

SEMI-CONDUCTING HYDROCARBON OIL SYSTEMS

THESIS

PRESENTED TO

**THE SWISS FEDERAL INSTITUTE
OF TECHNOLOGY, ZURICH**

FOR THE DEGREE OF

DOCTOR OF NATURAL SCIENCE

BY

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**ACCEPTED ON THE RECOMMENDATION OF
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BRUNNER & BODMER ZOLLIKON

1950

TO MY PARENTS

* * *

I wish to sincerely thank in particular for their co-operation, help and advice during the course of this work, Professor E. Baumann, Director of the Institute for Applied Physics, (Swiss Federal Institute of Technology), Professor Dr. R. Sanger, Dr. N. Schaetti and Dr. F. Held of the Section for Industrial Research (AfiF) of the above Institute. Further, I wish to express my appreciation to the members of the Swiss School Board and the Swiss Federal Institute of Technology with whom I have come into contact during my two and a half years study at the Federal Institute, and whom I have found ever ready to offer me assistance.

C O R R I G E N D U M

SEMI-CONDUCTING HYDROCARBON OIL SYSTEMS

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		Drawing of Measuring		Measuring Apparatus No.3
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SEMI-CONDUCTING HYDROCARBON OIL SYSTEMS

INTRODUCTION

1. General

The series of investigations reported herein were carried out with a view to gaining information concerning the physical-chemical nature of various semi-conducting hydrocarbon oil systems. Previous work done in the Institute for Technical Physics on such oil systems, although not systematic, showed anomalies in their physical properties and pointed to the desirability of performing a series of systematic investigations with the base oils in use.

Such liquid insulators or semi-insulators are important, for example, for their use as transformer oils. The most suitable oil mixtures found up to the present time use as a base either one of two colloidal petroleum oils obtained from the Shell Oil Company and designated by them CY1 oil and BE2 oil. The BE2 oil has been found the better of the two. To these bases is added an electrolytic salt, magnesium oleate. In addition small quantities of tricresyl phosphate and naphthenic acid or just ethyl ricinoleate are added to the oil base before the electrolyte, which for one thing render it more soluble in the mixture. CY1 is a pure linear chain hydrocarbon oil while BE2 is cyclic. Before preparing an oil mixture the base oils are fractionally distilled under high vacuum (HVD) in a specially constructed distillation apparatus and the fraction most suitable with respect to vapour pressure, light absorption, etc., used. The chosen fractions are then slowly filtered under vacuum at below 0°C to remove the waxes.

Hexaline naphthenate was also experimented with as a possible base, but its properties were found difficult to control mainly due to the widely varying acid amounts in its various fractions after production and distillation. However, in contrast to the CY1 and BE2 oils, the electrolytic salt could be readily dissolved directly in the hexaline naphthenate for use, without employing additional substances.

These investigations are also very interesting when considered apart from their application to the oil mixture itself in its technical application as an insulating oil, etc. Firstly, they deal with electrical conductivity in non-aqueous solutions, a field that has until lately been subordinated, at least from the point of view of actual work on the subject, to conductivity in aqueous solutions. Moreover, the dispersion medium is unusual in

that it is a viscous hydrocarbon oil of low dielectric constant (D.C.) - a colloid.

Secondly, using magnesium oleate we enter the field of 'colloidal electrolytes', a classification recognized only some 38 years ago and just establishing itself as a separate and important branch of colloid science. The results of the investigations reported here are most interesting and meaningful when viewed in the light of previous work done and theories developed in this field of colloidal electrolytes.

2. General Method of the Investigations

The method of investigation employed was the noting of the variations of the three properties of specific (volume) electrical conductivity (χ), viscosity (k) and refractive index (n) when magnesium oleate was systematically added in increasing quantities to basic ('starting') oil mixtures formed using one of the three oil bases - CY1, hexaline naphthenate and BE₂ oils. The total amount of oleate added in each test varied from 14 to 21%. Measurements were made of these properties after each oleate addition at 0, 10 and 20°C, except in Test No.1, where measurements were made also at 5 and 15°C.

When tricresyl phosphate with naphthenic acid, or just ethyl ricinoleate were used with the oil bases to form the starting mixtures, they were added in just the same proportions as used in the best oil combinations found using that particular base. Moreover, and as is only correct, exactly the same substances as employed in the previous oil systems were used in these tests as far as possible.

In the beginning (Test No.1) two additional properties were measured - capillarity and dielectric constant. In both cases however, it was apparent that the measurement method used was quite inaccurate, the error of measurement undoubtedly obscuring the true variation of the property. Thus the dielectric constant measuring arm specially constructed at the start, was later cut away from the apparatus. The capillarity measuring tube is included in the conductivity cell and could be safely left.

In all tests the oil mixture was first degassed and then kept under a vacuum of from 1.4 to 3.5 x 10⁻²mm. of mercury for the duration of the test to exclude gases and moisture.

3. Summary of the Starting Mixture Compositions

Test No.		
1	Cyl oil 10/7 (filtered at -10°C)	+ A
2	Cyl oil 9/6 (filtered at -2°C)	+ B
<hr/>		
3	Hexaline Naphthenate 4th Fr. HVD (6)	
	(Acid number = 17.3)	
4	Hexaline Naphthenate 4th Fr. HVD (6)	
	(Acid number = 4.49)	
5	"	+ A
6	"	+ B
<hr/>		
7	BE ₂ oil 4th Fr. 2nd HVD (unrefined)	+ A
8	"	+ B
9	" (refined)	+ B

A = tricresyl phosphate, 4th Fr. 2 Lt. Dist. App. 1.00 %
 + naphthenic acid, barrel 1 HVD (6) 5 0.75 %
 B = ethyl ricinoleate, 2nd Fr. HVD 305 3.00 %

All compositions are percent by weight. The proportions given under 'A' are those used in oil mixture "Lau 84", and that under 'B', in oil mixture "E 39".

The actual compositions of the starting mixtures used, which vary but little with the ideal proportions given above, are given in the section "EXPERIMENTAL" following.

The amount of magnesium oleate used in the original Lau 84 oil was 5.37 %, and in the E 39 oil, 2.5 %.

LITERATURE SURVEY

1. Electrolytic Solutions

a) General

The monumental discovery by van't Hoff 1) in 1887 that solutions which readily conduct electric current possess freezing points, boiling points, osmotic pressures, and vapour pressures characteristic of a special class of systems, and the simultaneous and even more important discovery of Arrhenius 2) that such systems contain electrically charged particles, or ions, marked the beginning of an organized theoretical and experimental investigation of conducting solutions. The science of solutions is very complex and has evolved its own numerous experimental methods, and has required for its clarification many branches of mathematical physics, such as thermodynamics, statistical mechanics, electrostatics and hydrodynamics. Van't Hoff first systematically applied thermodynamical methods to solutions. Gibbs' system of thermodynamics developed earlier 3), however, was not at first employed.

Walden 4) in 1887 showed that Ostwald's rule 5), derived from numerous experiments with basic organic and inorganic sulphonic acids, that - the more compact the anion is, the smaller is its conductivity, i.e. its ionic velocity, is also perfectly valid for the fatty acid soap series. Also the results showed the ionic velocity not to be dependent on the weight, but the number of atoms in the ionic complex.

On the appearance of the ionic theory, Ostwald 6) applied the law of mass-action to the solutions which he'd been studying and found that in practically all cases this law held true, and that the empirical relationships which he had previously discovered were readily interpreted in the light of this law. However, when applied to solutions of the mineral acids and bases and the neutral salts - "strong electrolytes", he found this law did not hold as it did for the organic acids 7).

Soon after the discovery that ions exist in solutions, it was realized that the electrostatic forces between the ions must play an important role in determining their properties, but not until 1923 was an exact theory of dilute solutions of electrolytes evolved with Debye's 8) formulation of the inter-ionic attraction theory.

b) Non-aqueous Solutions

In media other than water, Bjerrum's 9) theory of ionic association, developed from consideration of the factors which determine the

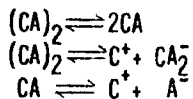
extent of ionic association, or more particularly, the formation of ion pairs under the influence of Coulombic forces, has indicated, and experimental results confirm 10), that the ions of all electrolytes tend to associate more as the dielectric constants of the media decrease. Accordingly, all electrolytes are partially associated, or "weak", in media of low dielectric constants, and classification of electrolytes into strong and weak becomes somewhat arbitrary.

When strong electrolytes are dissolved in solvents of very low D.C., the simple Coulomb forces are sufficient to cause ionic association at extremely low ionic concentration. In this case, the ions, not acting as part of an associated ion-pair, or more complex aggregate, are so far apart that short-range repulsive forces are negligible and the effect of the ionic atmospheres is also very small 11).

Investigations were made at an early date to supplement the results obtained in aqueous solutions by experimental data in other solvents. The earliest of these is that of Kablukoff 12), who investigated the conductance of hydrochloric acid in ether and alcohols. Later, numerous investigations were carried out in non-aqueous solvents, but the results could not be interpreted at the time. Not only did the mass-action law not hold, but the empirical dilution laws, which accounted fairly well for the results in aqueous solutions, failed in these non-aqueous solvents.

The earliest data confirmatory to the mass-action law in non-aqueous solutions are due to Franklin and Kraus 13) who found fairly satisfactory agreement with that law in the case of a number of typical salts dissolved in liquid ammonia, provided the dilutions were sufficiently great. Later Dutoit 14) and his associates at the University of Lausanne, found that in a considerable number of solvents typical salts yield solutions which conform to the mass-action law at high dilutions.

Kraus and Bray have published an excellent and thorough resumé 15) of the work with conducting solutions, both aqueous and non-aqueous, done up to 1912. They conclude that: (1) all electrolytic solutions are subject to the same dilution law; (2) at high dilutions the mass-action law applies to the results of conductance measurements; (3) in solutions whose ion concentration exceeds a value lying between 0.001 and 0.0001 normal (N), a divergence from the mass-action law becomes appreciable. Further, the D.C. is considered to be the controlling factor in electrolytic dissociation, both in dilute and concentrated solutions. On the basis of insufficiently precise transference numbers, they rejected the suggestion of Schanov 16) that the presence of complex ions and molecules,



might explain the deviation from the mass-action law for the simple ionization represented by the last equilibrium. Twenty years later Kraus with Fuoss 17) 18) brilliantly applied these equilibria to the interpretation of the conductance curves of salts in solvents of low D.C.

When the D.C. of the solvent is in the order of 10 or less, a minimum is observed in the conductance curves in dilute solution. With further decrease in D.C., the minimum becomes more distinct and its position shifts in the direction of increasing dilution.

To account for the increase in the number of ions per mol as the solute concentration increases, Fuoss and Kraus 19) postulate the combination of ions with ion-pairs to form "triple ions".

Stewart 20), commenting on the relation of D.C. to electrolytic conductivity, says the higher the D.C. the less will be the tendency to form ion-pairs as the force between the ions will be smaller. With low D.C. solvents, association is much more noticeable, and it has been suggested that at high concentrations there will be a further association to form ion triplets. This should have an interesting effect on the conductivity, for these ion triplets will have a resultant charge, enabling them to act as current carriers. Consequently, on passing the point of triple ion formation there should not be a decrease in conductivity similar to that arising from the formation of ion-pairs. Further, such an inflection has been observed in the conductivity curve and attributed to this cause - but only in non-aqueous solutions.

Association into more complex aggregates than triple ions should be expected in solvents of very low D.C., and progress has already been made in the numerical consideration of quadrupole formation from ion-pairs. The existence of quadrupoles is implied by the inflection just above the minima in the conductance-concentration curves for alkyl-ammonium salts in benzene 21) 22) and dioxane 23), and by the apparent molecular weights of the solutes derived from cryoscopic data 24) 25).

The influence of ionic size and structure upon conductance and association has been brought out in a number of studies 26). Elliott and Fuoss 27) have experimented also with incompletely substituted ammonium salts in tricresyl phosphate. Electrolytic polarization phenomena have also been found by Fuoss and Elliott in solutions of tributylammonium picrate in tricresyl phosphate (D.C. 6.92) at 40° 28). This polarization phenomena appeared when the con-

ductivity was measured on a direct current (d.c.) bridge. It was observed that the apparent resistance increased with time if the bridge voltage was kept on, until eventually a steady asymptotic resistance value much higher than the alternating current (a.c.) or initial d.c. value was reached 29). Commenting on this they say the increase in resistance is not due to the permanent depletion of the solution through electrolysis. The approach to the limiting conductance is exponential; the appearance in the exponent of the square root of applied voltage times elapsed time suggests that the increase is due to the formation of a space charge near the electrodes which reduces the voltage gradient in the volume between the electrodes. Measurement of these polarization rates is suggested as a method of determining diffusion constants in non-aqueous solution.

These observations are especially interesting as very similar phenomena have been observed during the course of the experiments on which this report is based. Such increases of resistance to an asymptotic value were noted in solutions of very low conductivity, i.e. in non-aqueous naphthenic- or paraffin-base oils containing either none or only very little tricresyl phosphate and naphthenic acid or ethyl ricinoleate, with none or very little magnesium oleate electrolyte. At higher electrolyte concentrations this phenomenon was not observed. In noting this the d.c. conductivity was measured as explained under "EXPERIMENTAL", the voltage being applied before each measurement before the charge on the electrodes had dissipated to zero from the previous voltage application (and measurement). The asymptotic resistance value was reached from 4 to 10 minutes after the initial voltage was applied.

c) Liquid Semi-dielectrics

Conductivity and viscosity research in the same field as this treatise, that is, employing viscous petroleum base oils of low D.C. and electrically only semi-conducting, almost insulating, as the solvent, is quite lacking. Gemant 30) attributes the small amount of knowledge in the field of insulating liquids to two main reasons: first, the technique of measurement is complicated by the high resistance of the systems; secondly, on theoretical grounds reproducible results can be expected only if the concentration of the metal ions in the liquid phase is finite and definite, a condition difficult to obtain with insulating liquids.

Successful measurements with liquids having D.C. down to 10^{-17} have been carried out by Hartley, Harned and co-workers 31). The conductance of these systems is, however, above, say 10^{-9} mho/cm. Gemant 32), experimenting with semi-conducting liquids, 10^{-9} to 10^{-12} mho/cm., and with a D.C. of 2.6, used frequencies of 1000 to 3000 cps in his conductivity measurements. The frequency at which the conductivity of these solutions is measured is irrelevant, at least in the

acoustical range, a variation in the conductivity with frequency in this range being expected only in heterogeneous systems. In discussing his results he points out that it is impossible to apply the Debye-Hückel theory for weak electrolytes to determine the dissociation constant, K , and the limiting equivalent conductance, Λ^0 (17), due to the degree of dissociation and the equivalent conductance, Λ , being too small to allow reasonable extrapolation to zero concentration. However, he has been able to use the approximate equation valid for very weak electrolytes -

$$\Lambda^2 c = \Lambda^2_0 K$$

(c being the molar electrolyte concentration), as the ionic concentration is so small as to make the activity coefficient practically unity. In other words one need not consider the Debye-Hückel effect. A plot of the measured data, according to the equation above, should reveal if the electrolyte behaves as a normal weak electrolyte, or deviates from this behaviour by formation of complex ions, such as found by Fuoss and Kraus in solutions of tetraisoamylammonium nitrate in dioxane-water mixtures (Fig. 1).

Higher paraffins, such as CYL oil, found in lubricating oils, although not high polymers as their chain length does not exceed 40, have high viscosities because of the interaction of numerous groups having relatively small attractive forces, the large number of interacting groups making up for the relatively weak attraction forces (33). Since they contain only hydrogen and carbon their D.C. are low and independent of frequency, and depend on temperature only through the density. Any d.c. conductivity or a.c. (alternating current) loss in them is due to the presence of electrolytic or polar impurities (34). This is true of all dielectrics - not only liquid dielectrics.

Experimental efforts (35) to realize the ideal liquid dielectric through successive stages of purification and distillation have resulted in progressive decreases of electrical conductivity down to a certain point only. The last traces of conductivity in liquids are attributed to ions caused by radio active influence. As in gases we find in these liquids, for low continuous stresses, that Ohm's law is obeyed, for higher stresses a saturation region with current constant under increasing stress, and then a rapid increase of current with further increase of stress, leading finally to breakdown as the result of secondary ionization. As stated, these relationships are found only in carefully purified liquids (36) (37).

