decreases very rapidly with concentration at room temperature being $(Al(OH)L_2)_{30}$ for 0.1% and $(Al(OH)L_2)_{4000}$ for 1%; although at 50°C it remains constant at $(Al(OH)L_2)_{30}$ over a wide range falling towards $(Al(OH)L_2)_6$ at 0%.

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.

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 0.01 N 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.

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

Osmotic pressure of $Al(OH)L_2$ in benzene. The osmotic pressure divided by concentration decreases very rapidly with concentration at room temperature being $(Al(OH)L_2)_{30}$ for 0.1% and $(Al(OH)L_2)_{4000}$ for 1%; although at 50°C it remains constant at $(Al(OH)L_2)_{30}$ over a wide range falling towards $(Al(OH)L_2)_6$ at 0%.

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 L from $(Al(OH)L_2)_{400}$ to $(Al(OH)L_2)_{30}$ with rise of temperature, the specific viscosity of L 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 J.W.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.

3. Thermodynamic Stability.

The question of the thermodynamic stability of the various forms and states of a system is of fundamental importance, since spontaneous changes within it always proceed 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 conditions 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 utlimate products 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 are described in the preceding section is the simplest method

of obtaining the relative stability of the initial and final state. We can thus summarize these observations as follows:

A. Pure Soap Systems.

(a) 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 temperature of transition to jelly.

(b) 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 (1) the jelly often reverts spontaneously to gel at lower temperatures and (2) 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 without becoming a jelly.

(c) 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.

(d) 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 $Al(OH)L_3$ 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% $Al(OH)L_3$ 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 more stable than either gel or 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 jelly.

B. Fuel Thickeners in Hydrocarbons.

The above statements referring to pure soap systems are probably true also for Napalm and thickened fuels, and may be applied to several aspects of the problem.

(a) Ultimate time limits of storage. From a practical point of view it appears that in Napalm and related aluminum soap systems only the jelly form has the desirable properties of stringiness and plasticity while the gel is too crumbly and the sol too fluid to make an acceptable thickened fuel.

The proof of the thermodynamic stability of jelly shows

that it is not a priori impossible to prepare thickened fuels having and indefinite storage stability over a limited range of temperatures.

(b) Temperature of dispersion. It is well known that Napalm requires an increasingly long time to disperse as the temperature is lowered, and at a sufficient low temperature the soap only swells and no dispersion occurs even after long periods. We have found that at least some Napalms show this behavior in isooctane at room temperature. It is very probable that below a certain temperature in any given solvent and concentration the two-phase gel-sol system is the stable one and no length of time will cause the formation of a homogeneous jelly unless the system is changed, as for example by the addition of a "low temperature peptizer".

(c) Low temperature stability. Although a Napalm jelly may not be thermodynamically stable below the temperature at which it cannot be formed spontaneously, from a practical point of view once it is formed, it may be stable enough due to the extreme slowness of reversion. This seems to be the general case although under extreme conditions syneresis has been reported for Napalm.

Aluminum stearate fuels seem to be more susceptible to reversion and this has been reported for various mixtures as structural instability with separation and opacity of the fuel. It is probable that those aluminum stearate fuels which do not show any indication of such structural instability are definitely stable at the storage temperature and that their preparation at a higher temperature is necessitated mainly by consideration of rate rather than of equili[illegible]

(d) Ageing or maturing. The drop in viscosity upon storage for prolonged periods of time has been often studied and called "ageing" or "maturing". Its occurrence suggests that the mixture is in the form of an unstable jelly tending towards a sol. The frequent occurrence of this effect suggests that the jelly to sol change, while slow, is not subject to requirements such as prevent in general reversion of Napalm jellies to gels (a process involving at least practical crystallization).

This suggests further that in order to form a mixture of stable viscosity one must try to reach the final state of liquefaction during the preparation because there is little likelihood of preventing a slow evolution towards an equilibrium state.

The situation with respect to the two opposite trends toward reversion to gel, reversion and liquefaction may be analogous to supercooling and superheating of a liquid. The former may lead to a permanent metastable state while the latter may not.

4. 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 "crystallized" one, a large two phase zone between gel and sol forms is present below about 40°C and the gel-jelly transition temperature rises to about 50°C as indicated in Figure 50 . The exact position of these 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 Figure 51.

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 (Figure 52

For other aluminum soaps and for other solvents it appears that the phase diagram retains its overall character

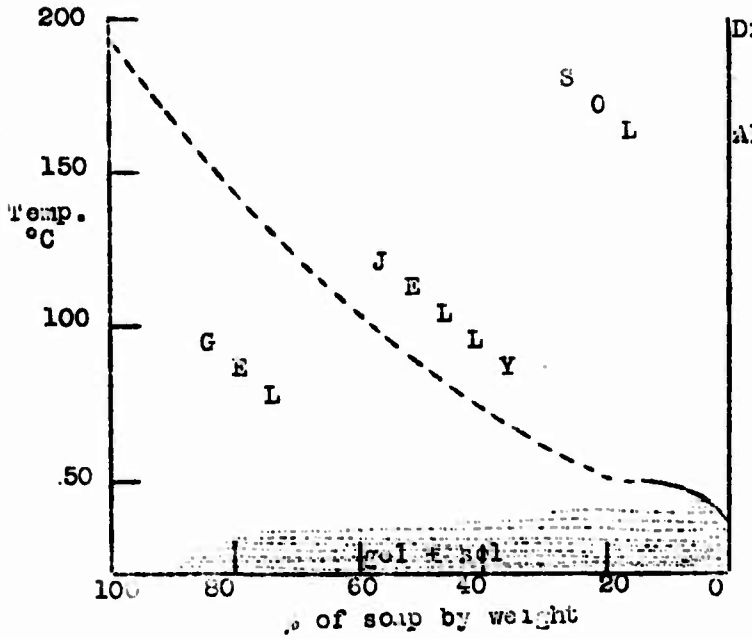


Figure 50
Outline of Phase Diagram of the System "Crystallized" Al(OH)L_2-Cyclohexane

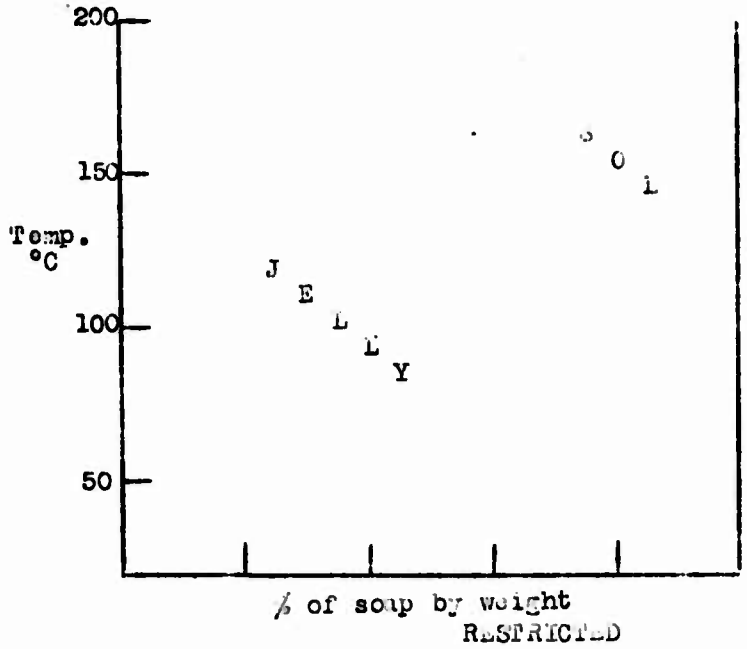


Figure 51
Outline of Phase Diagram of the System "Recovered from Jelly" Al(OH)L_2-Cyclohexane

Outline of the phase diagram of the $Al(OH)L_2$-cyclohexane and $Al(OH)L_2$ - isooctane systems.