The dominating cause of dielectric loss in the better known insulating liquids is a conductivity of relatively high value, which under continuous

potential, persists for only a very brief interval, say in the order of 1 second. The more highly purified the liquid, the greater the difference between the initial and final conductivities. Some oils which have excellent insulating power show little or no difference between the short time and long time conductivities.

Work carried out at the Detroit Edison Company (U.S.A.), 38) 39) 40) 41) 42), particularly by Gemant 43), approaches most closely the original research work reported here. Investigations by these researchers have been carried out to give in sight into the problem of insulating oil deterioration. Piper and his co-workers 38) used a saturated paraffin hydrocarbon oil, specific gravity 0.8860 at 15.6° C and a steady d.c. conductivity from 30 to 80° C of 0.2×10^{-14} mho/cm., which was first dried and degassed at 80° C under an approximate pressure of 1 mm. mercury, as solvent. To approximate the soluble oxidation products occurring in transformer oils on deterioration, stearic acid and mixed naphthenic acids were added to this oil in amounts up to 11 % and the d.c. conductivity measured. Their conclusions were that the effect of oxidation on an insulating oil is to increase both its power factor and conductivity. Their results are shown in fig. 3.

Later 39), they point out that their observations are in opposition to those of Sommerman 44), who claimed that on adding organic acids, phenol and stearic acid, to a mixture of paraffins, the true short time conductivities increased little, if at all, although the final conductivities increased greatly. Their results on the other hand show that organic acids as well as many other types of oxygen-containing compounds, have only a small influence on the conductivity of insulating oil "as long as such compounds are in true solution in the oil". Sommerman's conductivity increases were probably due to the mutual action of an impurity which he knew to be present in one of his paraffin constituents and the added substances.

Gemant 43) employed a typical hydrocarbon transformer oil of viscosity 0.14 poise at 25° C, D.C. 2.18, and an electrical conductivity of 1×10^{-14} mho/cm. at 25° C. To this he added two- and three-component electrolyte systems -

- tributylamine - oleic acid - o - cresol
- tributylamine - myristic acid - α - naphthol
- tributylamine - oleic acid

His results (figures 4, 5 and 6) and conclusions are very interesting. Appreciable conductivities at relatively low concentrations of the electrolyte were obtainable only in a three-component system. In solvents such as xylene or benzene, because of their higher D.C., approximately 2.4 and 2.29

at 20°C respectively 45), two-component systems are sufficient to cause reasonably high conductivities, although even in these solvents the three compounds together are far more effective. None of the three possible combinations in pairs of the three materials added, produced a conductivity noticeably higher than that of the oil alone.

Jacobs and Othmer 41) used soybean lecithin, trade name "Gliddol" (ca. 30 % lecithin, 40 % cephalin and 30 % adhering soybean-oil), as the inhibitor, adding it to a Pennsylvania stock S.A.E. 30 lubricating oil with a high viscosity index. Viscosity maxima at about 0.1 % Gliddol were observed (figure 7).

Piper and Kerstein 42) in their oil-paper dielectrics studies, added lauryl sulphonic acid to liquid paraffin. The a.c. conductivity at 80°C and 60 cps increased sharply at first from 0.001×10^{-12} mho/cm. then levelled off to about 8×10^{-12} mho/cm. as the acid concentration was increased from 0 to 0.6 % by weight (figure 8).

2. Colloidal Electrolytes

a) General

This terminology was originated by Dr. J.W. McBain, who began his exact study of colloidal soap solutions in 1910. Since 1911 he and his co-workers have made many publications on this subject. He applied this term to substances which dissociate to form simple non-colloidal ions in sufficiently dilute solution, but which reversibly associate to form colloidal micelles or clusters which contain ions of both signs in more concentrated solutions. These colloidal electrolytes, having soap-like properties, have a hydrocarbon group and an anionic or cationic group, and include the soaps, organic detergents, and the dyes.

Soaps and other organic detergents and wetting agents consist of a hydrocarbon portion containing from about 8 to 20 carbon atoms and at least one ionizable group 33) (figure 9).

Gonick and McBain 46) have supplied cryoscopic evidence for the existence of micellar association also in aqueous solutions of non-ionic detergents. These micelles are similar to those formed by colloidal electrolytes except for the absence of ionization.

McBain showed that soap solutions combined a low concentration of osmotically active particles, often much less than that calculated for no ionic dissociation, with a relatively high conductivity, and he pointed out that this anomaly could be explained by the formation of aggregates, termed micelles,

of soap ions 47).

Kortüm 48) views the combination of high conductivity with an unexpectedly low osmotic pressure as the distinguishing characteristic of a colloidal electrolyte. These micelles would clearly exert little osmotic activity but could still have considerable conductivity. The equilibrium between the micelle and the simple long-chain ions appears to obey the law of mass-action, and explains the disappearance of colloidal properties on sufficient dilution.

In dilute soap solutions soaps behave substantially like the simple inorganic electrolytes (e.g. KCl) with regard to both conductivity and osmotic effects. At somewhat higher concentrations the osmotic effects begin to deviate markedly from ideal behavior, their values falling below those calculated from Raoult's law. The change in electrical conductivity however, does not parallel the changes in osmotic effects. The observed values of conductivity remain quite high and are much higher than would be expected from the osmotic behaviour 49).

That the high degree of conductivity was not due to hydrolysis of the soap was definitely proved shortly after the original observations were made. Thus, this discrepancy between osmotic and conductivity behaviour led McBain to postulate the formation of a colloidal particle or micelle formed by association of the long-chain fatty acid anions and bearing a high electric charge. These micelles are of colloidal dimensions, usually 20 to 1000 Å in diameter. Practically all the anionic and cationic surface active agents show the same general behaviour, and are generally referred to as colloidal electrolytes. Besides the charged or ionic micelles, there may exist, in solutions of colloidal electrolytes, micelles with relatively low net charge. The non-ionic surface active agents form only neutral micelles in solution. Their colloidal behaviour is simpler of description because the electrical effects are absent 50).

Umstätter 51), who has done considerable work in the aggregation and structure field mainly through employing viscosity measurements, has shown that with lower temperatures heavier micelles are formed in any micelle bearing solution. Some of his results are shown in figures 10 and 11.

The conductivity curves for the various types of colloidal electrolytes are all qualitatively similar (see figure 19).

Pauli 52) added inorganic acids to various proteins and studied the resulting viscosity and electrochemical effects. McBain 53), speaking on Pauli's results, points out that the discrepancies reported by Pauli, resulting from a com-

parison of the viscosity of the acid- and alkali-albumins as measured mechanically, with the unexpectedly high mobility of these same viscous ions when measured by means of electrical conductivity, are a general phenomenon with such colloidal electrolytes. He agrees with Pauli in assuming excessive hydration of the highly charged micelles (possibly as a result of their electrical charges). This would account for their abnormally high mechanical viscosity and at the same time for their mobility being only normal.

Hartley has analysed the conductivity phenomena in detail (54), and he points out that micellar aggregation has three main consequences:

- a) the viscous drag is reduced
- b) the ionic atmospheres of oppositely charged gegenions exert a much increased 'braking effect'
- c) some of the gegenions will adhere to the micelle owing to its high charge and thus be forced to travel in the opposite direction to that of the free gegenions.

Under ordinary conditions b) and c), which tend to reduce the equivalent conductivity, outweigh a), which causes an increase of viscosity, so that the conductivity falls on aggregation.

With colloidal electrolytes at very high field strengths the reduction in atmosphere effects (ions move too rapidly for atmospheres to form) sets free some of the bound gegenions, and the conductivity rises on aggregation due to the Stokes law effect now preponderating (see curve for 200 KV/cm. in figure 12).

Kortüm (48), discussing the Wien effect with colloidal electrolytes, has this to say - at high field strengths the strong rise of the conductivity occurs in exactly the same concentration area in which the sharp drop of the normal conductivity begins, while at lower concentrations the effect is small and of the same order as the Wien effect as measured with ordinary electrolytes, i.e. Δ_{∞} , the equivalent conductance at infinite dilution, is not exceeded here.

The customary temperature-coefficient of conductivity involves three separate factors for any electrolyte and five for a colloidal electrolyte. The first two are the specific mobilities of the two ions, of which those with the lowest mobility have the highest temperature coefficient; the third is the change of dissociation with temperature, while in the case of the colloidal electrolyte there is the further factor of the change in equilibrium between ions and ionic micelles in addition to the temperature coefficient of the latter itself.

Three-component colloidal electrolyte systems have been investigated by various researchers. With partially miscible systems such as phenol-water or cresol-water, addition of soap lowers the critical solution temperature, a fact known as long ago as 1886.

The viscosity and conductivity of fatty acid soap solutions in the presence of phenols and electrolytes have been studied in particular by Angelescu and his co-workers 55). They find that at a fixed soap concentration, the viscosity shows a maximum at a certain phenol concentration, the maximum becoming less marked with rise in temperature. Weichherz and Saechtling 56) investigated sodium oleate, phenol and water systems, obtaining also viscosity maxima (see figure 13).

Moore 57) checked the results of Weichherz and Saechtling using a more rigorously purified sodium oleate. In the oleate-phenol-water systems even more pronounced viscosity maxima were obtained. In producing these maxima, p-cresol, guaiacol and creosol were about as effective as phenol, but in the case of catechol, resorcinol and o-bromophenol, the maxima were not so marked, or even, at lower oleate concentrations, non-existent. Of all the phenolic substances examined, p-cresol showed the most pronounced effect, maximum viscosity at 20°C of the system containing 90% water being around 100 - 200 poise (figures 14 and 15).

The viscosity-concentration curves for the homologous sodium soap solutions in water have been found by Hess, Philippoff and Kiessig 58). The curves are all similar, the viscosity increasing slowly with the concentration then rapidly as concentrations in the range of 10% are reached, as seen in figure 16).

Concerning the bivalent magnesium oleate, the electrolyte used in these oil systems and in the investigations reported herein, Bhatnager 59) and his associates have carried out studies on its properties. The peculiar behaviour of magnesium oleate in contra-distinction to zinc oleate in giving electrically conducting solutions in benzene (D.C. 2.29 at 20°C) is probably ascribable to its solvation, leading to the formation of micelles and its consequent behaviour like a colloidal electrolyte. The presence of such micelles in a benzene solution of magnesium oleate is also indicated by the observation that magnesium oleate, in contrast to zinc oleate, lowers the interfacial tension between benzene and water to a considerable extent and can be used as a good emulsifying agent.

Lewkowitzsch and Bhatnager have pointed out that the bi- and tri-valent soaps are not simple chemical compounds, but complex absorption compounds and their

composition varies considerably with the amount of monovalent soap and the precipitating electrolyte used. Master and Smith (60) observed that magnesium oleate carried down with it from solution sodium oleate.

It is clear from the preparations by Bhatnager and his associates that the metal and the acid are not present in stoichiometric ratio. The same has been found by Ostwald and Riedel (61) for magnesium palmitate and stearate, who also pointed out that the oleates of these metals are colloidal in nature. From observations during analyses and preparation, it is suggested by Bhatnager and co-workers, that when sodium oleate is in excess the oleate micelles are absorbed by the metal oleate particles and form a negatively charged colloidal solution, but when magnesium ions are in excess they are absorbed and coagulate the metal oleate as a positively charged precipitate. From the melting points of the samples prepared, it is evident that pure magnesium oleate is a yellow mass which can be powdered (while the other samples are sticky).

It was found that zinc and magnesium oleates obtained from solutions containing the electrolyte in excess are the most soluble in benzene, suggesting the formation of complex salts as postulated by Cady (62). Negligible freezing point depressions in benzene solutions of these oleates further showed that true solutions are not formed. Similar tests in camphor showed magnesium oleate to be doubly associated in this solvent.

The viscosity increases linearly for these two oleates in benzene, magnesium oleate giving a more viscous solution. Similar viscosity results were obtained by Ostwald and Riedel.

It has been shown (63)(64) that a study of the magneto-optical rotation of alkali soaps can furnish evidence as to the formation of ionic micelles. Bhatnager and his associates showed that the magnetic rotation of zinc oleate in benzene remains constant whereas that of magnesium oleate varies with the concentration indicating micellar formation.

They conclude from the difference in behaviour of zinc and magnesium oleates, that whereas zinc oleate may be regarded as a gel, magnesium oleate behaves more like a colloidal electrolyte.

An interesting summary of the dielectric constants of various magnesium oleate solutions measured at a frequency of 4×10^8 cps by various investigators (65) is given here:

Solvent	Oleate %	°C	D.C.
kerosene	5	20	1.2
carbon tetrachloride, CCl ₄	8	19	2.0
benzene, C ₆ H ₆	20	20	2.2
cotton seed oil	5	20	2.6
pyridine, C ₅ H ₅ N	15	25	11.0
capronitrile, C ₅ H ₁₁ CN	5	18	13.0

Dielectric constants of some oleates alone (65), measured at a frequency of 4×10^8 cps are:

	°C	D.C.
oleic acid	20	2.4
aluminum oleate	20	2.4
ferric oleate	20	2.6
sodium oleate	20	2.7
copper oleate	20	2.8
lead oleate	18	3.2
isobutyl ricinoleate	21	4.7

The following electrical conductivities are also reported in the literature:

- 66) oleic acid $< 2 \times 10^{-11}$ mho/cm. at 15°C
- 67) paraffin oil 7×10^{-17} mho/cm.
- 67) petroleum 3×10^{-13} mho/cm.

b) Critical Concentration

It is generally accepted that the aggregates or micelles begin to form in large amounts only when a definite concentration range is reached (68) and that this range is relatively narrow (50). Bury and his co-workers (69) have demonstrated, on the basis of the mass-action law, that the concentration range within which micelles begin to form in large amounts should be fairly narrow. This is particularly true where the aggregate is fairly large (20 or more ions) and is formed by the association of single ions. These investigators suggested the term 'critical concentration' for this range and it has been universally accepted.

The critical concentration can be obtained from measurements of conductivity or from measurements of one of the colligative properties of the solution.

The colligative properties can be represented in terms of the osmotic coefficient representing the number of particles in solution expressed as a fraction of the maximum number that would exist if the substance were completely dissociated 33).

In the neighbourhood of the critical concentration all physical properties which have been measured with sufficient accuracy suffer a rather abrupt transition 48). At concentrations well above the critical the behaviour is that of a colloidal electrolyte and there is no doubt that the paraffin-chain ions are almost all aggregated into micelles 70).

According to Schwartz and Perry 50) the critical ranges occur at lower concentrations and are sharper as the chain length increases. Moreover, temperature is not as important a factor as chain length in determining critical concentration. The cationic colloidal electrolytes show the break at the critical concentration more sharply than the anionic.

It is also evident that with the higher (C_{16} and up) members of the series, the first sharp dip in the curve is followed by a gradual levelling off through a minimum followed by a slow rise in the equivalent conductivity. This minimum corresponds to a second major change in the bulk properties of a solution. McBain's view is that here large amounts of a micelle larger than the ionic micelle and having only a small net charge, called the 'neutral colloid' 71), begins to form.

Another recently developed method for studying critical concentrations is due to Klevens 72) who has found that the refractive index of surface active solutions changes abruptly at the critical point. The critical values found by this method are again the low values corresponding approximately to those obtained by the conductivity method.

When gross properties such as conductivity or osmotic coefficient are plotted against concentration, sigmoid (S) type curves are generally obtained. These can be considered to consist of three different ranges - a pre-critical range, a range in which the magnitude of the effect being measured changes rapidly with the concentration, and a third range where the curve levels off or even changes the algebraic sign of its slope. This indicates that the nature of the micelle itself changes with concentration, or else that there is more than one type of micelle present. In view of the large amount of data which has been accumulated using many different techniques it is not surprising that a completely satisfactory theory to the structure of micelles is so difficult to develop. A major difficulty lies in the fact that the critical concentration values vary in several instances depending

on which particular effect is being measured 50).

Corrin and Harkins 73) have published some interesting information concerning the effect of salts on the critical concentration. It is shown that the behaviour of the colloidal aggregates of long-chain electrolytes cannot be described in terms of the principle of ionic strength or the related Debye-Hückel relationships. The depression of the critical concentration of such electrolytes is related only to the concentration of that ion of the added salt that bears a charge opposite to that on the colloidal aggregate. The nature of the other ion is without effect.

Within each class of detergents, i.e. anionic or cationic, the depression of the critical concentration brought about by equal amounts of salt is, in the cases investigated, greater the lower the critical concentration of the detergent.

The above relationships, and the fact that the form of the mass law usually applied to colloidal electrolytes is found to be invalid, indicates that they form 'a new type of electrolyte in which salt ions of the same charge as the colloidal aggregate are repelled to such a distance as to give independence of the magnitude of the charge per ion', with dependence upon only the sum of the charges on all such ions, in the formation of the aggregate. With ions of ordinary salts these ions are sufficiently close together to give the well known high dependence on the charge per ion.

c) Micellar Structure Theories

There are at the present time two leading schools of thought in this field 50), one represented by J.W. McBain 74), and the other by G.S. Hartley 54).

Hartley postulates essentially only one type of micelle, which is formed in substantial amounts at the critical range by association of ions. Below the critical range only free ions exist in solution. The rapid fall in the conductivity and osmotic coefficient is due to the association of "gegenions" (counter-ions, - ions of opposite charge) with the micelle. The later rise in the values of the conductivity and osmotic coefficient is either due to association of the gegenions or to Debye-Hückel effects (changes in the ionic atmospheres around the micelles) 75). The micelle itself is roughly spherical in shape.

In fig. 18 is represented a spherical micelle in dilute soap solution (\approx ca. 1 %) surrounded by positive gegenions.

This spherical micelle has a radius of rather less than the length of the

fully extended molecule, e.g. ca. 20 Å for the C₁₆ chain salts, and in this case it would contain about 50 molecules and have a molecular weight of about 14,000. The number of constituent molecules is found by dividing the size of the micelles by the volume of a single molecule. The hydrocarbon chains have been drawn irregularly to indicate that they are in a liquid state of aggregation. The majority of gegenions are (statistically speaking) attached to the micelle and move with it.

For example, in the case of sodium dodecane sulphonate, the ionic micelle is composed of the C₁₂H₂₅SO₃⁻ ions. Associated with this micelle are a number of Na⁺ ions, the gegenions. The number of gegenions associated with a single micelle varies with concentration, temperature, etc.

This theory of Hartley's does not account for the large lamellar micelle deduced from x-ray data.

McBain holds that all the data can only be explained on the basis of different types of micelles. The two general types of micelles are the small, spherical, highly conducting micelle and the large, lamellar, poorly conducting micelle. This latter structure he identifies with the so-called 'neutral colloid'. McBain has repeatedly pointed out that this term is a misnomer, since the micelles actually conduct electric current, although much more poorly than the ionic micelles (76). The ionic micelles form from simple ion pairs and progressively larger aggregates even in very dilute solution. At the critical point lamellar micelles begin to develop. They increase in size and amount until enough are present to produce an x-ray pattern.

The idea that several kinds and sizes of colloid particles exist in detergent solutions, and that their relative concentrations depend on total detergent concentration, temperature, etc., is very persuasive, and undoubtedly has more supporters than the single micelle type theory.

Consideration suggests that colloid particles begin to form by progressive association of ions and ion-pairs, and that all the different sizes and modes of packing can occur in proportion to their efficiency in removing insoluble parts of the molecules from contact with the solvent and in accordance with the respective requirements of the principles of mass-action (77).

Van Rysselberghe (78) has developed a mathematical treatment which interprets osmotic, conductivity, and migration data of dilute solutions on the basis of an "average inclusive micelle", the size and charge of which vary. He has also measured the conductance of non-aqueous solutions of magnesium and calcium perchlorates (79).

McBain (80), speaking on the recent interpretations of colloidal electrolytes

suggested in several quarters, says that a reexamination of the experimental evidence for soaps emphasizes that these interpretations are based on a failure to consider the osmotic data obtained from freezing point and lowering of vapour pressure. The reinterpretation is incompatible with these thermodynamic data, because the osmotic effects are here far greater than can be accounted for by colloidal and simple ions as deduced from conductivity. Simple molecules and ions (or simple neutral ion-pairs of identical formula), and only those, are present in substantial amounts. These precede the formation of neutral micelles. In this range the solutions contain not more than a very slight amount of colloid, probably ionic, micelle.

It is pointed out that at much higher concentrations, where aggregation to colloidal electrolytes has occurred and the relation between conductivity and osmotic data reversed, the neutral micelle of McBain and collaborators has been confirmed by x-ray observations, and that this, together with the ionic micelle likewise postulated, is still the most plausible explanation of all the evidence for all concentrations.

At present, in view of the overwhelming x-ray evidence (81) there is practically no doubt as to the existence of lamellar micelles. In view of all previous evidence, the existence of a smaller and more highly conducting micelle must also be conceded.

According to Hoerr and Ralston (82), recent x-ray absorption studies have confirmed earlier investigations in which two forms of micelles differing considerably in size were separated by ultra-filtration through semi-permeable membranes. These studies all agree definitely that two different forms of micelles exist in aqueous solutions of colloidal electrolytes. One of these forms is laminiferous, being a crystalline particle consisting of alternate layers of undissociated molecules of paraffin chain salt. This micelle is quite the larger of the two forms. It would possess very little ability to conduct electricity due to its undissociated nature and any charge that it possesses is merely that of an ordinary colloid particle. The other micelle form is a spherical particle consisting of paraffin chain ions with the paraffin chains inward and the polar groups at the surface, being essentially a minute droplet of crystalline fluid. This micelle would possess high conducting ability due to the fact that its charge would be the sum of the charges of the ions of which it is composed, these charges being concentrated in a relatively smaller volume than occupied by the individual dispersed ions.

In view of the variations among the x-ray studies concerning the structural details of the micelles, it seems evident that there are probably several

stages of association and dissociation between the two forms.

Many investigators 83) 84) 85) 86) 87) 88) 89) 90) 91) 92) 93) believe a long-chain hydrocarbon molecule takes a somewhat linked or curled shape, intermediate between a tightly rolled up mass and the rigid linear configuration assumed by Staudinger 94). Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains, but the configurations of intermediate extension predominate statistically.

Howell and Robinson 95) from a study of the conductivity of aqueous solutions of long-chain alkyl sulphates 96), suggested that at the critical concentrations "the anions are unable to pass one another owing to electrical repulsion and that on electrolysis they therefore move as a complete lattice-like loose network". At the concentration for the minimum of the equivalent conductance curve they assume that the "network falls into lamellar micelle formation" (see figure 21). The force tending to prevent micelle formation is the charge on the anion. The force tending to promote micelle formation is the hydrophobous nature of the chain, and this is proportional to its length. Hence the tendency for two long-chain anions to coalesce is proportional to the square of the chain length.

It follows that with a partially dissociated electrolyte, since the repulsive force is less, micelle formation should begin earlier, i.e. when the inter-molecular distance is greater, It further follows that, since micelle formation results in further dissociation of the electrolyte, increase of temperature should facilitate micelle formation.

McBain, Dye and Johnston 97) present conductivity measurements for the homologous series of straight chain sulphonic acids from C_2 to C_{14} , together with data for density and refractive index. This data shows the gradual transition from the behaviour of fully dissociated electrolytes for the lower homologs to the higher homologs. The latter approximate to complete dissociation in extreme dilution, then rather suddenly lose much of their conductivity through association of ion-pairs and ions to form colloidal particles of low conductivity, but after a well-defined minimum in moderately dilute solution regain some of their conductivity through increasing formation of better conducting or ionic micelles.

McBain and Salmon 98) in catalysis and emf tests using the potassium and sodium salts of the soaps, showed that the higher soaps in solution, quite apart from the small amount of free alkali present, exhibit minimum conductivity in 1/10 or 1/5N solutions. In higher concentrations the conductivity rises appreciably up to 1/2N or 1N solutions, where a maximum is

observed. The higher soaps are the most colloidal, and the potassium soaps contain more colloid than the sodium soaps. It is just these cases that exhibit the minimum in 1/10N solutions. The better conducting and less colloidal potassium laurate (C₁₂) and the sodium soaps do not show a minimum until 1/5N solution is attained.

Gonick and McBain (99) (100) in tests with hexanolamine oleate have shown that this colloidal electrolyte follows Brady's curve for branched chain compounds in its osmotic coefficients, and calculated the critical concentration therefrom. Brady (101) found that if the osmotic coefficient is plotted against the logarithm of the molality, the resulting curves for all colloidal electrolytes of the same type are parallel between the critical concentration and that at which the transition to colloid may be considered complete. In all the compounds covered by Brady's generalization one of the ions is monatomic (Na⁺, K⁺ or Cl⁻), the difference in the slopes of the osmotic coefficient-logmolality curve thus depending solely on the structure of the colloidogenic ion.

Hydrolysis has been shown to occur to only a slight extent in concentrated soap solutions, so it cannot in any case be adduced to explain an appreciable part of the good conductivity exhibited by soaps (102). The soaps show moderately good conductivity even in concentrated solutions. Indeed, in many cases, the conductivity curve, after passing through a minimum, rises on further concentration to a maximum, a phenomenon otherwise practically unknown in an aqueous solution. This effect is more pronounced at 18°C than at 90°C (note figure 19). The oleates differ entirely from the soaps of the saturated fatty acids in that sodium oleate is a much more typical soap in this respect.

The increase in conductivity must be due to the replacement of the simple oleate anion by an ionic micelle of higher mobility. Thus the effect of decreasing dissociation is more than counterbalanced by this replacement. Finally, however, a maximum is reached where the steadily diminishing dissociation of the colloidal electrolyte itself overbalances all other factors.

In concentrated soap solutions, i.e. 10-50 % soap, many striking differences from the dilute solutions in the physical properties are seen. For example, the viscosity is usually anomalous, and the original isotropic solution becomes doubly refracting upon shear (streaming birefringence); also, certain systems even show definite elastic properties (e.g. ammonium oleate). Such behaviour is indicative of a change from the spherical micelle to a more

asymmetric type such as a rod or plate (figure 20).

J. W. and M. E. L. McBain 103), in discussing the effect of the departure from the spherical shape on the viscosity by colloidal particles and large molecules, state that the measureable effect of even an extreme change to an elongated structure is too low to explain the high viscosity which 0.1% of certain colloids, such as nitro cotton, impart to solvents in which they are dissolved. The chief cause is attributed to a structural viscosity due to entanglement and local adherence of molecules and particles, effectively immobilizing a disproportionate amount of the solvent in comparison with the amount of the colloid itself. Where the viscosity reaches a maximum in dispersions of reversible, emulsoid, or hydrophilic colloids, one of their marked characteristics, is called by Alexander "the zone of maximum colloidity" 104). Above this zone the viscosity decreases with coarser subdivision as the Brownian motion becomes sluggish (about $100\mu\mu$), and below which it also decreases as molecular dimensions (about $5\mu\mu$) are reached, and the Zsigmondy-Brownian movement becomes violent. In concentrated solutions of potassium oleate for example, the equivalent conductivity is three times that of the oleate ion and equal to that of the potassium ion 102).

In concentrated solutions almost all of the long-chain ions are in aggregates. At concentrations above 15% these solutions give an x-ray pattern 58) 81) from which Hess and Gunderman 105) have deduced that at these concentrations at least some of the detergent is in the form of a lamellar repeating array consisting of alternate layers of water and double long-chain molecules (figure 21). There is no direct evidence that the chains are actually normal to the layers as shown. The overall dimension of the micelle are also unknown 106.)

A further support for the lamellar model comes from solubilization experiments. Certain water insoluble materials such as hydrocarbon, are soluble in detergent solutions. On the other hand, solubilization studies also show that if such a lamellar structure exists, it cannot be the only type of micelle in solution, since the change in long spacing is seldom enough to account for all the material solubilized 107) 108), and in some cases solubilization occurs with no change in long spacing (109).

The variation in spacing with large amounts of added salts is opposite in sign to that predicted, indicating that processes are occurring in this case not taken into account in the simple model. However, the variation with smaller amounts of added salts is again in qualitative agreement with that predicted from double layer theory.

Although some discussion still centers upon the structure of the micelle and

whether one or two types exist, it is generally agreed that the physical properties of soap solutions are due directly or indirectly to the occurrence of micelles.

d) Solubilization

For some time McBain and his collaborators have defined the term "solubilization" to include all cases in which otherwise insoluble material is brought into thermodynamically stable solution by incorporation within or upon stable colloidal micelles (110) (111). For this there are three possibilities, all of which occur. First, attachment to the external polar groups; second, interlayering within the McBain and Hess micelles between the hydrophobic layers; and third, interpenetration between the molecules or ions of the micelle. This is the explanation here suggested for the many colloids which solubilize hydrocarbons and yet do not form McBain or Hess molecules for geometrical reasons. Hydrocarbons do not dissolve in or fully wet hydrocarbon chains of parallel oriented fatty acids or soaps, such as films on water, or spherical micelles.

In 1923 McBain suggested one form of micelle which consists of two layers of soap molecules or ion-pairs partially dissociated and arranged side by side, with the two hydrocarbon layers inside. Mattoon, Stearns and Harkins (112) have recently found x-ray evidence for the existence of the McBain micelle.

From 1937 to 1942 Hess and his associates and others discovered through x-ray examination that the McBain lamellar micelles can repeat in parallel arrangement, separated by definite layers of water, thus giving a long spacing equal to the double length of the molecule plus that of the layer of water (77) (see figure 21).

With the higher fatty acid soaps, the water holding capacity per mol of sodium soap increases rapidly as the molecules become larger. Oil solubilized into soap solutions is believed to be taken up between the ends of the soap molecules arranged in various possible structures as shown in figure 22.

It seems unlikely that much penetration between the chains occurs, since the short spacing of ca. 4.4 \AA , which is undoubtedly the usual side chain spacing as found in many liquid hydrocarbons, is unaffected by these dissolved oils. The viscosity of these concentrated soap solutions seems to fit in quite well with the above structures. For example, in sodium oleate solution the viscosity-concentration curve turns up very rapidly around 10% soap, and from the streaming double refraction (Snellman 113) concluded that the transi-

tion to large micelles occurs over the concentration range 6-10 %. It is just over this range that the transition would be expected, and where the long x-ray spacing first becomes detectable.

Pink 114), in his water-in-oil emulsion studies using magnesium and calcium oleates, shows them to be much more readily wetted by oil than by water.

Sodium oleate with 18 carbon atoms exhibits intermediate values for the paraffins and cyclic hydrocarbons but excels in solubilizing aromatic and polar compounds. It is therefore clear that neither the carbon atom chain of the detergent nor its polar groups alone determine the solubilizing power, but that certain favourable and unfavourable combinations as well as occasional specificities, overlie the general regularities observed.

The extent of solubilization varies considerably for any given detergent with the type of oil used. McBain and Richards 115), after detailed studies of numerous organic liquids and synthetic detergents in soap, concluded that oils of low molecular weight are more readily solubilized, the solubility decreasing rapidly with increasing molecular weight or molar volume. Polar oils are more readily solubilized than non-polar.

The theory that has most in its favour states that solubilization is accomplished by the lamellar micelles. It has been noted that these micelles have alternate head-to-head and tail-to-tail spaces in their structure. The space between the head layers is filled with water. In a solution of pure detergent the intramicellar spacing between the head layers becomes greater as the dilution is increased indicating that more water molecules have moved into this region. When an oil is introduced into the system, the oil molecules enter the intramicellar spaces between the tail layers and become essentially a part of the micelle. This is indicated by x-ray diagrams, which show an increased spacing of these layers when solubilized oil is present. X-ray studies have also been made which show that some solubilization may take place between the parallel long chains as well as between the layers of tail ends 50).

Lawrence 116), commenting that systematic work on gels in dispersion media other than water is almost entirely lacking, has prepared a number of pure soaps and examined the optical and mechanical properties in nujol (a non-polar, high boiling hydrocarbon similar to medicinal paraffin). Clear mobile solutions can be obtained on heating to ca. 200°C, in which the soap molecules are probably aggregated with their polar groups together (i.e. opposite configuration to that in water) as seen in the figure 24. Changes depend on

the cation and are also very much affected by alcohols, phenols, amines, fatty acids, etc., which appear to act as peptizers in these non-aqueous systems also.