Figure 52

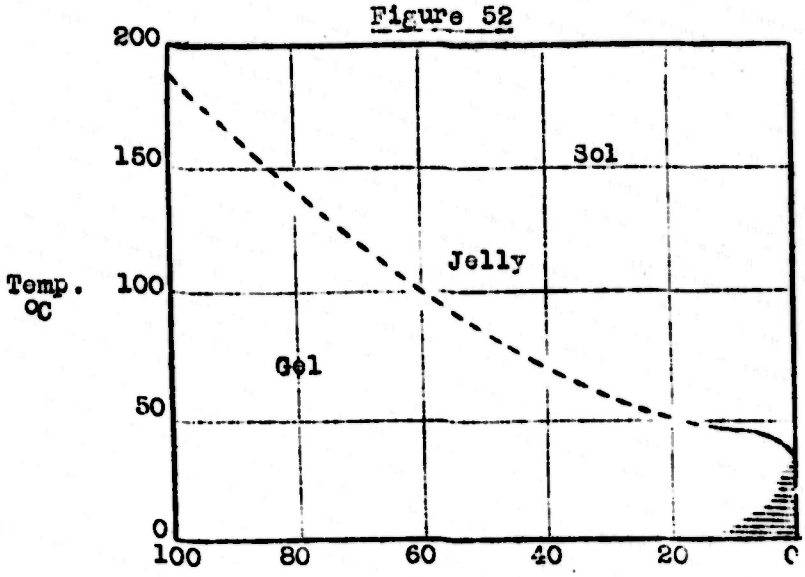
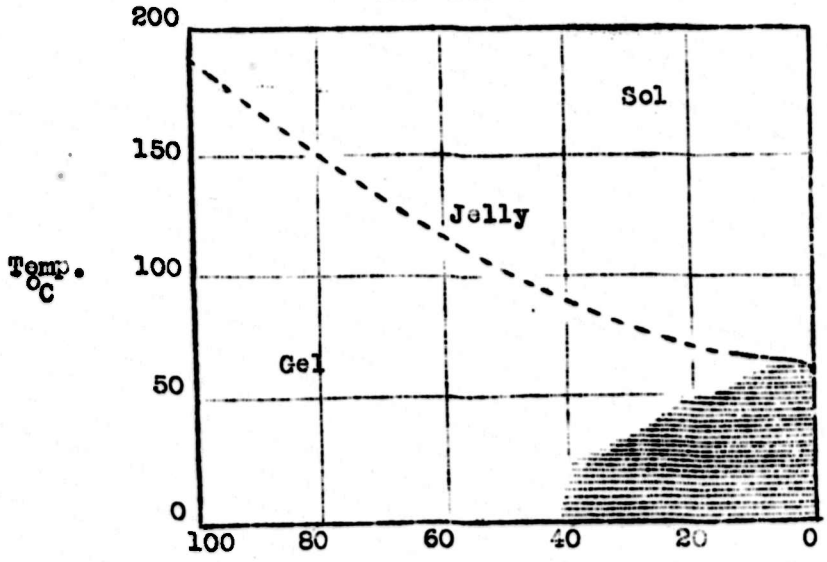


Figure 53



and the variations are similar to those produced by the nature of the soap, but more marked.

Thus with isooctane and "original" dilaurate the transition temperature is some 25°C higher than in cyclohexane and the two phase region at room temperature is greatly extended (Figure 53).

5. Forces Operative When 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. There is not enough information available yet to decide all details of this picture, but a few remarks may be made.

a. The Two Types of Thickening.

There seem to be two radically different mechanisms of thickening of hydrocarbons by aluminum soaps whether pure or of the Napalm type.

One is homogeneous dispersion and thickening to form a stringy, elastic jelly which may appear as a rigid elastic jelly in more concentrated systems. The other thickening action is by the physical contact of swelled lumps of gel which may or may not have reached their limit of swelling.

The second type of thickening action is exemplified by our observations of Nuodex Napalm in cyclohexane at room temperature which seems to exhibit a limited swelling to a gel form which then is essentially in indifferent equilibrium with any supernatant solvent or sol. If the system is concentrated enough to allow physical contact of the swelled lumps at or below the swelling limit of the soap, then the system will be effectively thickened.

Dilute Oronite on the other hand appears to be the most satisfactory soap to demonstrate the thickening action obtained by a homogeneous soap-solvent jelly system. It seems almost incredible that only 0.1% Oronite was enough to form a homogeneous, stringy, elastic jelly with all the cyclohexane.

It appears probable that in either case 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.

However in the gel type of thickening only (or mainly) pre-existing bonds between relatively large and crystallized primary particles and mechanical contact of large lumps is effective while in the jelly type of thickening new easily formed and reformed bonds are effective between smaller and less crystalline primary particles. The latter is essentially the same mechanism which operates to form jellies of sodium oleate in water.

(a) 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 $CaOL_2$ grease above and below the melting point of the soap (83-84°C). His results are reproduced in Figure 54, 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 $Al(OH)L_2$-cyclohexane mixtures was measured in the neighborhood of 196°C, which is the melting point of the pure soap. The results shown in Figure 55 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

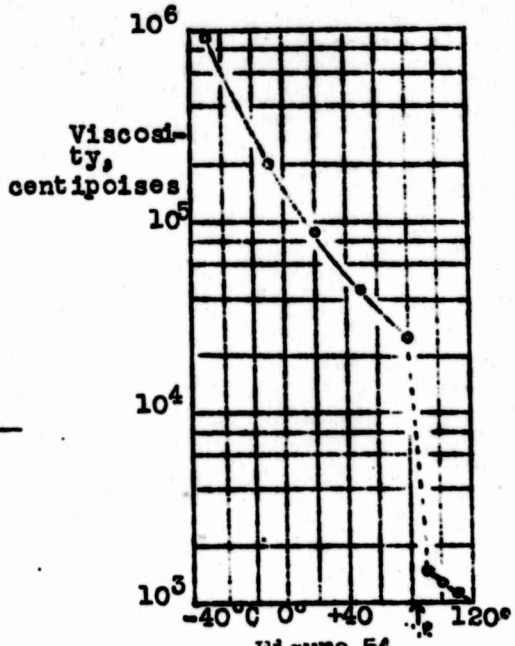


Figure 54

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

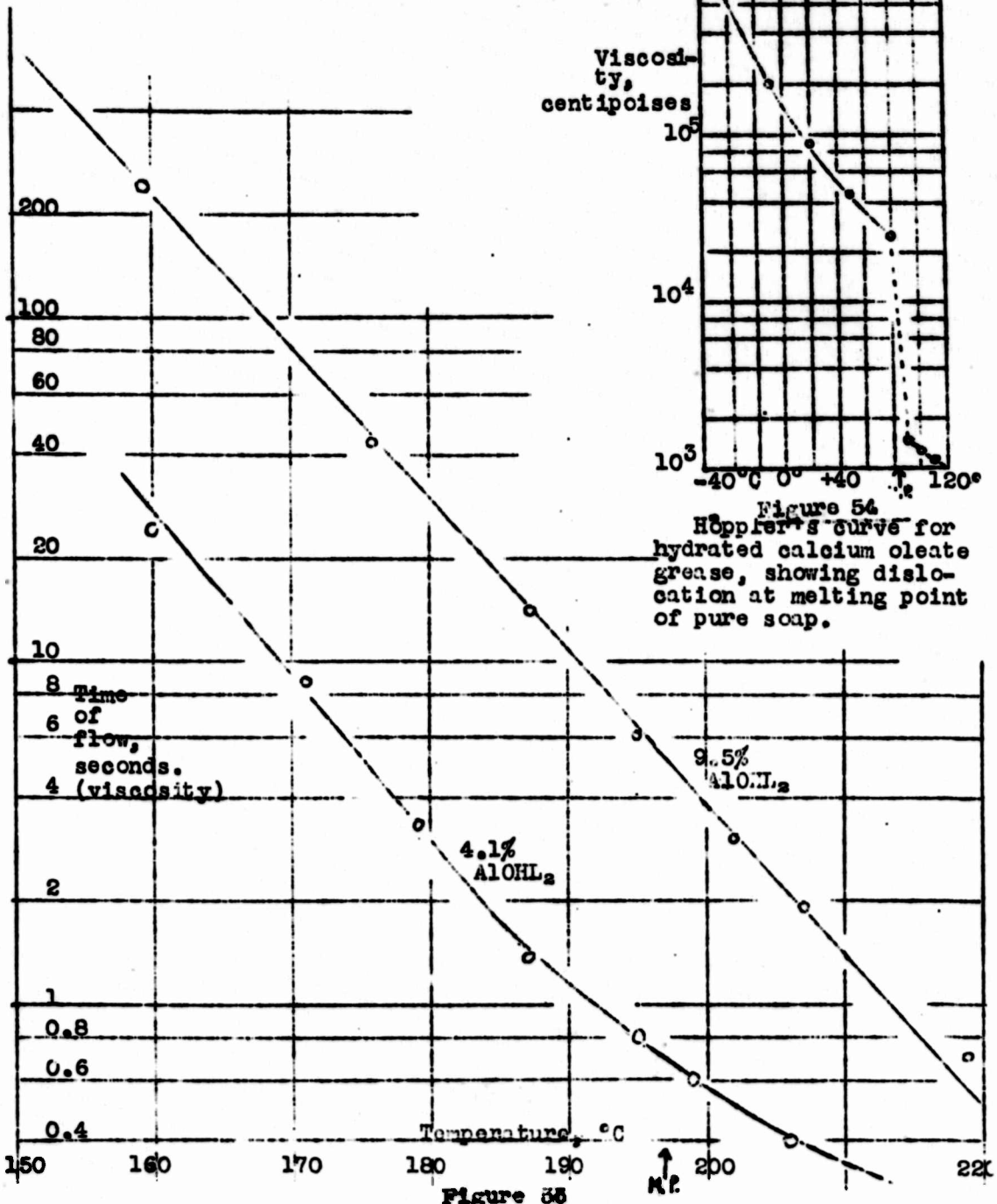


Figure 55

Viscosity of aluminum dilaurate-cyclohexane systemsas function of temperature, showing no discontinuity at melting point of soap.

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.

(b) In water association of alkali soap molecules is due to the great affinity of water molecules for each other 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.

(c) 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 the sodium stearate hydrocarbon system has been mentioned in our September 1943 report and has since been confirmed and expanded in this laboratory outside this contract, and reported on pages 149-152 of our Yearly Report and pages 61 - 64 of our October 1944 Report.

CHAPTER V

ADDITIVES WITH ALUMINUM SOAPS IN HYDROCARBONS

In this chapter are collected data on the effect of known additives on systems such as were examined in the preceeding chapter. It may be noted that any system containing gasoline or Napalm contains much more than only soap and hydrocarbons, but these other substances were usually not considered because the nature is largely unknown.

In this chapter we consider first some observations on systems comprising pure soaps and the evidence for double decomposition of soaps with acids, then the various additives to Napalm gasoline jellies, and finally experiments with aluminum cresylate.

1. The Behavior of Pure Aluminum Soaps Alone, Mixed, and With Added Fatty Acids.

A. Qualitative Tests.

A large number of qualitative tests has been performed on small amounts of several aluminum soaps in a large excess of isooctane, ASTM precipitation naphtha, and di-ethyl ether to determine the effect of solvent, of other soaps, and of various added acids on the behavior of the soap. Unextracted and acetone-extracted samples of aluminum laurate, stearate, oleate, and naphthenate were examined. The composition of the extracted samples corresponded substantially to di-soaps, while the unextracted originals contained three-quarters of an equivalent of fatty acid above that corresponding to di-soap.

The results of the many experiments which are tabulated in the January 1945 Report and discussed in the December and January Reports, lead to the following conclusions:-

(a) Effect of solvent. In all cases ether was the poorest solvent, isooctane was next, and the ASTM precipitation naphtha dispersed best. In most experiments isooctane was used.

(b) Effect of the physical state of the solid soap. It has been pointed out in previous reports that the solubility and other physical properties of a soap depend on its physical state and can be changed by treatment or method of preparation. This became evident once again in these studies. A stearate prepared at 25°C from an aged potassium soap

solution (having a high ash after extraction) was inert or slightly swollen under conditions which swelled a stearate prepared from a fresh potassium stearate solution (having a low ash after extraction). Furthermore an unextracted laurate prepared at 25°C was much more readily swollen than one prepared at 80°C. In fact the more reactive stearate was more easily dispersed than the less reactive laurate. In other words differences in physical state can overshadow differences in chemical composition.

(c) Effect of acid from which the soap is derived. In practically all cases under comparable conditions the naphthenate was most completely dispersed and the stearate least. The oleate is similar to the naphthenate and the laurate is similar to stearate.

(d) Effect of previous extraction of the soap. In all cases unextracted soaps of a given acid dispersed much more completely and much more easily than the extracted ones. This difference was marked, especially in the case of the oleate which dissolved completely and rapidly in case of the unextracted soap, and surprisingly enough swelled only moderately in case of the extracted soap (di-oleate).

(e) Action of unextracted soap or of acid. It appears that the fatty acids which are present in unextracted soap or are added later can interact with the soaps, tending to reach an equilibrium. In other words, stearate in the presence of oleic acid approaches the behavior of oleate in the presence of stearic acid. However, a complete equilibrium is not easily reached. In the unextracted soaps, where

the acid is in intimate contact with the soap, its effectiveness as a disperser is greatly increased. Thus while there seemed to be no interaction when extracted soaps of two acids were placed together in the solvent, and the particles of each behaved as if they were alone, there was a definite interaction between unextracted soaps, the more readily dispersible definitely aiding the swelling and dispersing of the other.

The presence of acid in the soap seems to favor dispersion of soap derived from it but it is quite certain that extracted soap in the presence of added acid does not disperse quite as much, and certainly not as rapidly as the original unextracted soap.

When extracted and unextracted soaps of the same acid were placed in the solvent together their behavior was at first independent, the unextracted soap swelling and dispersing more than the extracted one. After about two days, however, the particles belonging to the two soaps could not always be distinguished, and their behavior was intermediate between that of the extracted and unextracted soap of the same acid.

In mixtures of an acid with a soap from different acid, the dispersing or dissolving action of various acids differs markedly, naphthenic and oleic acid being most effective, while stearate acid is least.

(f) Effect of unsaponifiable from acetone extract of Napalm. This had no appreciable effect on the swelling and dispersion of the soaps.

B. Solubility of Aluminum Stearate in Isooctane.

Aluminum stearate is completely insoluble in isooctane at 30°C even in the presence of stearic acid.

During the preparation of distearate by extraction with isooctane in the batch extractor (Figure 108 October) it was found that an extract of 120 cc. of isooctane obtained at room temperature after a 10 hour contact with 5 grams of unextracted distearate contained 0.5 grams of stearic acid which had no ash content within experimental error (0.02%). Another extract obtained at 30°C under similar conditions contained 0.2 grams of stearic acid and also no detectable ash. In these experiments the solution tested was completely clear after filtration through fritted glass.

C. Additives in the System Aluminum Dilaurate-Cyclohexane.

A few systems were observed in sealed tubes. In most cases the systems became jellies or sols readily at room temperature.

Nitrobenzene proved to be much less effective as a liquefier than lauric acid and methyl alcohol more than octyl alcohol. These experiments are described in the October 1944 Report pages 21-23. This line of investigation has not been continued because Napalm gasoline systems seemed more adapted to a general survey as described below.

This work showed however that peptizers have essentially the same action on pure soap as on Napalm and cause a general lowering of temperature of all the phase boundaries of the phase diagram (p.186).

Comparison with sodium soaps. The question of whether or not the same "peptizers" would "peptize" both aluminum and sodium soaps was asked of us, and the following systems were accordingly prepared. To anhydrous systems containing 3% by weight of sodium stearate in cyclohexane were added 10% nitrobenzene, 2.5% lauric acid and 2.5 methanol, respectively.

The system with nitrobenzene showed no appreciable swelling of the sediment of the soap over a period of several weeks. However, the nitrobenzene was sorbed from the cyclohexane, the soap layer becoming a bright canary yellow. The system containing lauric acid changed considerably. The soap

swelled about 8-fold and though still white and opaque, it dispersed in discreet particles which float in the clear liquid. Methanol produced a profound change in the soap. It swelled about 15-fold, and half of that swelling occurred in the first 30 minutes. The soap was originally a fine powder but formed swollen granules and loose aggregates. The granules were surrounded by a film of clear jelly, and the rest of the solvent was a clear sol.

Sodium stearate was put into cyclohexane containing 1% lauric acid. It was found that the sol above the soap contained only about 0.25% lauric acid.

Thus these additives which "peptize" aluminum soaps have also a definite action upon sodium soaps in hydrocarbons. While the difference is marked between the effect on the two soaps it promotes dispersion and swelling in both.

2. Metathesis (Double Decomposition) of Aluminum Soaps with Other Acids in Hydrocarbons.

The results of the preceding and following sections suggested strongly that aluminum soaps react with acids in hydrocarbons. To establish this the following experiments were performed, using pure aluminum laurate and benzoic acid.

As mentioned in previous reports, aluminum dilaurate, especially in the presence of lauric acid, gives a clear solution in benzene. Benzoic acid alone also gives a clear solution. When these two solutions are poured together a white, extremely light precipitate appears within a few seconds, and in dilute solutions settles out slowly.

In one experiment such a precipitate from an equivalent mixture (2 mols of acid to 1 mol of soap) was separated, washed and the acid split therefrom. It had an acid number

of 442 corresponding to a mixture of about 90% benzoic + 10% lauric acids. It melted between 100 and 120°C. The filtrate was evaporated and ashed but no ash was detectable. This shows that all the aluminum was precipitated and the precipitate consisted mainly of aluminum benzoate.

In another experiment 3.11 grams of unextracted aluminum laurate were placed in 100 cc. of a solution containing 4.35 g. of benzoic acid. After standing overnight at room temperature a white bulky precipitate and a clear supernatant liquid were present. The precipitate was separated by filtration, washed repeatedly with benzene and dried. The dried soap had an ash content of 17.7% and the acid split therefrom had an acid number of 426 mg. KOH per gram. This corresponds to a mixture of 20% lauric acid with 80% of benzoic acid in the reaction product and the ash indicates that the soap is somewhat on the mono side of a di-benzolaurate. The theoretical ash value for a di-soap, based on an acid number of 426, is 16.63. The filtrate was evaporated yielding 5.5 g. of free acid whose ash content was less than 0.1%.

In view of the technique used it is possible that some laurate particles remained occluded in the precipitate and could not react with the benzoic acid and that some hydrolysis occurred during the various operations. There is no doubt, however, that in this experiment also the bulk of the lauric acid originally combined with aluminum has been replaced by benzoic acid.

3. Additives to Napalm.

A. The Various Effects.

It is desirable to be able to modify the properties of Napalms in order to adapt them to special conditions or uses. Thus for bomb fillings it is desirable to have a long setting time during which Napalm-gasoline mixtures may be poured into the bombs and finally became a strong jelly resisting excessive shattering. For flame thrower fuel it is desirable in general to have a short stir time to facilitate field mixing and a soft stringy jelly for best flame effect. Under conditions of high temperature it may be necessary however to slow down the setting time in order to make field mixing possible.

The pressure loss in conduits, and flight characteristics of a flame thrower fuel depend to a large extent on the

variation of viscosity with rate of shear and modifications of this variation may be desirable for best results.