The "plastic" stage for magnesium oleate in nujol was between 203 and 90°C. A true gel is optically empty in that individual particles cannot be detected ultramicroscopically although a weak Faraday-Tyndall cone is usually visible. It is now generally accepted that gels have a fibrillar structure. For the fibrils to hold the solvent it is obviously necessary that they be numerous and therefore of very small cross-section. Gelation requires adhesion of the particles into a three dimensional structure, and is caused by reduction of solubility - by cooling a hot solution, by salting out, or by removal of the stabilising ions of a hydrophobic sol. In the plastic and gel stages, the hydrocarbon tails are in kinetic agitation which prevents the soap's molecules forming into their regular lattice. The behaviour of a given soap depends on both cation and hydrocarbon tail. Gels of the oleates have a much lower rigidity than those of the corresponding stearates. This latter fact has been illustrated in our laboratories when stearate and oleate salts were dissolved in CY1 oil during eidophore production research - the resulting stearate mixtures were gel-like and firmer than the oleate mixtures at corresponding salt concentrations.

In connecting with polymerization phenomena, careful x-ray measurements by Harkins, Mattoon and Corrin (81) (107), and Mattoon and Mittelman (117), showed that the polymer molecules are ejected from the micelles as soon as they have reached a certain size and the x-ray spacings of the micelles return to their original value. As long as monomer is available in the system, the micelles are filled up again and the sequence of solubilization, activation, and initial propagation is repeated (118). Harkins, Mattoon and Corrin describe this process as follows:

"Thus, micelles which have been utilized as loci for the formation of polymer may be used over and over again as the reaction proceeds, so that the soap micelles would continue as loci through the entire course of the polymerization reaction, if it were not for a factor introduced by the polymer particles formed. These contain monomer, and the polymer-monomer particles absorb a monolayer of soap. Thus, soap present in the micelles changes into absorbed soap. This causes the disappearance of the micelles at some yield of polymer, which, with the standard formula, appears to be below 20 %."

EXPERIMENTAL

1. Apparatus

a) Measuring Apparatus - Electrical Conductivity and Viscosity

There were three measuring apparatus employed, known as "Apparatus No. 3, 5 and 6". All were constructed of high quality 1 mm. thick 'soft' glass and consist of three sections - the reservoir and degassing section with a volume of 500 - 550 cc., the electrical conductivity arm and the viscosity arm. Apparatus No. 3 can be seen in figure 26.

Figure 29 is the actual size drawing of the apparatus from which the three vessels were constructed. The point at the top of the viscosity arm (seen both in the drawing and figure 26) for centering the metal ball was omitted and the top left rounded as it was found that gases collected there during the tests.

Figure 27 shows the conductivity measuring cell with the capillary measuring tube (not used). In figure 28 the electrode arrangement can be seen more clearly. The electrodes are composed of two vertical, bright, 0.085 mm. thick platinum plates, each approximately 11.5 by 6.5 mm. and from 2 to 3 mm. apart. Each plate is secured to its glass support by three platinum wires sealed into the glass, the top one of which is connected to the spiral platinum contact wire in the hollow glass support tube leading to the outside to connect into the circuit.

Figure 30 shows the viscosity measuring arm with the two horizontal lines approximately 3 cm. apart circling the tube, between which the fall-time of the 0.050 cm. diameter steel ball is measured.

Also, as required by this method, the measuring lines are equally spaced between the top and bottom of the arm, so that the fall-velocity is measured in the middle of the tube axis.

Convenient volumes of the liquid under test for the two arms are, in cc.:

	Apparatus No. 3	5	6
Conductivity arm	28	38	35
Viscosity arm	65	75	65

In practice it was found better to put a little more of the liquid than the volume actually required into the reservoir, i.e. 100 to 120 cc.

A ground glass joint protruding horizontally from the center of the apparatus fits into a female joint on the high vacuum line for support and degassing. At this joint a high quality vacuum grease (Soft Grade High Vacuum Grease, W. Edwards and Co., London, Ltd.) is used to ensure a perfect seal. The apparatus can be turned about the axis of this joint to effect degassing and filling of the two measuring arms.

b) Zeiss Abbe Refractometer - Refractive Index

The refractive index was measured using a direct reading Zeiss Abbe Refractometer reading to 0.0001, and employing an ordinary tungsten filament light bulb as light source. The refractometer was so made that the prism and liquid could be liquid - (in this case 'industrial alcohol') cooled or warmed for readings at various temperatures. The thermometer was built in and could be read to 0.5^oC.

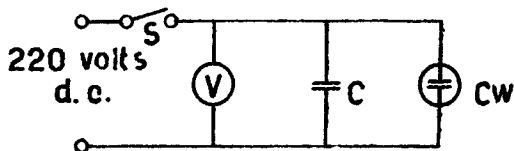
Since not strictly absolute values, but only comparative variations of the refractive index were of interest, the thermometer was considered to read correctly and no correction was made for the lack of sodium light source.

2. Formulas and Constants

a) Electrical Conductivity

1) General

The direct current (d.c.) 'fall-in-potential' method was used, the electrodes, with a d.c. voltmeter and condenser of known capacitance in parallel, being charged to a certain tension, the circuit broken, and the time for the voltage (as indicated by the voltmeter) to fall from an initial to a lower voltage measured. This fall-in-potential time is inversely proportional to the conductivity of the liquid surrounding the electrodes. Schematically, the circuit is shown here -



where S = switch

V = voltmeter (0-300 volts d.c.)

C = condenser

CW = conductivity cell

The appropriate equation for the specific (volume) conductivity, χ , is thus -

$$\chi = \frac{C_w \cdot C \cdot \ln \frac{V_1}{V_2}}{t} \text{ mho/cm.} \quad (119)$$

where C_w = resistance capacity of the electrode arrangement,
or, more commonly, the "cell constant" (cm.⁻¹)

C = condenser capacity (F, farads)

V_1 = initial voltage (volts)

V_2 = final voltage (volts)

t = discharge time from V_1 to V_2 (seconds)

In all tests V_1 and V_2 were 200 and 100 volts respectively and therefore -

$$\ln (\text{natural logarithm}) \frac{V_1}{V_2} = \ln 2 = 0.6931$$

It was first necessary however, to standardize the condensers (C) and determine the cell constants (C_w) of the three apparatus.

2) Condenser Standardization

For this a Siemens and Halske 'Small Capacity Measuring Bridge', with a supplementary condenser for the three larger capacities, a Siemens and Halske 'Magnetic Hummer', earphones, and a two volt storage battery were used. The correct capacities were quickly found by connecting the unknown condenser into the bridge and current supply circuit, balancing the bridge, and reading off the indicated capacity value.

For the variable condenser (B31²) only the largest capacitance of 1254 $\mu\mu\text{F}$ was measured using the bridge. The smaller capacities down to 175 $\mu\mu\text{F}$ were then calculated from the discharge time through an oil mixture at constant temperature, as the capacity measuring bridge was not accurate enough at the lower values.

The results are tabulated here -

Condenser	Capacity given as	Standardized as
831 ² -Cambridge Instrument Co. Ltd., England	100 $\mu\mu$ F	175 $\mu\mu$ F
	200	278
	300	372
	400	473
	500	566
	600	670
	700	768
	800	866
	900	958
	1000	1047
	1100	1150
1200	1252	
C6/1-Solar Mfg. Corp., N.Y.	0.0066 μ F	0.0044 μ F
	0.052 μ F	0.049 μ F
19648-Xamax A.G., Zurich	0.4 μ F	0.49 μ F

The condensers were standardized just before and after the measurements and the same values obtained. The smaller, variable condenser had previously been found to vary over a long period of time.

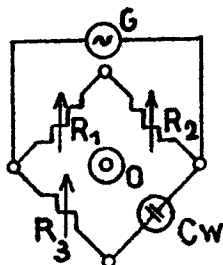
3) Cell Constant Determination

This was accomplished by measuring the resistance of the electrode arrangement in a solution of known conductivity.

Potassium chloride solution, widely used in conductivity work, was used. The conductivities of its solutions at different temperatures have been accurately determined and checked by several researchers (20). All care and precautions were taken in preparing the solutions and in cleaning the conductivity cell. Merck's (Darmstadt) 'Kalium Chloratum pro Analysisi' was used in fresh, double distilled water to make up a 0.01N solution (i.e. 0.7456 grams of potassium chloride per liter).

A Wheatstone bridge arrangement was used to measure the cell resistance, employing a Philips oscillograph as balance indicator and a Philips frequency generator for the alternating current (a.c.) input.

The measuring circuit is shown here schematically -



- where R_1 , R_2 and R_3 = Siemens and Halske variable plug resistance boxes, 0.1 to 111,111 ohms
 C_w = conductivity cell
 O = Philips oscillograph
 G = Philips frequency generator

The resistance could be measured to ± 1 ohm which is an error of less than 1% over the range measured. Except for Apparatus No.6, where the cell constant was determined for all three temperatures, 0, 10 and 20°C, the resistance was measured only at the middle temperature of 10°C. As seen from the results (below) the cell constant varies very little over the 20° temperature range, and thus it was considered safe to use only the middle (average) constant at 10°C for all the calculations.

The results are tabulated here -

Apparatus No.	Temperature °C	Specific Conductivity mho/cm.	Resistance ohms	Cell Constant cm. ⁻¹	Average Constant cm. ⁻¹
		χ	R	$(\chi \cdot R)C_w$	C_w
3	10	0.001020	194	0.198	0.198
5	10	0.001020	182	0.186	0.186
6	0	0.000776	199	0.154	0.156
	10	0.001020	153	0.156	
	20	0.001278	123	0.157	

This value for Apparatus No. 3 is the final one. However, prior to this determination the apparatus was damaged and repaired, but first used in measuring

certain conductivities reported later, in Tests No. 2 and 7. It then had a slightly lower cell constant of 0.194 cm.^{-1} , and where it was used with this value will be found indicated in the "MEASUREMENTS and RESULTS" chapter.

The greatest accuracy was obtained using a 0.4 volt input at a frequency of 2 kilohertz. Frequencies up to 10 kilohertz led to the same results and so we can therefore assume that by measuring at 2 kHz we are safely above the polarisation frequency range (Wien effect) for the resistance measuring method used and its accuracy. New measurements after a four month period of use produced the same results.

4) Resulting Equation Constants

The cell constants and capacity values can now be set in the conductivity equation given previously (page 34), and we arrive at an equation constant for each combination of apparatus and condenser used, which must only be divided by the discharge time, t , to give the specific electrical conductivity of the liquid in reciprocal ohm-centimeters (mho/cm.).

For example, using Apparatus No. 3 and the smallest capacity of $175 \mu\text{F}$ we have

$$\begin{aligned} C_w &= 0.198 \text{ (cm.}^{-1}\text{)} \\ C &= 175 \times 10^{-12} \text{ (F)} \\ \log \frac{V_1}{V_2} &= 0.6931 \end{aligned}$$

and setting in the equation gives -

$$\begin{aligned} X &= \frac{0.198 \cdot 175 \times 10^{-12} \cdot 0.6931}{t} \\ &= (2.39 \times 10^{-11}) \cdot t^{-1} \text{ mho/cm.} \end{aligned}$$

the so-called 'equation constant' here being 2.39×10^{-11} .

The equation constants are given below, as well as the capacitance signs used later for convenience in tabulating the results -

Sign	Capacity	Equation Constant $\times 10^{-11}$		
		Apparatus No. 3	5	6
o	$175 \mu\text{F}$	2.39	2.24	1.88
	278	3.78	3.55	2.98
	566	7.71	7.24	6.06
	1047	14.3	13.4	11.2
	$0.0044 \mu\text{F}$	60.4	56.7	47.6
	0.049	673	631	529
+	0.49	6730	6310	5290

The specific conductance ranges of these cells possible with this drop-in-potential method are approximately from 6.7×10^{-9} mho/cm. using the largest capacity of $0.49 \mu\text{F}$ with Apparatus No. 3 and a discharge time of 10 seconds, to 1.6×10^{-14} mho/cm. using the smallest capacity of $175 \mu\text{F}$ with Apparatus No. 6 and a discharge time of 20 minutes. A discharge time of less than 10 seconds is not accurate, nor is a discharge time of more than 20 minutes accurate due to current leakages.

b) Viscosity

1) General

The 'falling-ball' method is here used. A small spherical steel ball of 0.05 mm diameter is allowed to fall from the top of the arm down the axis of the vertical viscosity tube. Its time of fall between two horizontal circular lines drawn on the glass is measured and is proportional to the liquid's viscosity.

In this method, based on the free fall of a sphere through a liquid in a cylindrical vessel, we can use the Stokes-Ladenburg-Faxen equation to give the viscosity, k . This equation is -

$$k = \frac{2}{9} \cdot g \cdot R^2 \cdot \frac{S - S_0}{V(1 + 2 \frac{R}{\infty})(1 + 3.3 \frac{R}{h})} \text{ poise} \quad \begin{matrix} 121) \\ 122) \end{matrix}$$

where g = acceleration of gravity = 981 (cm./sec.²)

R = ball radius = 0.025 (mm.)

V = ball fall velocity = $\frac{d}{t}$ (cm./sec.)

d = distance between measuring lines (cm.)

t = ball fall time between lines (seconds)

S = ball density = 7.8 (gm./cm.³)

S_0 = liquid density (gm./cm.³)

∞ = vessel radius (cm.)

h = vessel height (cm.)

(1 poise = 1 dyne second cm.⁻² = cm.⁻¹ gram second⁻¹)

The physical dimensions of the viscosity arm are -

Apparatus No.	3	5	6
d (cm.)	3.0	3.1	3.0
∞ (cm.)	1.68	1.65	1.65
h (cm.)	9.82	11.45	10.07

A former member of the Institute for Technical Physics employed a Höppler Viscometer of similar dimensions to the viscosity measuring arms above, in tests to prove the validity of the Stokes-Ladenburg-Faxen equation. The same oil used in both apparatus gave results in excellent agreement with one another and within the accuracy of measurement.

2) Resulting Equation Constants

Substituting the dimensions and constants in the equation given previously (page 38), we can obtain easily handled equations for each of the three apparatus, in which only the liquid density, S_0 , and ball fall time, t , must be set to give the viscosity, k .

Using Apparatus No. 3 as an example we get -

$$k = \frac{2}{9} \cdot 981 \cdot (0.025)^2 \cdot \frac{7.8 - S_0}{\frac{3.0}{t} (1+2.1 \frac{0.025}{1.68})(1+3.3 \frac{0.025}{9.82})}$$

$$= 0.04226 (7.8 - S_0) t \text{ poise.}$$

Similarly, for Apparatus -

$$\text{No. 5, } k = 0.04229 (7.8 - S_0) t \text{ poise}$$

$$\text{No. 6, } k = 0.04225 (7.8 - S_0) t \text{ poise}$$

The liquid density used for each of the nine separate tests was that of the 'starting mixtures' at the middle measurement temperature, 10°C. These densities are given for each test in the "MEASUREMENTS and RESULTS" tables following.

3. Materials Used

The CY1 petroleum oil is a paraffin-base hydrocarbon from the Shell Oil co., England (through Lumina A.G., Zurich), and is of a linear configuration. As received it had a specific weight of 0.894 at 20°C, viscosity of about 2.7 poise at 20°C and 0.40 poise at 50°C, refractive index of 1.4996 at 20°C, and a flame point of 225°C. After further distillation and filtration, the fractions suitable as to vapour pressure ($< 1 \times 10^{-6}$ mm. mercury) had refractive indices from 1.485 to 1.55 at 20°C, a dielectric constant of approximately 2.2 at room temperature, and an almost unmeasurable electrical conductivity.

The BE₂ oil, now universally called 'Carnea oil 41', obtained from the same source as the CY1 oil, is an acid purified naphthenic-base petroleum oil, and thus is essentially of a cyclic configuration. It is not highly purified (refined) and its delivery specifications are: specific weight 0.929 at 20°C; viscosity ca. 4.03 poise at 20°C and 0.51 poise at 50°C; and flame point ca. 210°C.

The naphthenic acid was obtained from the commercial acid (Lumina A.G., Zurich) having a molecular weight of 150-400. This commercial acid was fractionated and the middle of the three Fractions obtained further fractionated to six fractions. The 5th and 6th fractions, colourless and favourable as to vapour pressure and with a molecular weight of 250 to 280, were then used for the production of the systems investigated.

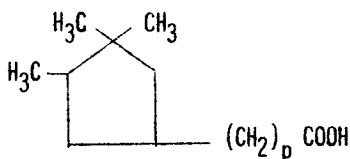
True naphthenic acids are probably normal constituents of all crude mineral oils to the extent of 0.03 to 8% (23). Generally, oils rich in paraffins are low in naphthenic acids and vice versa. These acids are the carboxylic derivatives of cyclo-paraffin hydrocarbons and have found extensive application in the form of their metallic salts. They also find use in reducing the viscosity of colloidal solutions and preventing gelatinizing of tung oil on heating. The separated oils are impure but by distillation a purity of about 93% can be obtained. Specific gravities are usually in the range of 0.96 to 0.99, and acid numbers, 165 to 315 (24).

It has been shown that naphthenic acids contain three classes of acids which differ in hydrogen content (25):

$C_n H_{2n+1} COOH$ are chiefly paraffin carboxylic acids and occur in the lower boiling fractions of the mixture.

These acids contain 6 or 7 carbon atoms and are colourless..

$C_n H_{2n-1} COOH$ or structurally -



Mainly a more or less highly alkylated five-carbon ring or a double carbon ring, while in the side chain, $p=0$ to 5 or more. Compounds of $p=0$ predominate and of $p=0$ are a minority. These acids are chiefly those containing 8-12 carbon atoms and may include some paraffin carboxylic acids. Bell (26) lists nine such acids of this type containing from 6 to 14 carbon atoms that have been isolated from crude oil, and having boiling point ranges increasing from 215 to 310°C with increasing number of carbon atoms.

$C_n H_{2n-3} COOH$ includes acids containing 12 to 23 carbon atoms.

The commercial acids are combinations of these and thus liable to wide variations when obtained from different sources.

Hexaline naphthenate was made by combining the suitable naphthenic acid fractions with cyclohexanol (hexalin). The resulting ester is, of course, cyclic

with 5 and 6 carbon atom rings. Cyclohexanol (Siegfried A.G., Zofingen), $C_6H_{11}OH$, is a colourless, oily, hygroscopic liquid of molecular weight 100.16, density 0.9624 at 20°C, boiling point 161.5°C (127), specific gravity 0.937 at 37°C and refractive index 1.465 at 22°C (124). It is sparingly soluble in water but infinitely soluble in benzene, turpentine, carbon disulphide and miscible with most organic solvents and oils.

Tricresyl phosphate (tolyl phosphate) (Siegfried A.G., Zofingen) was obtained by distillation of the commercial product to obtain a fraction suitable as to vapour pressure. It is a colourless, practically odourless isomeric liquid mixture of formula $(CH_3C_6H_4)_3PO_4$, molecular weight 368.36 grams (127), refractive index 1.554-1.556 at 25°C, boiling point 410°C at 760 mm. mercury and 275 - 280°C at 20 mm. mercury (124), specific gravity 1.170-1.180 at 20°C, and dielectric constant of 6.92 at 40°C and 60 cps (27). The fractions used in the eidophore production have a viscosity of around 6.2 poise at 0°C and 2.0 poise at 10°C, and an electrical conductivity of about 65×10^{-11} mho/cm.

Ethyl ricinoleate $C_{18}H_{33}O_2C_2H_5$, was made by treating ricinoleic acid with ethyl alcohol. Its density is 0.918 at 15°C and 0.914 at 20°C, molecular weight 326.29, refractive index 1.4626 at 20°C, and boiling point 258°C at 13 mm. mercury. It possesses an optical rotatory power of 4.48 at 15°C (65).

The magnesium oleate was purchased commercially (Siegfried A.G., Zofingen) and further purified by crystallization from alcohol. It was then sealed in 500 cc. air tight glass containers after drying, and taken from this supply only as needed. It is a yellow, slightly hygroscopic powder of formula $(C_{18}H_{33}O_2)_2Mg$, and molecular weight 587.21 (127).

Magnesium oleate is an unsaturated substitution compound from the ethylene or olefine series, and usually made by the double decomposition method from magnesium chloride and sodium oleate, the product being crystallised from alcohol and dried. Nearly insoluble in water, it is soluble in alcohol, ether, benzene, linseed oil, etc.

Because of its reasonable cost, inertness towards textiles, and effectiveness at low concentrations, magnesium oleate finds use in the textile cleaning industry since it raises the electrical conductivity of the solvent to a point where the electrical charges from the vigorous motion of the textiles are dissipated as they form.

Further information concerning these materials, their properties and reactions, and those of related compounds, is to be found in the "LITERATURE SURVEY" chapter.

4. Liquid Compositions Tested

While in making up the starting mixtures for each of the nine tests it was attempted to have the proportions of the added substances ('A', tricresyl phosphate and naphthenic acid and 'B', ethyl ricinoleate) as close as possible to those of the oils 'Lau 84' and 'E 39', as mentioned previously (page 9) the actual proportions varied slightly and are given below in percent by weight -

Test No.	Basic Substance		Added Substances		
			Tricresyl Phosphate	A Naphthenic Acid	B Ethyl Ricinoleate
1	CY1 oil (10/7 filtered at -10°C)	98.26	1.00	0.74	
2	CY1 oil (9/6 filtered at -2°C)	97.080			2.920
3	Hexaline naphthenate (4th Fr. HVD(6) Acid No.-17.3)	100.00			
4	Hexaline naphthenate (4th Fr. HVD(6) Acid No.-4.49)	100.00			
5	Hexaline naphthenate (4th Fr. HVD(6) Acid No.-4.49)	98.258	0.998	0.744	
6	Hexaline naphthenate (4th Fr. HVD(6) Acid No.-4.49)	97.076			2.924
7	BE ₂ oil (4th Fr. 2ndHVD unrefined)	98.264	0.983	0.753	
8	BE ₂ oil (4th Fr. 2nd HVD unrefined)	97.074			2.926

Test No.	Basic Substance	Tricresyl Phosphato	Naphthenic Acid	Ethyl Ricinoleate
9	BE2 oil (4th Fr. 2nd HVD refined)			97.078 2.922

5. Procedure

a) Magnesium Oleate Addition

1) General

After a series of measurements air is let into the apparatus and the viscosity ball retrieved using a magnet. Then the oil measuring apparatus is emptied of its oil contents into a weighed, 1 liter, round-bottomed, long-necked pyrex glass flask. This was facilitated by using a special long-stem funnel, so that no liquid remained behind on the flask's neck. When cool the flask and oil were weighed, and the weight of the oil found.

A small quantity of magnesium oleate was taken from one of the sealed glass ampules and stored in an air-tight flask for use during each series of measurements. Sufficient oleate (1-1.5 grams) was then transferred to an air-tight weighing bottle as required to raise the oleate content of the oil mixture by approximately 1%, and added to the oil in the long-necked flask through a smooth paper tube, so that it all landed directly on the oil's surface and non adhered to the flask's neck. The weight difference of the weighing bottle plus magnesium oleate before and after the addition, weighed to the nearest 0.0001 gram, then gave the amount of magnesium oleate added.

The oleate was dissolved and the mixture made uniform throughout by heating and agitation under a vacuum of ca. 3×10^{-2} mm. mercury to thoroughly degas the mixture.

It was found impractical and unnecessary to filter the mixture after each addition due to the high loss of liquid by so doing, the results of the measurements remaining essentially the same whether filtered or not. All care was taken throughout to avoid contamination of the liquid. Only Tests No. 1, 3 and 7 were filtered after every other oleate addition.

The measuring apparatus and weighing flasks were thoroughly cleaned by using one after the other, several fresh quantities of trichlor ethylene, ethyl alcohol, and lastly, ether.

They were then either evacuated to dryness or dried by compressed filtered air.

The new mixture was then poured warm into the reservoir of the cleaned measuring apparatus, the steel ball put in, the apparatus connected into the vacuum line, and vacuum applied. By gentle heating and agitation of the oil in the reservoir it was thoroughly degassed. Then, by carefully turning the apparatus about the axis of the vacuum joint into its upright position (figure 26), the two measuring arms could be filled with the appropriate volume of liquid and the next series of measurements begun. During measurements the mixture remained always under a vacuum of from 1.5 to 3.5×10^{-2} mm. mercury.

2) Sample Calculation

The sample calculation given here is for Test No. 1, 4th addition (between measurements No. 4 and 5). All figures represent grams except where otherwise shown.

Flask + ring support + oil = 427.60
 Flask + ring support = 211.10
 Hence oil weight = 216.50

Weighing bottle + oleate (1) = 16.8807
 Weighing bottle + oleate (2) = 14.2187
 Hence magnesium oleate added = 2.6620

Oil composition following 3rd (previous) addition:

CY1 oil	225.282
Tricresyl phosphate	2.292
Naphthenic acid	1.691
Magnesium oleate	<u>7.8466</u>
Total weight	= 237.1116

Hence, composition after 4th addition:

Constant = 216.50 = 0.9131
 237.1116

(an actual weight divided by a calculated weight)

CY1 oil = 225.282 x 0.9131	= 205.705
Tricresyl phosphate = 2.292 x 0.9131	= 2.093
Naphthenic acid = 1.691 x 0.9131	= 1.544
Magnesium oleate = (7.8466 x 0.9131)	
+ 2.6620	= <u>9.8267</u>
Total weight	219.1687

Thus, magnesium oleate % (by weight) = $\frac{9.8267 \times 100}{219.1687} = 4.484\%$

3) Calculation Accuracy and Loss per Run

The compositions were calculated after each addition by combining an actual weight with a theoretical (calculated) weight, as noted above. The theoretical weights, for example, of the four components in Tests No. 1, 5 and 7 when added gave a total weight differing by at most only $\pm 0.01\%$ from the actual, when weighed to the nearest 0.01 gram.

Between successive measurements the loss of oil from pouring in and out of the two vessels varied from 3 to 11 grams, following the operations of emptying, addition, mixing and pouring into the measuring apparatus again.

b) Measurement

1) General

For temperature control both an electric cooling machine employing freon (CCl_2F_2) (Autofrigor A.G., Zurich) and a dry ice cooling apparatus were used, each in conjunction with a thermostat. Both conductivity and viscosity measurements could be carried out simultaneously using the two thermostats.

The two thermometers used for the cell constant determinations and all the tests were graduated in $1/10^\circ\text{C}$ and could be read to 0.05°C . They were first compared with a precision thermometer before use. The precision thermometer being considered correct, the two thermometers used did not differ from it by more than $\pm 0.05^\circ\text{C}$ at the temperatures of 0, 5, 10, 15 and 20°C . The small corrections necessary were taken into account during measurement, however.

Glass cooling vessels were made specially to fit about the two measuring arms of the measuring apparatus, alcohol being used as the cooling medium in the cooling vessels. In the case of the viscosity arm, it was entirely immersed in the cooling liquid.

Vacuum was obtained by an oil vacuum pump (Micafil A.G., Zurich) driven by an electric motor (Brown Boveri & Co., Baden).

2) Electrical Conductivity

The circuit employed for this d.c. drop-in-potential method has been shown previously (page 33).

After allowing time for constant temperature to be reached, at least an hour, and more at the lower temperatures, the measurements were made as follows - 220 volts d.c. were passed through the circuit until the voltmeter showed a constant value (a few seconds), the circuit was then broken and the time for the potential as shown by the voltmeter to drop from 200 to 100 volts taken

with a stop-watch reading to 1/10 second. This was repeated until at least three consecutive results in good agreement with one another were obtained, indicating that the temperature was constant throughout the liquid. The average of these results was then taken for use in the conductivity equation (pages 33 and 37) to give the conductivity at that particular temperature. This average measured time is that given in the "MEASUREMENTS and RESULTS" to follow.

As an example of the measuring accuracy, using the measurements for Test No. 1, an overall average deviation of $\pm 0.39\%$ or ± 0.27 seconds, at an overall average measuring time of 68 seconds was obtained. This shows that the results have an inaccuracy of only 0.3% using the largest capacity ($0.49\mu F$) to less than 0.5% using the smallest ($175\mu F$).

3) Viscosity

The falling ball method here employed is easily carried out and quite suitable for our liquids and conditions, giving accurate and reproducible results.

After a suitable length of time was allowed for constant temperature to be attained throughout the liquid, the small steel ball was raised to the top of the vertical viscosity arm with either a permanent or an electro-magnet. The cooling vessel was briefly removed from about the arm in order to do this, then replaced. The time required for the ball to fall down the axis of the arm, between the two horizontal measuring lines, was then taken using a stop-watch reading to 1/10 second. This was repeated with slight pauses between measurements, until at least three consecutive results in good agreement with one another were obtained. The average of these results was then taken as the result at that particular temperature, and set in the viscosity equation (pages 38 and 39) to obtain the viscosity. This average result is that reported under "MEASUREMENTS and RESULTS".

As the magnesium oleate content reached high proportions in the mixtures containing CY1 and BE2 oils, the viscosity reached very high values, and it was only practical, due to the extremely slow fall of the ball, to make one or at most two measurements, making sure that more than sufficient time had first been allowed for constant temperature to be reached. At very high oleate concentrations it was sometimes not possible to measure the viscosity at all, the mixture being practically solid at $20^{\circ} C$ and under. Such cases have been noted in the "MEASUREMENTS and RESULTS".

An analysis of the measurements made in Test No. 1 shows an overall measurement deviation of only $\pm 0.60\%$ or ± 0.74 seconds for consecutive measurements. Therefore, the average result variation is ± 0.215 poise for consecutive measurements, meaning the results are accurate from $\pm 2.3\%$ at the lowest viscosity measured (9.32 poise), to $\pm 0.009\%$ at the highest measured (2318.3 poise).

4) Refractive Index

One reading was made with the refractometer at each temperature. Only a drop of the mixture was required for each series of measurements, and this was transferred from the mixing flask to the prism with a clean glass rod. The prism was cleaned each time with cotton baton soaked, one after another, in trichlor ethylene, ethyl alcohol, and lastly, ether.

Due to the very thin layer of liquid required, arriving at a constant temperature was no problem. Either one of the thermostats was used for the temperature control.

Measuring to 0.0001, the result accuracy is better than 0.01 %.

MEASUREMENTS and RESULTS

These are tabulated on the pages (48 to 73) immediately following. Under each test is given the composition of the starting mixture, its density at 10⁰ C, and which of the three measuring apparatus was used.

Each set of measurements and results is shown in two adjacent columns, the left hand one giving the conductivity measurements and under it the viscosity measurements, in seconds, and opposite, in the right hand column, the resulting values of these properties. The refractive index value, being read directly, is given in the right hand 'result' column. Above each two column set of measurements and results is given the number of the measurement and under it the magnesium oleate % by weight in the mixture.

The measurement temperature is indicated to the left of Measurement No. 1 and repeats similarly for each set of measurements and results, although only mentioned the first time. The conductivity and viscosity units are also only indicated for Measurement No. 1, but hold similarly for the following sets.

Between each conductivity measurement and result is given a symbol, which, when compared with the legend included in Test No. 1 (page 48), and also given under "FORMULAS and CONSTANTS" (page 37), shows the capacitance used for that particular measurement.