Thus at least two different properties of Napalms have to be controlled, the rate at which a jelly is formed, and the viscosity of this jelly. "Peptizers" have been frequently used to modify both these properties. They seem in general to accelerate the formation of jelly and liquefy it at the same time. Otherwise inert dehydrating agents such as silica gel added to the soap stiffen the jelly markedly, presumably by removing water which is a liquefier.

We found that substances added to Napalm gasoline jellies produce a number of <u>independent</u> effects upon flow properties, which are differently combined in different additives. An additive may be a liquefier or stiffener, and simultaneously either an accelerator or retarder of gelation. In addition to these four groups of properties we find a further independent alternative; an additive may either decrease or increase ("dilatancy") apparent viscosity with increase in rate of shear. Mixtures of additives may have intermediate effects combining those of the separate additives.

It therefore appears possible to modify independently as desired:- liquefaction or stiffening, acceleration or retardation of stir time and set time, increase the variation of viscosity with shear or produce more nearly Newtonian behavior or dilatancy.

Other properties of the jellies may also show independent variations with various additives.

B. Nomenclature.

(a) Peptizer. 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 Mack'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 liquefaction 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.

In connection with Napalm it is preferable to avoid the loose use of the word peptizer for all additives since these may be stiffeners or liquefiers, retarders or accelerators. Retarders have not been known previously. All four properties of additives might be useful and it may be desirable to control them independently. They may depend further upon temperature and concentration of the additive.

(b) Polar dompounds. "Peptizing" agents are frequently referred to as "polar compounds". This term has at least 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 dinitro benzenes, 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. We compared their efficiency as liquefiers (Yearly 141-144), and found that there is little to choose between the most polar and the least polar in their reduction of the viscosity of Napalm jelly although they are both effective. After five days the times of flow under gravity were:

ortho	1
para	1.1
meta	3.0
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 polar and that various carboxylic acids all having the same COOH group can have widely different and even opposite effects.

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

C. Experimentsl.

The technique employed is described in our November (p. 35-36) and December (p. 22). It consisted essentially in preparing comparative series of Napalm jellies of exactly the same weight by volume concentration of 4.00% and observing their viscosity by the dropping ball method as well as other properties. The results are tabulated in Tables XXVI to XXX of the December Report and in our January 1945 Report. The additives were in general used in equivalent amounts at two levels of concentration. Many of them are shown in the following graphs, one equivalent to 0.5%, the other to 2.5% lauric acid in the solvent.

D. Results of the survey.

(a) Effects on viscosity and formation of jelly.

(i) Liquefiers and accelerators. The best example of this group are the lower alcohols, the xylenols; but it is illustrated also by the fatty acids between 6 and 16 carbon atoms.

(ii) Liquefiers and retarders. The typical examples are the C_2 - C_4 fatty acids; also Staybellite rosin; and to a lesser extent dilute K and N rosins ; and dilute cyclohexane carboxylic acid.

(iii) Stiffeners and retarders. Benzoic acid is the best example, also concentrated cyclohexane carboxylic acid.

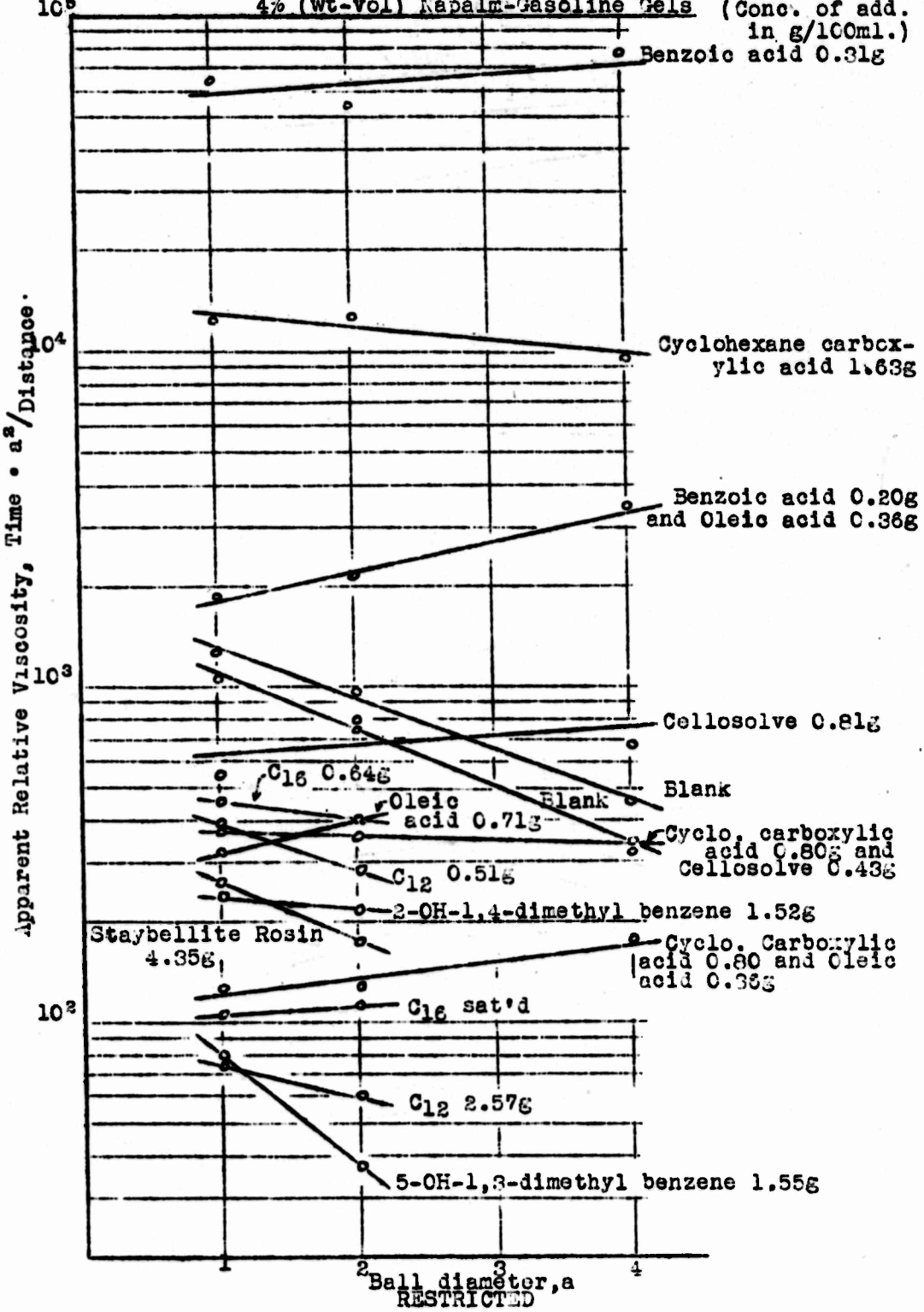
(iv) Stiffeners and accelerators. This behavior seems to be rare but it is shown by higher concentrations of N and K wood rosins.

(v) Variation of apparent viscosity with shear (Effect of ball diameter). As already mentioned the apparent viscosity of these gels depended on the diameter of the ball used for measurement, and this dependence differed for various additives.

In other words, on a graph of viscosity vs. shearing force, additives may not only change the position of the line parallel to the blank but may also change its slope in either direction. This may occasionally lead to an intersection of the two lines in the experimental region so that an additive may appear as both a stiffener and softener depending on the

Figure 56

Characteristic Plasticity Effects Of Various Additives On 4% (wt-vol) Napalm-Gasoline Gels (Conc. of add. in g/100ml.)



conditions of flow. Ethyl cellosolve shows this effect in some of the experiments in Figure 56 .

Only in a limited number of gels was it possible to use balls of three sizes for measurements as the rate of fall increased with the square of the diameter in Newtonian liquids and much faster in most jellies. Figure 56 shows a few characteristic graphs of this effect for various classes of additives.

The frequent crossing of the lines shows that softening properties of an additive are independent of the effect upon the slope of the variation of apparent viscosity with shear. Oleic, benzoic, and cyclohexane carboxylic acids and cellosolve tend to slope the line upwards (dilatancy), while the more active cresols and Staybellite rosins have the opposite effect.

(b) Effect of the various additives.

(i) The fatty acids. C_6 and above are accelerators and softeners. There is little difference in the accelerating action, but the softening effect decreases with increasing molecular weight. Below C_5 they may prevent setting completely at higher concentration.

Oleic acid is an accelerator and a pronounced softener and renders the jelly dilatant.

(ii) Naphthenic acids are accelerators and softeners. Added in higher concentration they seem to stabilize the gel.

(iii) Cyclohexane carboxylic acid is a retarder. At low concentrations it has a slight softening action

Figure 57

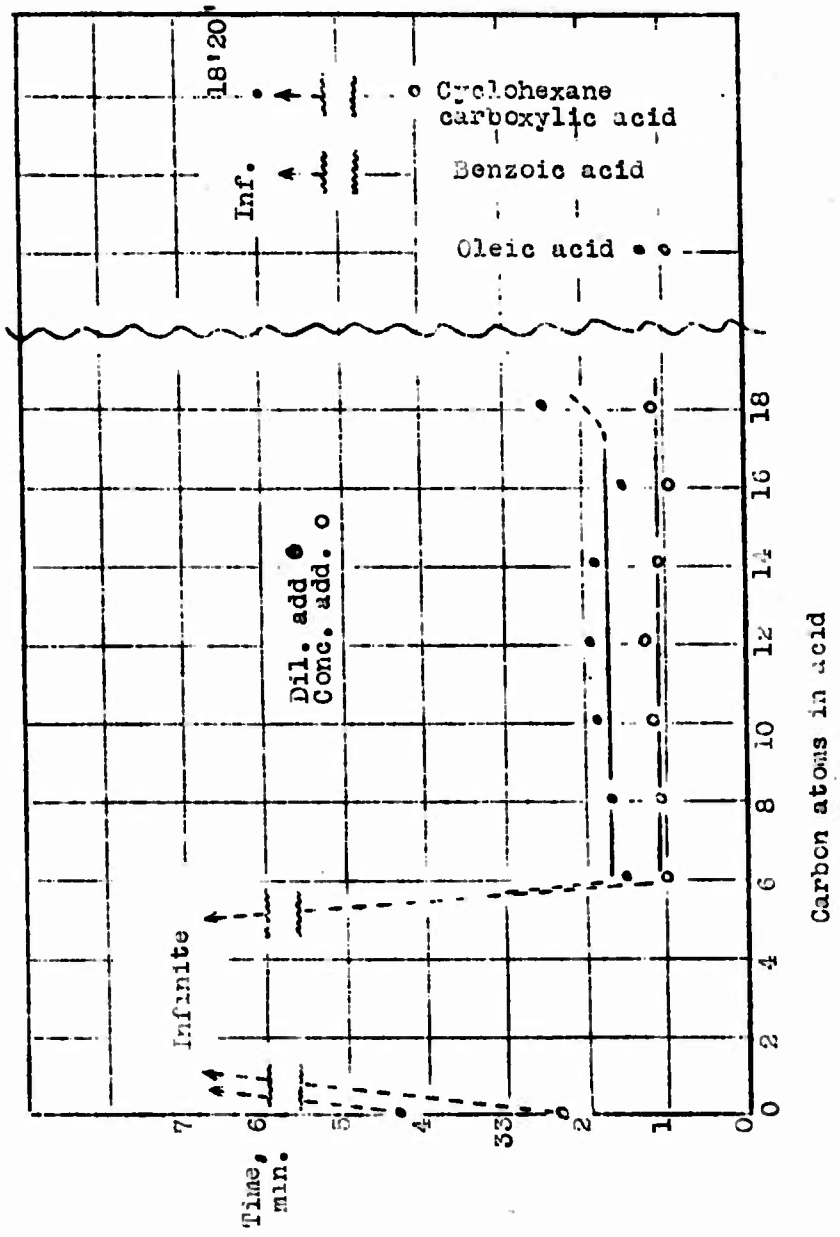
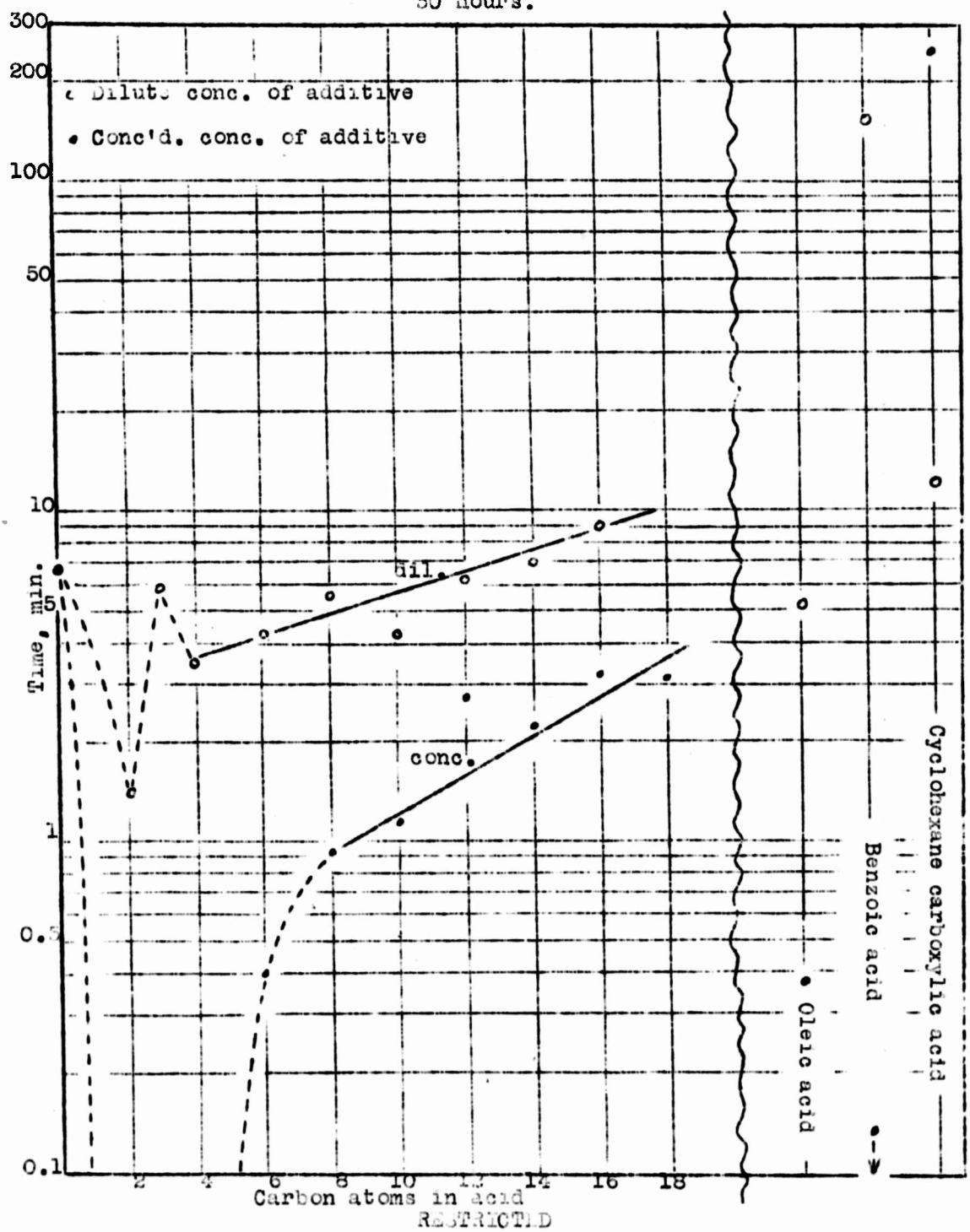

Set and stir times of Perro Napalm-gasoline gels with organic acids as additives
(conc. of acids are equimolar to 2.5%, wt-vol, of lauric acid)
Time, min.
Infinite
18'20"
Inf.
Dil. add ●
Conc. add. ○
Cyclohexane carboxylic acid
Benzoic acid
Oleic acid
Carbon atoms in acid
0
2
4
6
8
10
12
14
16
18
1
2
3
4
5
6
7

Figure 58

Falling ball viscosities of 4% Napalm-gasoline gels, containing organic acids at two levels of concentration, after aging for 50 hours.



but is a marked stiffener at higher concentration. With this stiffener we have not noted any separation or syneresis.