Test No. 1

Starting Mixture: CY1 oil 10/7 (filtered at -1 C)	98.26 %
Tricresyl phosphate 4th Fr. 2 Lt. Dist. App.	1.00 %
Naphthenic acid Barrel 1 HVD(6)5	0.74 %

Using Apparatus No. 5

Measurement No. 1
Magnesium oleate % 0.00

		0°C	0	secs.	0	$\times 10^{-11}$	mho/cm.
Conductivity							
Viscosity k			263.4	"	76.7		poise
Refractive index n					1.5129		
		5°C	0	"	0	$\times 10^{-11}$	mho/cm.
o C=175 $\mu\mu$ F			145.0	"	42.1		poise
V =278 "					1.5109		
x =566 "							
⤿ =1047 "		10°C	0	"	0	$\times 10^{-11}$	mho/cm.
Λ =0.0044 μ F			80.3	"	23.3		poise
= =0.049 "					1.5092		
+ =0.49		15°C	0	"	0	$\times 10^{-11}$	mho/cm.
			52.7		15.3		poise
Density, So, of the starting mixture at 10°C=0.928 gm/cm ³		20°C	0	"	0	$\times 10^{-11}$	mho/cm.
			32.6	"	9.46		poise
					1.5055		
2				3		4	
1.11				2.13		3.31	
407.0	o	0.00028	123.3	⤿	0.0932	86.3	Λ 0.658
262.5		76.2	266.9		77.4	266.0	77.2
		1.5124			1.5121		1.5118
236.8	o	0.00049	72.8	⤿	0.158	43.9	Λ 1.29
145.1		42.1	147.0		42.7	150.1	43.6
		1.5107			1.5103		1.5100
131.7	o	0.00087	41.3	⤿	0.278	26.4	Λ 2.15
83.2		24.1	85.1		24.7	89.5	25.9
		1.5089			1.5085		1.5082

Test No. 1 (continued)

753.0	o	0.00153	26.6	∩	0.432	15.9	∧	3.57
51.2		14.9	51.3		14.9	54.3		15.7
		1.5070			1.5068			1.5064
46.7	o	0.00246	16.6	∩	0.693	10.1	∧	5.62
32.1		9.32	33.3		9.66	33.5		9.72
		1.5052			1.5050			1.5046
		5			6			7
		4.48			5.50			6.45
48.9	∧	1.16	44.1	∧	1.29	43.1	∧	1.32
289.2		83.8	323.9		93.9	351.1		101.8
		1.5118			1.5112			1.5112
26.1	∧	2.17	23.0	∧	2.46	22.4	∧	2.53
259.5		46.3	178.4		51.8	188.8		54.8
		1.5099			1.5095			1.5093
14.7	∧	3.86	125.1	—	5.04	119.0	—	5.31
94.5		27.4	102.5		29.8	111.1		32.2
		1.5080			1.5077			1.5075
82.7	—	7.64	72.7	—	8.69	68.4	—	9.24
57.3		16.6	62.2		18.0	67.6		19.6
		1.5062			1.5059			1.5056
49.9	—	12.7	42.6	—	14.8	40.5	—	15.6
36.3		11.1	38.6		11.2	41.0		11.9
		1.5041			1.5041			1.5038
		8			9			10
		7.20			8.28			9.13
55.7	∧	1.02	115.4	∧	0.491	121.1	∧	0.469
530.3		153.8	3060		887.4	7994		2318.3
		1.5108			1.5106			1.5106
28.6	∧	1.98	56.1	∧	1.01	57.4	∧	0.989
272.1		79.0	1105		320.5	1962		569.0
		1.5090			1.5088			1.5088

Test No. 1 (continued)

154.3	—	4.10	28.0	Λ	2.02	27.8	Λ	2.04
153.2		44.4	446		129.3	673.4		195.3
		1.5072			1.5070			1.5070
83.3	—	7.59	14.8	Λ	3.83	14.3	Λ	3.97
88.4		25.6	224.3		65.1	289.8		84.0
		1.5053			1.5052			1.5049
47.2	—	13.4	8.2	Λ	6.92	8.0	Λ	7.10
53.9		15.6	119.6		34.7	145.8		42.3
		1.5035			1.5033			1.5031
		11						13
		10.14			12			11.44
					10.89			
217.7	Λ	0.260	115.0	Λ	0.493	36.0	Λ	157
			592.6		171.9	26885		137.7
		1.5099			1.5101			1.5102
110.8	Λ	0.511	53.4	Λ	1.06	19.6	Λ	2.89
			277.0		80.3	1357.6		69.6
		1.5081			1.5082			1.5083
50.0	Λ	1.17	30.4	Λ	1.87	10.4	Λ	5.45
			155.7		45.2	133.2		38.8
		1.5064			1.5069			1.5069
24.7	Λ	2.29	13.5	Λ	4.20	54.8	—	11.5
3120		905.1	88.5		25.7			
		1.5045			1.5048			1.5049
12.0	Λ	4.72	6.8	Λ	8.34	32.0	—	19.7
920		266.9	52.5		15.2			
		1.5028			1.5028			1.5028

Test No. 1 (continued)

14 13.69	15 15.52	16 19.68
563.2 Λ 0.101 quite firm 1.5097	655.0 Λ 0.087 quite firm 1.5090	100 o 0.0012 quite firm 1.5082
213.2 Λ 0.27 quite firm 1.5076	296.7 Λ 0.19 quite firm 1.5073	35 o 0.0033 quite firm 1.5071
119.1 Λ 0.48 quite firm 1.5064	125.8 Λ 0.45 quite firm 1.5055	14.6 o 0.0079 quite firm 1.5050
60.6 Λ 0.94 quite firm 1.5043	71.8 Λ 0.79 quite firm 1.5035	65.2 \odot 0.0176 quite firm 1.5031
30.6 Λ 1.85 quite firm 1.5027	30.7 Λ 1.85 quite firm 1.5018	47.6 \odot 0.0242 quite firm 1.5012

Test No. 2

Starting Mixture: CY1 oil 9/6 (filtered at -2°C) 97.080 %
 Ethyl ricinoleate 2nd Fr. HVD 305 2.920 %

Using Apparatus No. 6	Measurement No.	1						
	Magnesium Oleate %	0.00						
Conductivity	0°C	848.6	o	secs. 0.00221 x 10 ⁻¹¹ mho/cm.				
Viscosity k		175.4	"	50.9 poise				
Refractive index n				1.5114				
	10°C	750.0	o	" 0.00251 x 10 ⁻¹¹ mho/cm.				
Density, S _o , of starting mixture at 10°C = 0.926 gm/cm ³		55.1	"	" 16.0 poise 1.5076				
	20°C	420.0	o	" 0.00448 x 10 ⁻¹¹ mho/cm.				
		22.0	"	" 6.38 poise 1.5038				
	2		3	4				
	0.96		1.93	3.15				
11.2	o	0.168	55.0	∩	0.202	9.9	∩	1.13
176.3		51.2	174.4		50.6	167.8		48.7
		1.5111			1.5108			1.5105
13.1	x	0.463	24.8	∩	0.451	14.3	∧	3.33
58.0		16.8	57.2		16.6	60.6		17.6
		1.5073			1.5070			1.5068
10.3	∩	1.088	9.6	∩	1.17	60.5	∩	8.74
22.7		6.58	22.4		6.50	23.9		6.94
		1.5035			1.5032			1.5030
	5		6		7			
	4.10		4.97		6.06			
44.6	∧	1.07	46.2	∧	1.03	51.0	∧	0.934
221.0		64.1	255.7		74.1	380.9		110.4
		1.5099			1.5099			1.5097
14.0	∧	3.40	12.6	∧	3.78	14.6	∧	3.26
71.2		20.6	77.5		22.5	107.1		31.1
		1.5063			1.5063			1.5060

Test No. 2 (continued)

47.2	—	11.2	44.4	—	11.9	46.1	—	11.5
27.1		7.86	30.4		8.81	38.3		11.1
		1.5028			1.5028			1.5022
	8			9			10	
	6.87			7.84			9.01	
76.8	Λ	0.620	76.7	Λ	0.620	32.2	⊖	0.348
759.9		220.0	2040		592.0	too solid		
		1.5095			1.5096			1.5093
21.6	Λ	2.20	22.0	Λ	2.16	32.9	Λ	1.45
211.0		61.2	372.3		108.0	too solid		
		1.5058			1.5059			1.5056
6.4	Λ	7.44	73.2	—	7.22	12.2	Λ	3.90
66.2		19.2	102.7		29.8	519.6		151.0
		1.5021			1.5022			1.5019
	11			12			13	
	9.85			11.09			12.11	
25.7	⊖	0.436	49.4	⊖	0.227	32.7	x	0.185
too firm			too firm			too firm		
		1.5089			1.5089			1.5088
29.9	Λ	1.59	12.4	⊖	0.903	9.0	x	0.674
1680		487.0	too firm			too firm		
		1.5052			1.5052			1.5051
85.7	—	6.17	18.7	Λ	2.55	25.2	Λ	1.89
292.1		84.7	too firm			too firm		
		1.5015			1.5014			1.5012
	14			15			16	
	13.26			14.07			15.13	
37.2	x	0.163	38.5	x	0.158	48.1	x	0.126
too firm			too firm			too firm		
		1.5086			1.5085			1.5082

Test No. 2 (continued)

13.5	x	0.449	10.4	x	0.583	12.7	x	0.478
too firm			too firm			too firm		
		1.5048			1.5047			1.5044
7.6	⤿	1.47				8.8	⤿	1.27
too firm			too firm			too firm		
		1.5010			1.5010			1.5006

Test No. 3

Starting Mixture: Hexaline naphthenate 4 th Fr. HVD(6), (Acid No.=17.3)

Using Apparatus No. 5, Measurements 1-12

No. 3, Measurements 13-20, Cell constant $C_w=0.194 \text{ cm.}^{-1}$

and No. 3 repaired, Measurements 21-22, Cell constant $C_w=0.198 \text{ cm.}^{-1}$

		Measurement No.		1				
		Magnesium oleate %		0.00				
Conductivity	0°C	372.6	o	secs.	0.00600 x 10 ⁻¹¹ mho/cm.			
Viscosity k		138.3		"	40.0 poise			
Refractive index n					1.4995			
	10°C	114.4	o	secs.	0.0196 x 10 ⁻¹¹ mho/cm.			
		41.6		"	12.0 poise			
					1.4957			
Density, S ₀ , of the starting mixture at 10° = 0.978 gm/cm ³	20°C	44.2	o	secs.	0.0507 x 10 ⁻¹¹ mho/cm.			
		12.2		"	3.5 poise			
					1.4919			
	2							
	1.09							
		3						
		1.96						
					4			
					3.04			
80.4	V	0.044	64.0	x	0.113	150.7	⊖	0.089
90.1		26.0	94.1		27.2	95.2		27.5
		1.4999			1.4998			1.5000
49.3	V	0.072	34.7	x	0.209	45.8	⊖	0.292
29.9		8.6	29.6		8.6	28.7		8.3
		1.4961			1.4961			1.4963
18.0	V	0.197	19.2	x	0.377	18.4	⊖	0.728
11.3		3.27	11.3		3.27	11.6		3.35
		1.4923			1.4924			1.4926
	5							
	4.04							
		6						
		5.14						
								7
								6.30
243.8	⊖	0.055	123.3	⊖	0.109	66.2	⊖	0.202
103.0		29.6	105.7		30.5	103.5		29.9
		1.4990			1.4988			1.4985

Test No. 3 (continued)

60.1	☺	0.223	41.9	☺	0.320	18.0	☺	0.745
33.0		9.5	33.2		9.6	40.7		11.8
		1.4955			1.4949			1.4951
19.8	☺	0.676	14.8	☺	0.905	8.0	☺	1.67
12.6		3.65	13.7		3.96	14.6		4.22
		1.4920			1.4910			1.4913
	8			9			10	
	7.10			8.13			9.11	
23.8	☺	0.563	17.3	☺	0.874	58.8	Λ	0.965
102.5		29.6	105.7		30.5	105.4		30.5
		1.4983			1.4986			1.4982
10.1	☺	1.33	6.8	☺	1.97	17.1	Λ	3.32
39.6		11.4	39.4		11.4	33.4		9.7
		1.4977			1.4947			1.4946
4.3	☺	3.12	2.2	☺	6.09	5.9	Λ	9.62
14.6		4.22	13.2		3.82	13.9		4.02
		1.4911			1.4909			1.4910
	11			12			13	
	10.09			10.94			11.98	
40.5	Λ	1.40	18.6	Λ	3.05	23.4	Λ	2.53
105.7		30.5	101.2		29.3	103.9		29.9
		1.4980			1.4980			1.4979
12.3	Λ	4.61	65.4	—	9.65	70.7	—	9.32
36.4		10.5	33.7		9.7	35.4		10.2
		1.4944			1.4942			1.4939
5.6	Λ	10.1	26.8	—	23.6	29.4	—	22.4
14.3		4.13	12.9		3.75	14.1		4.06
		1.4908			1.4905			1.4900

14
13.04
68.9 - 9.57
107.3 30.9
1.4981

21.7 - 30.4
34.6 10.0
1.4942

11.5 - 57.3
15.1 4.35
1.4902

17
16.12

19.4 - 34.0
114.5 33.0

9.2 - 71.6
37.1 10.7

34.6 + 190.5
16.9 4.87

20
19.46

23.3 - 28.3
515.8 43.7
1.4971

7.9 - 83.4
47.3 13.6
1.4934

28.3 + 233.0
19.8 5.70
1.4896

15
14.00

54.2 - 12.2
100.6 29.0
1.4980

18.7 - 35.2
36.7 10.6
1.4938

8.5 - 77.5
15.4 4.43
1.4896

18
17.16

35.3 - 18.7
113.6 32.7

12.2 - 54.0
35.4 10.2

47.0 + 140.0
16.2 4.67

21
20.25

52.8 - 12.8
146.8 42.3
1.4960

15.0 - 44.9
49.1 14.2
1.4923

58.5 + 115.0
19.6 5.65
1.4887

16
15.03

30.9 - 21.3
110.8 31.9

10.2 - 64.6
35.8 10.3

40.3 + 163.5
15.1 4.35

19
18.26

30.7 - 21.5
152.4 43.9
1.4968

10.0 - 65.9
50.0 14.4
1.4931

38.1 + 173.0
19.9 5.73
1.4892

22
20.89

39.2 - 16.9
159.2 45.8
1.4970

13.3 - 49.8
49.5 14.3
1.4932

50.0 + 132.5
19.9 5.73
1.4893

Test No. 4

Starting Mixture: Hexaline naphthenate 4th Fr. HVD(6), (Acid No. = 4.49)

Using Apparatus No. 6 Measurement No. 1
Magnesium oleate % 0.00

	Conductivity	0°C	secs.		x 10 ⁻¹¹	mho/cm.
	Viscosity k	113,2	"	32.7	poise	
	Refractive index n			1.4984		
		10°C	secs.		x 10 ⁻¹¹	mho/cm.
Density, So, of the starting mixture at 10°C = 0.971 gm/cm. ³		32.8	"	9.48	poise	
				1.4945		
		20°C	45.9 o	secs.	0.041	x 10 ⁻¹¹
			11.4	secs.	3.29	poise
					1.4905	

	2		3		4
	0.89		2.29		2.97
93.5	☺ 0.120		36.2 x 0.168		33.6 ☺ 0.334
122.0	35.3		101.3 29.3		113.3 32.8
	1.4977		1.4976		1.4981
46.7	☺ 0.242		15.6 ☺ 0.718		40.3 Λ 1.18
25.1	7.25		31.0 8.96		30.6 8.85
	1.4941		1.4936		1.4942
22.2	☺ 0.505		27.2 Λ 1.75		15.2 Λ 3.13
12.5	3.62		11.6 3.35		12.3 3.56
	1.4906		1.4895		1.4903
	5		6		7
	3.95		5.01		5.95
49.1	Λ 0.970		22.1 Λ 2.15		10.9 Λ 4.37
104.6	30.2		102.0 29.5		104.5 30.2
	1.4980		1.4977		1.4977
16.7	Λ 3.85		68.0 — 7.78		36.1 — 14.7
30.4	8.79		31.5 9.11		31.3 9.05
	1.4941		1.4938		1.4940

62.9	—	8.41	27.3	—	19.4	15.1	—	35.0
12.2		3.53	11.6		3.35	11.9		3.44
		1.4902			1.4902			1.4902

8	9	10
7.02	8.11	9.14

49.8	—	10.6	32.1	—	16.5	30.9	—	17.1
104.5		30.2	108.6		31.4	109.2		31.6
		1.4978			1.4968			1.4978

18.8	—	28.2	11.2	—	47.2	10.3	—	51.4
30.6		8.84	35.1		10.15	35.8		10.35
		1.4940			1.4932			1.4938

76.3	+	69.4	42.1	+	125.6	35.4	+	149.5
12.0		3.47	12.6		3.64	13.1		3.79
		1.4902			1.4897			1.4900

11	12	13
10.00	10.94	11.79

27.2	—	19.4	26.0	—	20.3	28.0	—	18.9
108.2		31.3	133.4		38.6	144.6		41.8
		1.4974			1.4971			1.4965

74.6	+	70.9	70.9	+	74.6	83.6	+	63.3
36.7		10.60	38.8		11.21	43.9		12.7
		1.4936			1.4932			1.4931

28.6	+	185.0	24.4	+	217.0	29.2	+	181.0
15.2		4.39	15.7		4.54	16.4		4.74
		1.4900			1.4899			1.4896

14	15	16
12.79	14.01	15.24

26.0	—	20.3	23.1	—	22.9	27.8	—	19.0
157.4		45.5	169.8		49.1	208.6		60.3
		1.4969			1.4971			1.4965

83.1	+	63.6	68.0	+	77.8	75.7	+	69.9
47.5		13.73	50.0		14.45	59.5		17.20
		1.4934			1.4931			1.4928

26.6	+	199.0	24.7	+	214.0	27.1	+	195.1
18.4		5.32	18.9		5.46	23.7		6.85
		1.4898			1.4899			1.4891

	17 16.19		18 16.87		19 18.01			
30.0	-	17.6	26.9	-	19.7	32.3	-	16.4
272.0		78.6	242.1		70.0	331.6		95.8
		1.4966			1.4969			1.4966
96.7	+	54.7	77.8	+	68.0	94.8	+	55.8
82.0		23.7	69.8		20.2	97.4		28.2
		1.4929			1.4933			1.4929
34.2	+	154.7	25.3	+	209.0	31.8	+	166.7
27.8		8.03	25.5		7.37	34.3		9.91
		1.4892			1.4897			1.4892

Test No. 5

Starting mixture: Hexaline naphthenate 4th Fr. HDV (6) 98.258%
 (Acid No. = 4.49)
 Tricresyl phosphate 4th Fr. 2 Lt. Dist. App. 0.998%
 Naphthenic acid Barrel 1 HVD(6)5 0.744%

Using Apparatus No. 3 Measurement No. 1
 Magnesium oleate % 0.00

Conductivity	0°C	230.0	0 secs.	0.0104	$\times 10^{-11}$	mho/cm.
Viscosity k		117.4	"	33.9	poise	
Refractive index n				1.4990		
	10°C	84.2	0 secs.	0.0284	$\times 10^{-11}$	mho/cm.
		31.8	"	9.19	poise	
				1.4952		
Density, So, of the starting mixture at 10°C = 0.972 gm/cm ³	20°C	31.0	0 "	0.0771	$\times 10^{-11}$	mho/cm
		11.0	"	3.18	poise	
				1.4915		

	2		3		4
	1.06		2.06		3.08
144.0	x 0.0535	60.6	⊖ 0.236	36.0	⊖ 0.397
114.2	33.0	108.9	31.4	107.1	31.0
	1.4987		1.4984		1.4986
34.8	x 0.222	18.7	⊖ 0.765	50.0	Λ 1.21
29.6	8.55	30.6	8.85	31.6	9.14
	1.4949		1.4948		1.4949
11.1	x 0.695	7.0	⊖ 2.04	22.1	Λ 2.73
11.4	3.29	11.3	3.27	12.2	3.52
	1.4915		1.4913		1.4912
	5		6		7
	3.93		5.07		5.97
16.4	⊖ 0.872	33.6	Λ 1.80	24.6	Λ 2.45
102.0	29.5	105.2	30.4	104.4	30.2
	1.4987		1.4985		1.4985
24.0	Λ 2.51	11.7	Λ 5.16	78.5	— 8.57
31.1	8.99	31.4	9.08	32.0	9.25
	1.4949		1.4948		1.4948

9.0	Λ	6.71	42.7	—	15.75	32.1	—	21.0
11.2		3.24	11.8		3.41	11.6		3.35
		1.4910			1.4910			1.4911
	8			9			10	
	7.24			8.22			8.97	
9.2	Λ	6.56	10.9	Λ	5.54	41.5	—	16.2
102.6		29.7	102.7		29.7	111.0		32.1
		1.4979			1.4980			1.4980
35.1	—	19.2	34.3	—	19.6	13.1	—	51.4
32.2		9.31	31.1		9.00	33.0		9.54
		1.4942			1.4943			1.4943
12.6	—	53.4	14.2	—	47.4	51.0	+	132.0
11.7		3.38	12.4		3.58	12.4		3.58
		1.4905			1.4907			1.4905
	11			12			13	
	9.64			11.24			12.30	
39.3	—	17.1	25.2	—	26.7	23.7	—	28.4
107.2		31.0	125.0		36.1	129.7		37.5
		1.4977			1.4977			1.4977
13.0	—	51.8	8.2	—	82.1	7.4	—	91.0
33.3		9.63	36.1		10.43	39.2		11.32
		1.4940			1.4939			1.4939
50.3	+	134.0	30.6	+	220.0	27.6	+	244.0
12.4		3.58	13.5		3.90	14.9		4.31
		1.4904			1.4901			1.4901
	14			15			16	
	13.38			14.11			15.20	
20.2	—	33.3	20.5	—	32.8	20.3	—	33.2
132.7		38.4	135.5		39.2	148.3		42.9
		1.4974			1.4975			1.4971
62.9	+	107.0	59.0	+	114.0	61.5	+	109.4
40.3		11.64	43.9		12.68	47.3		13.69
		1.4937			1.4937			1.4933
24.2	+	278.0	23.0	+	293.0	23.4	+	288.0
15.8		4.57	16.2		4.68	17.6		5.09
		1.4902			1.4899			1.4895

	17 16.02		18 16.95		19 18.21	
20.5	- 32.8		21.3	- 31.6	22.1	- 30.4
166.4	48.1		189.2	54.7	234.5	67.8
	1.4972			1.4969		1.4970
58.1	+ 115.9		60.4	+ 111.3	64.5	+ 104.3
51.8	14.98		57.5	16.61	70.8	20.4
	1.4934			1.4969		1.4932
22.5	+ 299.0		21.8	+ 309.0	23.4	+ 288.0
19.0	5.49		21.5	6.21	25.6	7.40
	1.4897			1.4894		1.4895

Test No. 6

Starting mixture: Hexaline naphthenate 4th Fr. HVD(6) 97.076%
 (Acid No. = 4.49)
 Ethyl ricinoleate 2nd Fr. HVD 305 2.924%

Using Apparatus No. 5 Measurement No. 1
 Magnesium oleate % 0.00

Conductivity	0°C	325.0 o secs.	0.0069 x 10 ⁻¹¹	mho/cm.
Viscosity k		90.2 "	26.1 poise	
Refractive index n			1.4976	
	10°C	154.7 o secs.	0.0145 x 10 ⁻¹¹	mho/cm
		27.1 "	7.84 poise	
			1.4938	

Density, So, of the starting mixture at 10°C = 0.969 gm/cm³.

	20°C	55.2 o secs.	0.0406 x 10 ⁻¹¹	mho/cm.
		10.0 "	2.89 poise	
			1.4900	

	2		3		4
	0.78		2.18		2.87
32.0	o 0.070	50.4	☉ 0.266	17.0	☉ 0.788
80.8	23.4	82.1	23.7	83.1	24.0
			1.4971		1.4972
10.6	o 0.211	19.1	☉ 0.702	23.4	Λ 2.42
24.6	7.11	26.0	7.51	25.6	7.40
			1.4934		1.4934
11.4	x 0.635	6.2	☉ 2.16	9.4	Λ 6.03
9.6	2.77	10.0	2.89	10.0	2.89
			1.4897		1.4895
	5		6		7
	3.97		5.03		5.96
32.5	Λ 1.74	17.0	Λ 3.34	8.2	Λ 6.92
82.2	23.8	83.0	24.0	84.2	24.3
	1.4969		1.4968		1.4968
12.1	Λ 4.69	61.1	— 10.3	27.6	— 22.9
23.8	6.88	25.3	7.31	26.3	7.60
	1.4932		1.4931		1.4931

45.1	—	14.0	23.7	—	26.6	11.8	—	53.5
9.8		2.83	10.0		2.89	10.0		2.89
		1.4895			1.4895			1.4892
	8			9			10	
	7.03			8.05			8.90	
51.3	—	12.3	28.5	—	22.1	26.2	—	24.1
84.9		24.5	86.6		25.0	88.7		25.6
		1.4969			1.4965			1.4930
18.0	—	35.1	10.3	—	61.2	9.0	—	70.1
26.5		7.66	27.8		8.04	27.8		8.04
		1.4931			1.4928			1.4930
7.5	—	84.2				32.6	+	193.7
10.1		2.92	10.4		3.01	11.1		3.21
		1.4893			1.4891			1.4891
	11			12			13	
	10.13			11.05			12.08	
23.6	—	25.7	20.9	—	30.2	20.0	—	31.6
90.1		26.0	98.3		28.4	104.2		30.1
		1.4965						1.4963
9.8	—	64.4	63.7	+	99.0	60.4	+	104.5
28.7		8.29	31.2		9.01	34.8		10.05
		1.4928						1.4926
32.3	+	195.2	25.6	+	246.0	24.9	+	253.0
11.9		3.44	12.4		3.68	13.5		3.90
		1.4891						1.4889
	14			15			16	
	12.89			13.94			14.99	
18.0	—	35.1	16.2	—	39.0	14.4	—	43.8
109.6		31.6	111.6		32.2	114.2		33.0
		1.4962			1.4959			1.4958
50.7	+	124.4	49.3	+	128.0	45.6	+	138.2
34.1		9.85	36.5		10.55	37.9		10.9
		1.4925			1.4922			1.4921
20.0	+	316.0	19.3	+	327.0	18.3	+	345.0
14.3		4.13	14.4		4.16	15.2		4.39
		1.4888			1.4886			1.4885

17 16.11	18 17.00	19 18.09
15.0 - 42.1	15.9 - 39.7	15.5 - 40.7
129.7 37.5	148.5 42.9	
1.4958	1.4958	1.4959
46.6 + 135.4	49.6 + 127.1	39.5 + 159.8
43.4 12.53	46.1 13.22	47.3 13.68
1.4920	1.4920	1.4921
17.5 + 361.0	18.3 + 345.0	17.8 + 355.0
17.1 4.94	17.9 5.17	18.3 5.29
1.4882	1.4883	1.4884

Test No. 7

Starting mixture: BE₂ oil 4th Fr. 2nd HVD (unrefined) 98.264%
 Tricresyl phosphate 4th Fr. 2 Lt. Dist. App. 0.983%
 Naphthenic acid Barrel 1 HVD (6) 5 0.753%

Using Apparatus No. 5, Measurements 1-8
 and No. 3, Measurements 9-17, Cell constant Cw=0.194 cm⁻¹.

		Measurement No. 1	
		Magnesium oleate % 0.00	
Conductivity	0 ^o C	296.8 o secs.	0.00755 x 10 ⁻¹ mho/cm.
Viscosity	k	221 "	65.2 poise
Refractive index	n		1.5273
Density, S _o , of the starting mixture at 10 ^o C = 0.943 gm/cm ³	10 ^o C	315.0 o secs.	0.00711 x 10 ⁻¹ mho/cm.
		66.1 "	19.5 poise
			1.5239
	20 ^o C	317.0 o secs.	0.00707 x 10 ⁻¹ mho/cm.
		24.0 "	7.08 poise
			1.5201
	2	3	4
	1.14	1.96	3.16
344 o	0.0065	58.0 o	0.0386
212.5	62.8	212.1	62.6
	1.5267		1.5264
161.6 o	0.0139	17.8 o	0.126
65.2	19.2	65.2	19.2
	1.5230		1.5227
31.5 o	0.0711	6.3 o	0.356
25.2	7.44	23.9	7.05
	1.5193		1.5191
	5	6	7
	4.15	5.10	6.21
36.4 A	1.56	26.6 A	2.13
224.9	66.4	254.9	75.3
	1.5256		1.5254
			1.5250

10.8 \wedge 5.25
72.0 21.2
1.5219

3.4 \wedge 16.7
25.3 7.46
1.5183

8
7.10

31.6 \wedge 1.79
410.5 121.2
1.5246

8.0 \wedge 7.09
114.7 33.9
1.5209

26.3 --- 24.0
39.0 11.5
1.5173

11
9.97

73.3 \wedge 0.81
quite firm
1.5238

15.8 \wedge 3.74
470.3 136.2
1.5201

39.2 16.8
92.3 26.8
1.5164

7.8 \wedge 7.27
75.9 22.4
1.5217

2.5 \wedge 22.7
25.8 7.61
1.5181

9
8.23

45.4 \wedge 1.30
559.0 162.0
1.5239

10.4 \wedge 5.69
137.9 40.0
1.5203

29.4 --- 22.4
43.5 12.6
1.5170

12
11.09

187.4 \wedge 0.32
quite firm
1.5230

38.0 \wedge 1.56
quite firm
1.5192

7.9 \wedge 7.49
1320 383.0
1.5159

6.5 \wedge 8.72
85.9 25.4
1.5213

23.2 --- 27.2
31.1 9.18
1.5177

10
9.28

87.0 \wedge 0.68
quite firm
1.5239

16.0 \wedge 3.70
523.8 152.0
1.5202

43.9 --- 15.0
98.4 28.5
1.5165

13
11.96

225.6 \wedge 0.26
quite firm
1.5230

53.8 \wedge 1.10
quite firm
1.5192

12.2 \wedge 4.85
quite firm
1.5158

14
 13.02
 21.5 o 0.109
 quite firm
 1.5228
 26.3 ☺ 0.532
 quite firm
 1.5190
 27.7 Λ 2.14
 quite firm
 1.5154

15
 14.15
 24.7 o 0.095
 quite firm
 1.5222
 24.1 ☺ 0.581
 quite firm
 1.5182
 25.1 Λ 2.36
 quite firm
 1.5149

16
 15.36
 37.6 o 0.062
 quite firm
 1.5215
 42.3 ☺ 0.331
 quite firm
 1.5179
 50.0 Λ 1.18
 quite firm
 1.5142

17
 16.08
 28.2 o 0.083
 quite firm
 29.0 ☺ 0.483
 quite firm
 1.5171
 36.8 Λ 1.61
 quite firm
 1.5142

Test No. 8

Starting mixture: BE₂ oil 4th Fr. 2nd HVD (unrefined) 97.074%
 Ethyl ricinoleate 2nd Fr. HVD 305 2.926%

Using Apparatus No. 6 Measurement No. 1
 Magnesium oleate % 0.00

Conductivity	0°C	908.0	o	secs.	0.00207 x 10 ⁻¹¹	mho/cm
Viscosity k		157.6		"	45.7	poise
Refractive index n					1.5257	
Density, S _o , of the starting mixture at 10°C = 0.941 gm/cm ³	10°C	540.0	o	secs.	0.00348 x 10 ⁻¹¹	mho/cm
		51.3		"	14.9	poise
					1.5220	
	20°C	259.0	o	secs.	0.00726 x 10 ⁻¹¹	mho/cm
		18.5		"	5.36	poise
					1.5182	

2		3		4	
1.03		2.30		3.08	
18.6	o 0.101	44.5	Λ 1.07	38.7	Λ 1.23
155.8	45.2			178.2	51.2
	1.5252		1.5246		1.5246
8.6	o 0.218	14.0	Λ 3.40	11.1	Λ 4.29
50.4	14.6	51.0	14.8	57.8	16.8
	1.5216		1.5210		1.5210
3.1	o 0.606	4.9	Λ 9.72	3.8	Λ 12.5
19.0	5.51	20.3	5.81	21.8	6.32
	1.5180		1.5178		1.5171
5		6		7	
3.95		4.98		6.20	
33.2	Λ 1.43	36.2	Λ 1.32	33.0	Λ 1.44
190.6	55.3	232.8	67.5	280.0	81.2
	1.5242		1.5241		1.5235
10.6	Λ 4.50	10.5	Λ 4.54	10.0	Λ 4.76
61.6	17.9	73.5	21.3	84.4	24.5
	1.5208		1.5206		1.5200