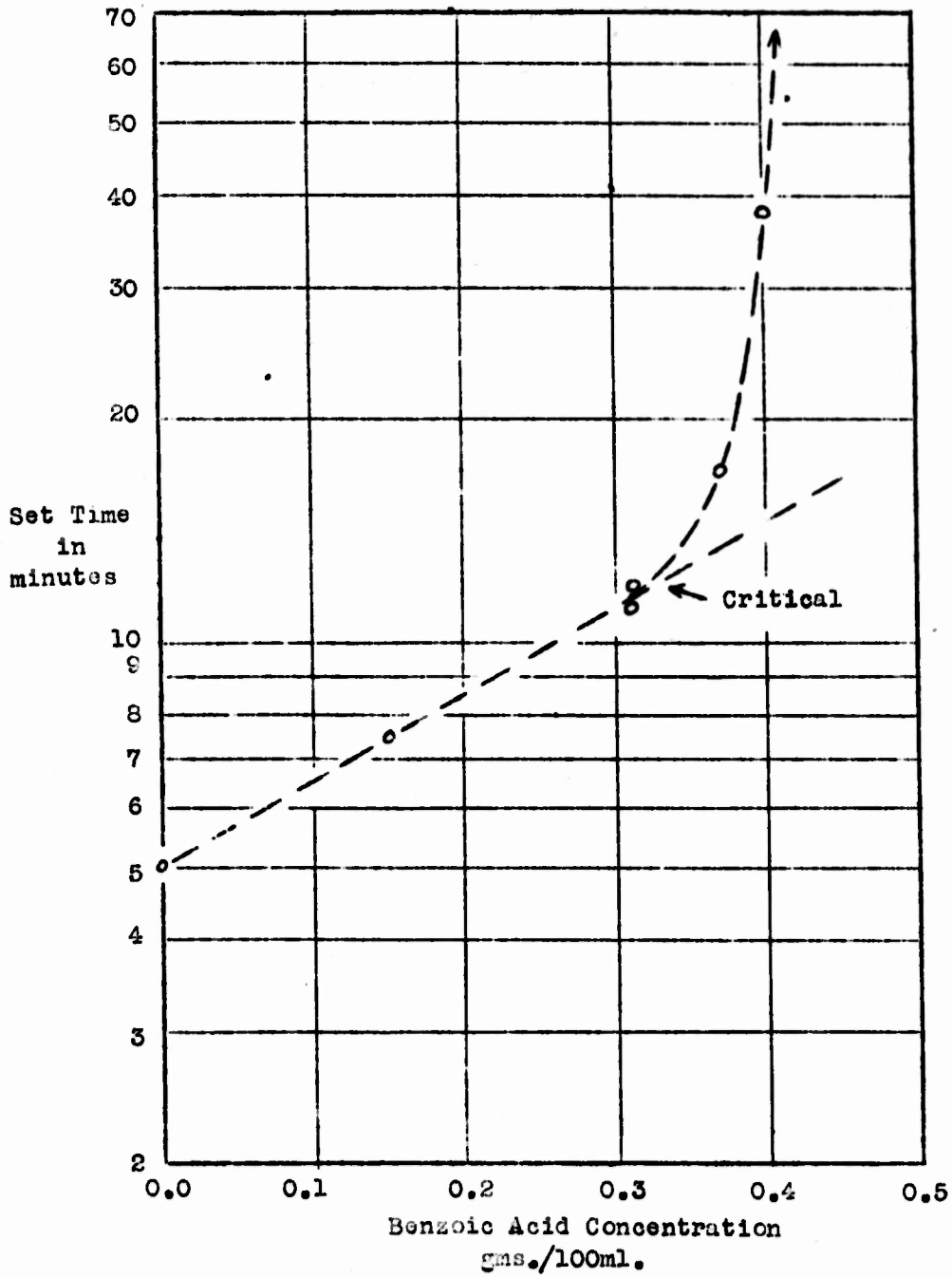
(iv) Benzoic acid: stiffening and breakdown by metathesis. Benzoic acid acts as a sitffener and retarder at low concentration, but completely prevents setting at high concentration. A further series of eight concentrations of this additive was prepared to study this effect. At concentrations below 0.33 g/100 ml. the jellies set, above 0.40 g/100 ml. they fail to set. The limitin. sample 0.40 g/100 ml. set within half an hour but after 20 hours was syneretic. In most of these samples it was observed that the swollen lumps of soap did not have the characteristic appearance of swellen Napalm, but a less lyophilic dense structure and that occasionally new particles which looked like plates of jelly appeared in the supernatant solvent. This led to the experiments on methathesis between aluminum laurate and benzoic acid described in the preceding section.

The set-time of these samples as a function of the concentration of benzoic acid is shown in Figure 59 . It will be noted that the samples which gave stable gels had set-times increasing exponentially with the concentration while the unstable ones set after a disproportionately long time.

(v) Specific effects of four pure isomeric Xylenols. A series of four isomeric xylenols showed that they were all accelerators and extremely effective softeners. However, they differed noticeably among themselves. Two regularities have been observed:-

Figure 59

The Effect of Benzoic Acid on the Set Time of Napalm-Gascline Gels.



(1) Closeness of a methyl group decreases the effectiveness of the hydroxyl group as a softener.

(2) The effect upon the decrease of viscosity with shear of a Napalm jelly varies greatly among the isomers, from a negligible one to the largest we have observed. This effect parallels the liquefying properties. The most effective is 4 - OH - 1,2 dimethyl benzene.

This is shown by the following Table VI , giving the structural formulae of the pure xylenols and the observed ball drop viscosities using 1/8" balls and the slope of the lines in Figure 60 .

The great effect of the best softeners upon the reduction of apparent viscosity with rate of shear may lead to a reversal of the softening power at sufficiently low rates of shear which was obtained in results of ball drop viscosities using 1/16" ball at low concentration.

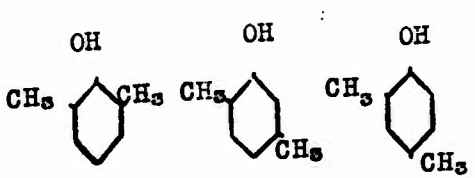
Figure 60 illustrates these observations.

(vi) Cellosolve is an accelerator that promotes dilatancy. The viscosity of the jellies containing ethyl cellosolve when measured with a small ball (1/16") appears to be smaller than the blank but the effect is reversed when a 1/8" ball is used.

(vii) Alcohols are effective accelerators as far as stir time is concerned but their softening action is so pronounced that the set time may be missed. The softening effect in our experiments decreases with increasing molecular weight even on an equivalent basis. Methyl alcohol softening

TABLE VI

Effect of Isomeric Xylenols on Viscosity and Plasticity

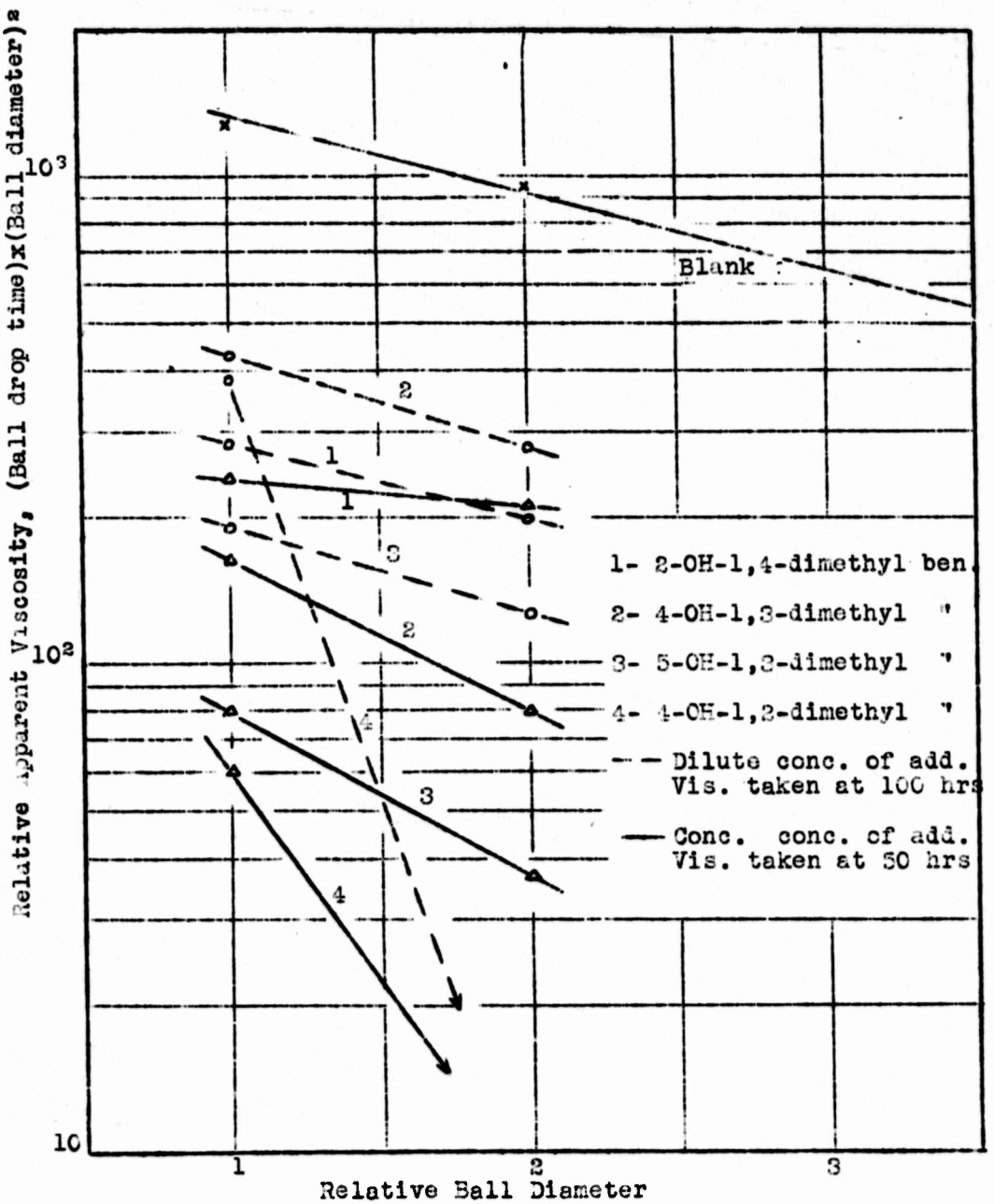
Isomeric dimethyl benzenes	2-OH-1,3 dimethyl benzene	2-OH-1,4 dimethyl benzene	4-OH-1,3 dimethyl benzene	3-OH-1,2 dimethyl benzene	5-OH-1,3 dimethyl benzene	4-OH-1,2 dimethyl benzene
Formulae in order of softening ability						
Slope of lines for concentrated systems (Fig. 144)	not tested	0.088	0.556	not tested	0.550	>1.300
Viscosity at 50 hrs. of Concentrated systems using 1/8" ball.	not tested	83	20	not tested	80	<10

NOT FOR PUBLICATION

RESTRICTED

Figure 60

Effect of Pure Xylenols On 4% Napalm-Gasoline Gels, At 22-26°C.



more effectively than equimolecular amounts of ethyl alcohol and these in turn more than octyl alcohol.

(viii) Rosins are accelerators and the stiffening effect of K- and N-wood rosin has been noted above. Hydrogenated "Staybellite" rosin acts as a softener.

(c) Other effects.

(i) Properties of mixtures of additives. A few experiments have been made with mixtures of two additives. In general it seems that the accelerating effect of one easily overcomes the retarding effect of the other. Effects upon variation of viscosity with shear seem to be intermediate. The softening properties vary irregularly but softening action seems to predominate.

(ii) Effects of concentration. Most of our experiments were made at two levels of concentration, one equivalent to 0.5% of lauric acid and the other to 2.5% of this acid. Figure 61 shows a few characteristic lines for the variation of viscosity(by the falling ball method) of Napalm gasoline jellies containing various additives as a function of concentration. It may be noted that in general the softening effect increased with concentration although the increase was in general far less than proportional to the amount of additive, but the stiffening effect, it seems, is often reversed at lower concentration.

(iii) Stringiness. The main conclusion as to stringiness is apparent from Figure 62 which is a plot of observed values vs. viscosity. In general stringiness increased as viscosity dropped and the stiff gels always were short.

Figure 61
Variation of Apparent Viscosity with Respect to the Concentration of Some Fatty Acids in 4% (wt.-vol.) Napalm-Gasoline Gels.

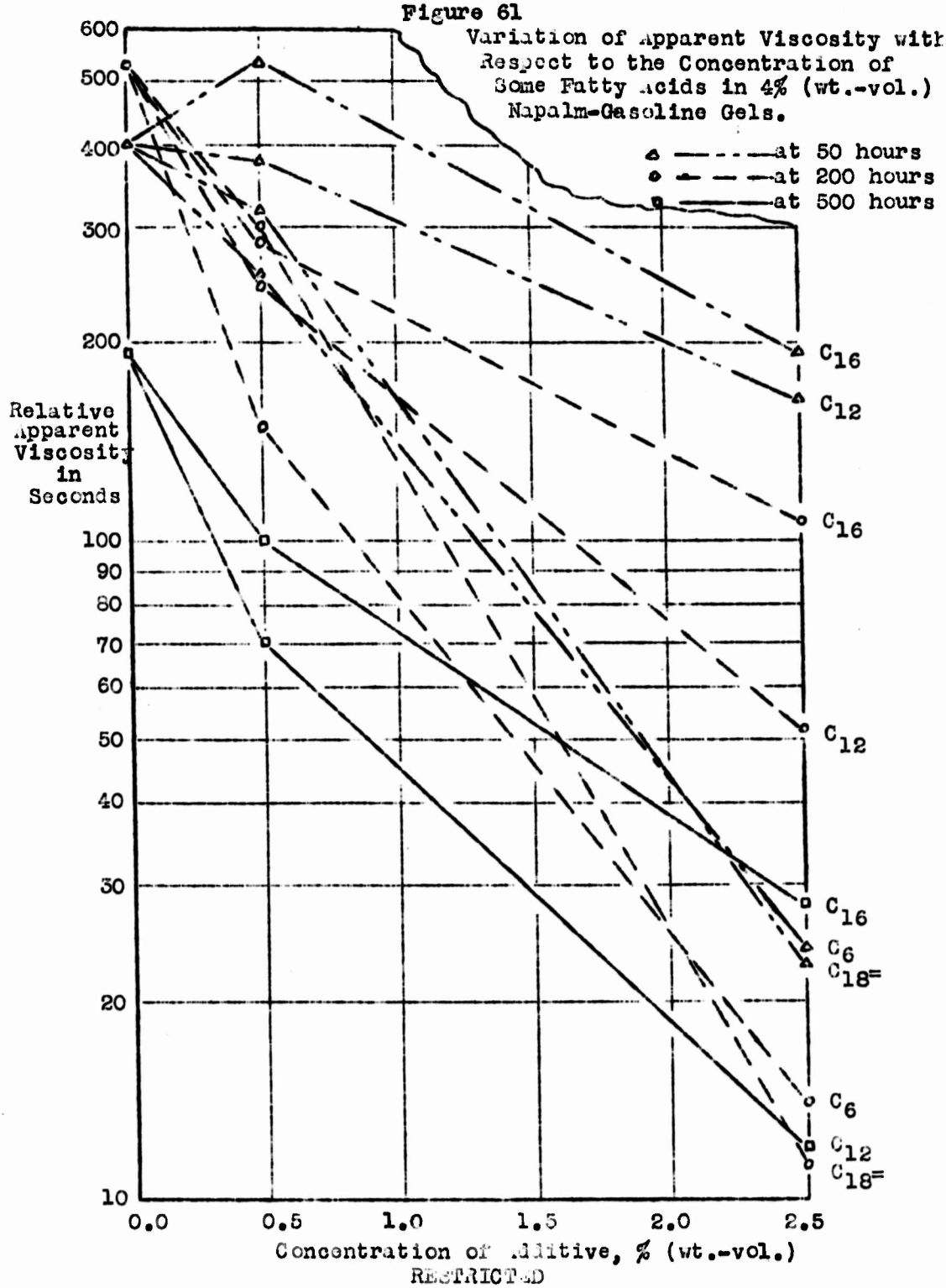
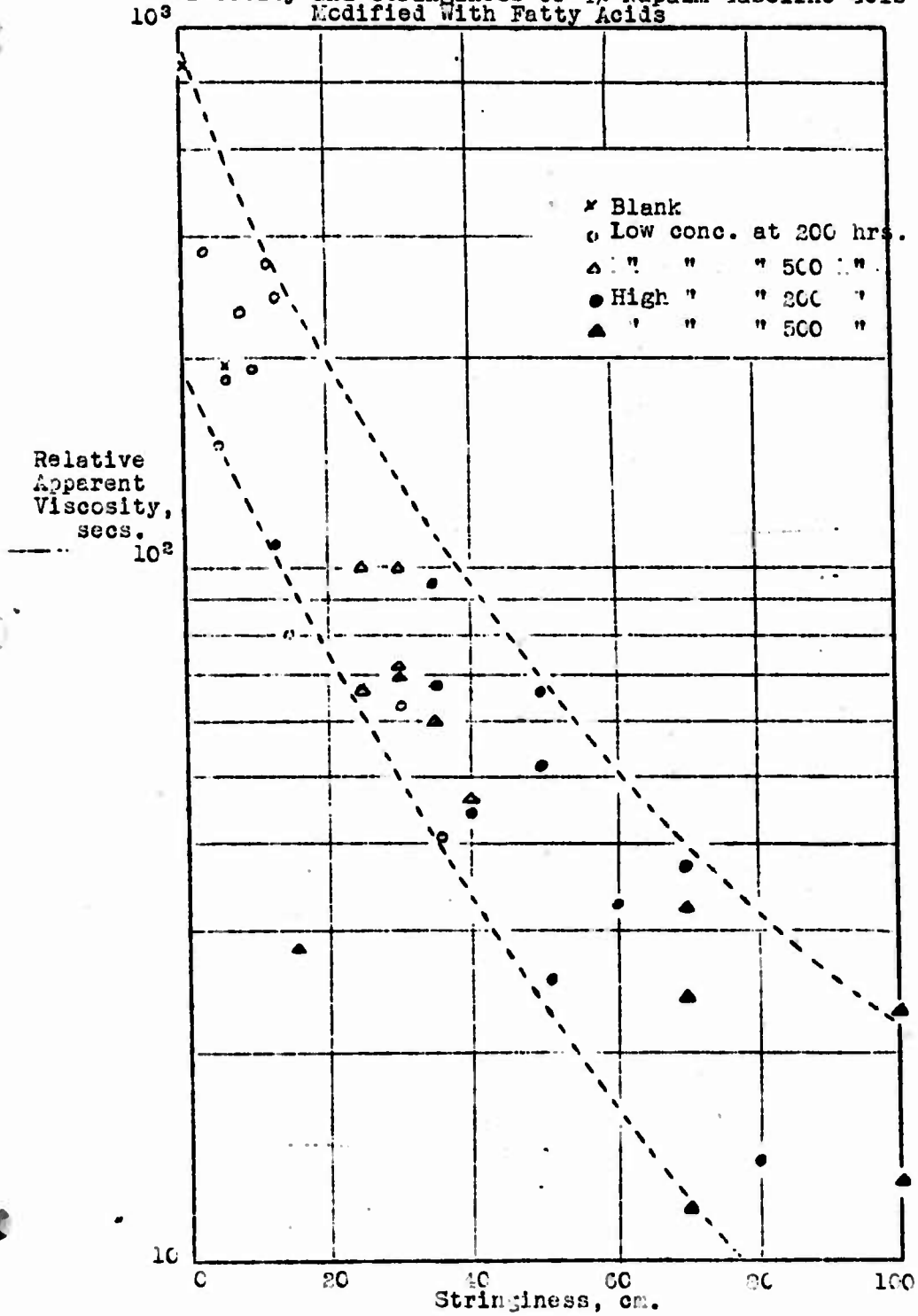
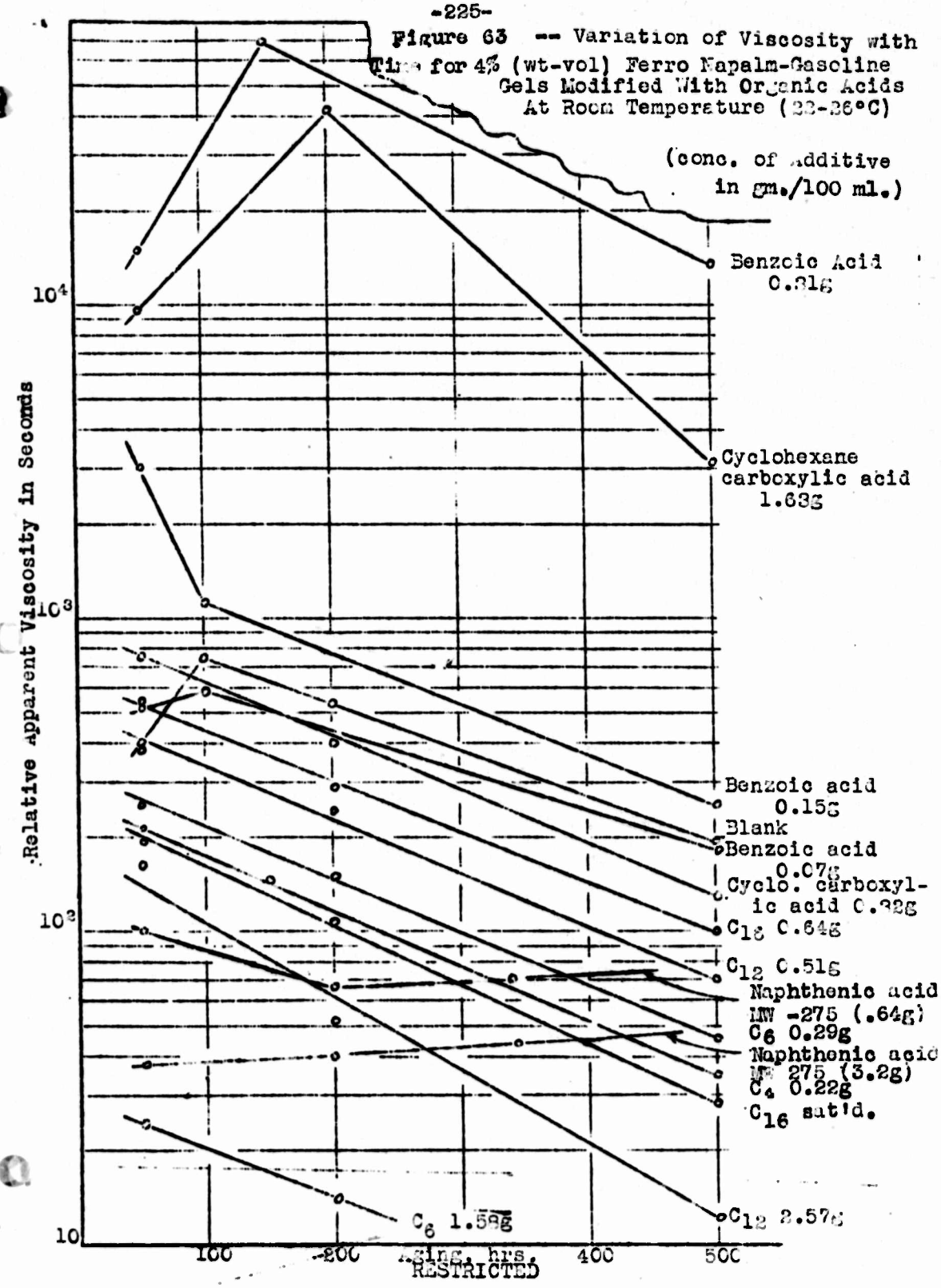


Figure 62
Viscosity and Stringiness Of 4% Napalm-Gasoline Gels Modified With Fatty Acids



(iv) Effect of time. Our results indicated that in general the softening effect continues over several hundred hours, dropping exponentially as shown by a few characteristic lines in Figure 63 . It must be noted, however, that the results are obtained at room temperature by successive measurements on the same sample (so that some moisture might be picked up each time) and stored in transparent glass bottles.

Figure 63 -- Variation of Viscosity with Time for 4% (wt-vol) Ferro Napalm-Gasoline Gels Modified With Organic Acids At Room Temperature (23-26°C)



4. Aluminum Cresylates and their Use in Studying the Properties of Thickened Fuels.

The rapid jellying of the thickened fuels prepared by mixing solutions of aluminum cresylates and solutions of fatty acids in gasoline or naphtha, as reported in the British Memorandum No. 415, seemed important in respect to the current study on gel-jelly transitions, peptization of these systems, and the nature of the existent phases themselves. Accordingly, the preparation and study of the aluminum cresylates was undertaken to supplement the work employing the usual methods of thickening fuels. Procedures described in the British reports were used in the preparation of these cresylates. The details of these preparations are discussed in our September Report p. 27-30.

Most of the jellying experiments were carried out using

a mixture of naphtha with 10% benzene and 3% oleic or stearic acid, with or without the addition of 1% o-cresol. There appeared to be no difference between the results with the two acids, and if the use of the o-cresol made any difference, it was masked by other variables. To this mixture was added 5% of a cresylate preparation made from 1.3 gm. Al and 24 ml. o-cresol, diluted with 20 ml. dried benzene; or a corresponding amount of cresylate in benzene solutions of other concentrations.

In no case did jellying occur as rapidly as quoted in the British report, i. e., starting in 30 seconds and becoming very elastic in one or two minutes. When the mixture was put into a tightly closed bottle and shaken, it usually did not form a firm jelly even after several weeks, but in most cases formed a firm skin over the surface, and thickened the naphtha to a slight degree. One sample was made from cresylate which had oxidized considerably in the air, and had been given the opportunity to absorb moisture. This sample was put into a tightly stoppered flask with a comparatively large air space, and after 24 hours had formed a firm elastic jelly which stood up for several weeks. Oxidation of the aluminum cresylate, absorption of moisture, or the presence of the large amount of air might have been responsible separately or in combination for the jellying.

Preparation of cresylate with 2 to 3% of iodine, as suggested in the British report, did not appear to make any consistent difference in jellying properties. Different preparations made in the same way did however show marked difference:

in jellying properties, indicating that what seem minor differences in technique cause important differences in results.

The discovery that contact with iron, air, etc. accelerated the jellying rate led to setting up a series of samples for comparison and observation. The only sample of cresylate. 13-P108-11, which formed jellies with the standard naphtha-benzone-oleic acid blend was used for this series. (See also September Tables X and XI). Skellysolvent B and petroleum ether (B.P. 55-85°C)were included, blended with 10% benzene and 3% oleic acid, for comparison.

The samples were made up in tightly capped bottles with as little air space above the contents as possible, and stored at room temperatures throughout the observation period. The sample through which the air had been bubbled formed large blobs of jelly during aeration and had thickened noticeably throughout to a short jelly within two hours. The addition of water to a sample resulted in an upward growth of a gelled area shaped like a mass of large crystals, starting at the bottom of the sample and engaging most of the liquid within 6 hours. Elastic stringy jellies were formed in the Skellysolve B and the petroleum ether in much less time than in the naphtha.

The elastic, stringy jellies were similar in appearance to good Napalm jellies in benzene and peptized aluminum soap jellies.

Thus the thickening of fuels by oleic acid and aluminum cresylate is evidently controlled by reactions which are not

well understood, but are very sensitive to certain catalysts . In view of the resulting difficulty of obtaining reproducible results further work along this line was abandoned.

J W. McBain

REEL - C

1358

A.T.I.

33601

~~RESTRICTED~~

TITLE: Fundamental Study of the Structure and Characteristics of Soap-Thickened Fuels

AUTHOR(S): McBain, James W.
ORIGINATING AGENCY: Stanford University
PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div 11

U

ATI- 33601
REVISION (None)
ORIG. AGENCY NO. (None)
PUBLISHING AGENCY NO. (None)

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
Dec '44	~~Restr.~~	U. S.	Eng.	229	tables, graphs

ABSTRACT:

A study of the structure and phase relationships of thickened fuels is given, in order to provide a more fundamental basis for understanding their properties. The problem was related to the Napalm program. A study of aluminum soaps is discussed. The phases and phase transitions utilized in the hydrocarbon systems are identified. Investigations were conducted to determine how water is held by Napalm. Methods are given for the purpose of distinguishing between free acid, sorbed or bound fatty acid, and chemically bound acid. Different Napalms are compared in pure solvents. Gel and gel structure and the effective additives are discussed.

EO 10501 dd 5 NOV 1953

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

DIVISION: Ordnance and Armament (22)
SECTION: Chemicals and Incendiaries (11)

SUBJECT HEADINGS: Incendiary thickness (50964)

ATI SHEET NO.: R-22-11-2