3.2	Λ	14.9	34.5	—	15.3	30.5	—	17.3
24.1		6.99	27.6		8.0	30.7		8.90
		1.5170			1.5168			1.5162
	8			9			10	
	7.21			8.28			9.02	
41.2	Λ	1.16	52.7	Λ	0.90	92.4	Λ	0.52
455.0		132.0	quite firm			quite firm		
		1.5230			1.5228			1.5228
10.8	Λ	4.41	13.0	Λ	3.66	23.4	Λ	2.04
122.0		35.4	259.0		75.1	quite firm		
		1.5194			1.5190			1.5190
36.0	—	14.7	39.3	—	13.4	58.6	—	9.02
40.3		11.7	65.2		18.9	346.8		100.6
		1.5158			1.5153			1.5152
	11			12			13	
	9.97			11.06			11.88	
75.1	Λ	0.63	26.3	∩	0.43	25.4	∩	0.44
quite firm			quite firm			quite firm		
		1.5224			1.5215			1.5215
16.0	Λ	2.98	25.6	Λ	1.86	28.0	Λ	1.70
quite firm			quite firm			quite firm		
		1.5186			1.5177			1.5180
48.0	—	11.0	69.5	—	7.61	74.6	—	7.09
156.2		45.3	1100		319.0	quite firm		
		1.5149			1.5139			1.5140
				14			15	
				13.05			14.15	
35.7	∩	0.314	39.1	∩	0.286			
quite firm			quite firm					
		1.5212			1.5204			
37.2	Λ	1.28	39.0	Λ	1.22			
quite firm			quite firm					
		1.5168			1.5169			
10.5	Λ	4.54	12.3	Λ	3.87			
quite firm			quite firm					
		1.5138			1.5134			

Test No. 9

Starting mixture: BE₂ oil 4th Fr. 2nd HVD (refined) 97.078%
 Ethyl ricinoleate 2nd Fr. HVD 305 2.922%

Using Apparatus No. 5 Measurement No. 1
 Magnesium oleate % 0.00

Conductivity	0°C	secs.					
Viscosity k							x 10 ⁻¹¹ mho/cm
Refractive index n							
		165.8		48.1	poise		
				1.5257			
	10°C	52.6	o secs.	0.043	x 10 ⁻¹¹		mho/cm
		52.8	"	15.3	poise		
				1.5222			
	20°C	9.0	o secs.	0.249	x 10 ⁻¹¹		mho/cm
		20.5	"	5.95	poise		
				1.5188			

Density, S_o, of the starting mixture at 10°C = 0.941 gm/cm³

2		3		4	
1.05		2.06		2.99	
46.5	⊖ 0.288	58.6	∧ 0.968	37.1	∧ 1.53
171.5	49.7	173.0	50.2	162.9	47.2
	1.5255		1.5254		1.5250
14.9	⊖ 0.900	21.1	∧ 2.68	11.1	∧ 5.11
52.4	15.2	53.2	15.4	53.2	15.4
	1.5219		1.5215		1.5212
27.4	∧ 2.07	8.2	∧ 6.92	32.9	— 19.2
19.9	5.77	20.9	6.06	22.8	6.61
	1.5181		1.5175		1.5175
5		6		7	
4.06		5.09		6.11	
31.4	∧ 1.81	26.4	∧ 2.15	23.6	∧ 2.40
181.4	52.6	195.1	56.6	236.0	68.4
	1.5246				1.5240
10.1	∧ 5.61	7.4	∧ 7.66	67.6	— 9.34
59.6	17.3	66.0	19.1	73.5	21.3
	1.5209				1.5201

24.9 — 25.4
23.7 6.87
1.5172

8
7.00

21.7 \wedge 2.61
269.1 78.0
1.5227

66.0 — 9.56
84.3 24.4
1.5191

22.0 — 28.7
30.5 8.85
1.5155

11
10.42

30.2 \wedge 1.88
1059.4 307
1.5221

87.3 — 7.23
235.4 68.3
1.5184

28.3 — 22.3
69.1 20.0
1.5148

14
12.89

33.0 \wedge 1.72
very firm
1.5212

78.9 — 8.00
287.9 83.5
1.5175

23.2 — 27.2
75.5 21.9
1.5140

24.6 — 25.6
25.2 7.31

9
8.15

29.0 \wedge 1.96
359.6 108.5
1.5224

72.5 — 8.70
101.1 29.3
1.5188

24.7 — 25.5
38.3 11.1
1.5151

12
11.06

31.1 \wedge 1.82
1069.5 310
1.5226

82.5 — 7.65
240.4 69.8
1.5188

23.7 — 26.6
71.6 20.8
1.5150

15
14.24

57.4 \wedge 0.989
very firm
1.5210

12.6 \wedge 4.50
1300 377.0
1.5174

37.0 — 17.06
244.8 71.0
1.5138

22.8 — 27.7
29.4 8.53
1.5163

10
9.21

30.3 \wedge 1.87
626.3 181.8
1.5226

83.5 — 7.56
162.8 47.2
1.5190

28.0 — 22.5
53.3 15.5
1.5157

13
11.89

34.7 \wedge 1.63
very firm
1.5218

82.9 — 7.62
269.8 78.1
1.5183

25.8 — 24.5
77.2 22.4
1.5147

16
15.10

61.4 \wedge 0.926
very firm
1.5210

13.4 \wedge 4.23
very firm
1.5171

38.1 — 16.6
426.6 123.8
1.5132

DISCUSSION of the RESULTS

The starting mixtures were so made up that it would be possible at the completion of the tests to compare the results and note the effects of the various components on the physical properties in the presence of the electrolyte, magnesium oleate, and also the effect of the oleate itself.

The results can be conveniently considered in three groups; the first, composed of those mixtures employing CY1 oil as base (Tests 1 and 2); the second, of those with hexaline naphthenate as base (Tests 3,4,5 and 6) and the third, of those with BE₂ oil as base (Tests 7,8 and 9). The concentrations indicated on the graphs are those at which the measurements were made.

a) CY1 Oil Mixtures

The graphical representations of the results of Test No. 1 are shown in figures 31 to 35.

The break in the viscosity curve where the viscosity begins to increase fairly sharply, at ca. 6.5% oleate concentrations, occurs at the first maximum in the electrical conductivity.

The second maximum in the conductivity at around 9.2%, after which it drops sharply to its lowest minimum, is where the viscosity again-begins increasing still more sharply to its highest maximum.

The maximum attained by the viscosity curve at about 10.1% occurs at the same place as the lowest minimum reached by the conductivity. Here also, the refractive index reaches a decided minimum.

The point where the viscosity breaks sharply upward again at about 11.4% is the point where the conductivity reaches its second and highest maximum, and the refractive index also reaches a maximum.

It can be seen that there is clearly a connection between the conductivity and viscosity - a sudden change in one being accompanied by an inverse change (i.e. as regards increase and decrease) in the other at the same electrolyte concentration. This relation is also shown by the refractive index, although not as clearly. However, in general, where a maximum or minimum in the conductivity occurs (and respectively a minimum or maximum in the viscosity), the refractive index also exhibits a corresponding maximum or minimum.

In figures 34 and 35 the results of the dielectric constant and capillarity measurements are shown. These measurements were made only for Test No. 1 and the results were not listed as their accuracy is doubtful, as mentioned before. However, marked changes in these properties occur at concentrations at which the other measured properties also undergo sudden variations.

Apparent is the general similarity of the D.C.-concentration curve with the conductivity curve, the maximum in the D.C. at about 7.2% comparing roughly to the conductivity maximum at approximately the same concentration. The minimum at about 8.2% corresponds also in both of these properties.

In general the capillarity (figure 35) follows the run of the viscosity, and the concentration areas of maximum and minimum in the capillarity and viscosity curves correspond to minimum and maximum respectively in the conductivity.

In Test No. 2, as seen in figures 36, 37 and 38, the same relationship holds true between the electrical conductivity and viscosity. As before, the refractive index also shows a relation, behaving similarly to the run of the conductivity curve, although by no means as markedly.

The use of tricresyl phosphate and naphthenic acid leads to conductivity values from 15 to 35% higher than when ethyl ricinoleate is used (with CY1 oil), up to the rises to the last maxima. Here, in the case of the tricresyl phosphate and naphthenic acid, is produced a maximum value 21% higher than the initial maximum, while the ethyl ricinoleate leads to a much less pronounced final maximum - 52% less than the initial maximum.

The initial maxima in both cases are at approximately the same electrolyte concentration (6.4 and 5.1%), as are also the second maxima and minima.

Up to the maximum in the viscosity curve, the tricresyl phosphate and naphthenic acid lead to slightly higher viscosities than the ethyl ricinoleate at corresponding concentrations. In the case of the tricresyl phosphate and naphthenic acid however, the viscosity minimum is much more pronounced and reaches a far lower value than in Test 2 employing ethyl ricinoleate. This is analogous to the conductivity results at the final maxima, the effect of the ethyl ricinoleate being here also far less noticeable.

As in the case of the conductivity, the tricresyl phosphate and naphthenic acid lead also to higher values of the refractive index than does the ethyl ricinoleate.

These observations concerning the CY1 oil base mixtures may be summarized as follows:

1. tricresyl phosphate and naphthenic acid with CY1 oil lead to higher values of the electrical conductivity, viscosity and refractive index than does ethyl ricinoleate;

2. there is a relation between the conductivity and viscosity in these two colloidal CY1 oil mixtures - abrupt changes in one being related to abrupt changes in the other; a sudden decrease in viscosity for a sudden in-

crease in the conductivity and vice versa;

3. the refractive index also enters this relation, although it is not so apparent, and follows in a less striking manner the general run of the conductivity where maxima and minima occur;

4. tricresyl phosphate and naphthenic acid lead also to more pronounced 'final effects' at higher electrolyte concentrations in the conductivity and viscosity, following the initial maximum and minimum respectively;

5. allowing for slight error in the method of electrolyte addition it is seen that the magnesium oleate reaches its point of greatest influence on the conductivity at the same concentration in both tests. Also, the falling off of its influence and the later rise in the conductivity to another maximum takes place at approximately the same concentration in both cases;

6. this observation (5.) would tend to indicate a definite molecular combination between the oleate and CY1 oil not influenced, or only very slightly, by the presence of the other substances;

7. in the case of the final maxima, however, the conductivity results especially show the influence of the extra substances. Either the tricresyl phosphate or naphthenic acid or both together, in combination with the magnesium oleate, lead to a surprising increase in the conductivity, while the ethyl ricinoleate bearing mixtures shows only a very small increase.

b) Hexaline Naphthenate Mixtures

In these four mixtures employing hexaline naphthenate as the base, there is a smaller variation in the three measured properties than in the previous two tests using the colloidal CY1 oil

The Test 3 results are seen in figures 39, 40 and 41. It is difficult to analyse the curves as they do not vary as markedly as those heretofore considered, nor as those for the BE₂ oil base mixtures to follow.

The break in the viscosity curve at 3% comes at the levelling-off area in the conductivity. The viscosity break at 11% takes place at a maximum value of the conductivity, while the break at 14% comes at another slight levelling-off area in the conductivity. The break at 17.2% comes at a minimum in the conductivity, and the last break at 19.5% (at 100°C), at the last and largest maximum value of the conductivity.

As with the CY1 oil, the refractive index appears in general to follow the electrical conductivity, especially with regard to the minima.

Figures 42, 43 and 44 represent the results of Test 4. At the first break in the viscosity curve at 10% the conductivity has just passed through a small levelling-off stage. At the second viscosity break at 14% the conduc-

tivity reaches its second maximum. At the maximum in the viscosity at 16.2% the conductivity shows a minimum. The last conductivity maximum at 16.9% occurs at a viscosity minimum. All three of the conductivity maxima reach approximately the same value. Further viscosity measurements at below 0°C would probably show up another viscosity break at around 10.9% to correspond to the conductivity maximum at this concentration. The well-defined maximum in the viscosity at 16.2% occurs at the lowest minimum of the conductivity curve.

Again the refractive index follows in general the conductivity with respect to the maxima and minima.

The viscosity-temperature graph for Test 4 is shown in figure 45. It is representative of the viscosity-temperature relation in all these tests - the viscosity decreasing regularly with rising temperature.

Test 5 results, shown in figures 46, 47 and 48, show the first definite break in the viscosity (figure 47) at 8.2% at a small levelling-off or decreasing area in the conductivity, as well as the second upward break at 9.6%. The break at 14.1% takes place at a maximum and much higher value of the conductivity. The final, highest, maximum of the conductivity takes place with the viscosity increasing still more sharply.

The refractive index, especially at the higher concentrations, follows the general run of the conductivity curve.

From an observation of figures 49, 50 and 51, representing the conductivity, viscosity and refractive index vs. oleate concentration for Test 6, the relation again seems to be - the first break in the viscosity curve between 9 and 10% (increase) occurs at either a small levelling-off or a decreasing area in the conductivity; the second, more pronounced break in the viscosity curve, takes place at a higher, maximum value, of the conductivity; where there are slight maxima or a levelling-off of the viscosity curve, there are corresponding small levelling-off areas in the conductivity curve.

Here, the refractive index only corresponds to the electrical conductivity as regards the maximum at about 8.9% at 10°C.

From Tests 3 and 4, which differ only in the acid (naphthenic) content of the hexaline naphthenate, Test 3 with 3.33% acid (acid no. = 17.3) and Test 4 with 0.865% (acid no. = 4.49), it is seen that up to the first conductivity maxima, both at an electrolyte concentration of ca. 11%, the extra acid represses the conductivity to only 1/7 to 1/9 the value obtained with the lower acid content mixture: i.e. a decrease in the acid quantity to 1/3.8 leads to

a conductivity increase from 7 to 9 times.

After this however, the extra acid exerts its influence. While the lower acid content mixture reaches no higher conductivity values than initially at 11% electrolyte concentration, the one with the higher acid content continues to increase through two maxima to approximately the same conductivity as the other, i.e. ca. 233×10^{-11} mho/cm. at 20°C at an electrolyte concentration of 19.5%.

As with the conductivity curves, the viscosity curves for Test 3 (higher acid content) vary more irregularly than in the lower acid content case in Test 4. In the case of the higher acid content the viscosity drops suddenly on the first electrolyte additions then remains fairly steady as does the lower acid content mixture, until an electrolyte concentration of ca. 14% is reached. In the case of the lower acid content, the viscosity rises quite sharply after 10% to fairly high values. In both cases the viscosity values are of the same order up to the main breaks in the curves.

Concerning the refractive index the values in both cases (Tests 3 and 4) are of approximately the same order, but the higher acid content in Test 3 produces a steeper drop, while the lower holds more to the horizontal with increasing electrolyte concentration.

When compared to the results of Test 4, using just hexaline naphthenate as the starting mixture, the addition of tricresyl phosphate and naphthenic acid to the hexaline naphthenate in Test 5 (both with the lower acid content) leads to an increase in the conductivity values up to 50% higher at the maxima. Ethyl ricinoleate with hexaline naphthenate in Test 6 (also lower acid content) gives still higher conductivities, increasing to ca. 80% higher values at the maxima.

With regard to the viscosity only the ethyl ricinoleate bearing mixture shows a marked deviation, being ca. 6% lower in value than the other two mixtures (Tests 4 and 5). The general run of all three viscosity plots is the same.

The refractive index curves have all approximately the same slope, with those for the ethyl ricinoleate containing mixture being slightly lower in its values. The plot for the ethyl ricinoleate bearing mixture is the most regular and those for the mixtures containing just hexaline naphthenate as starting mixture, the most irregular.

These observations of the results of the hexaline naphthenate base mixtures can be summarized as follows:

1. a relation between the electrical conductivity and viscosity is again evident. Where the first break in the viscosity curve occurs is gene-

rally a levelling-off in the conductivity curve. The next break is usually at a conductivity maximum, and the last (there being usually three), also at a maximum value of the conductivity;

2. well-defined maxima in the viscosity curve usually occur at maxima or levelling-off areas in the conductivity curve;

3. the refractive index again in general follows the run of the conductivity, although not as clearly as observed with the Cyl oil base mixtures;

4. a higher acid content in the hexaline naphthenate depresses the conductivity up to the first maximum, then the conductivity increases to approximately the same value as the maximum reached by the lower acid content mixture;

5. tricresyl phosphate and naphthenic acid increase the conductivity, and ethyl ricinoleate even moreso, when added to the hexaline naphthenate (of lower acid content);

6. the higher acid content in the hexaline naphthenate causes a greater fluctuation in the conductivity and viscosity but does not change the viscosity values essentially up to the main breaks;

7. following the main breaks in the viscosity curves the mixture with the lower acid content increases more sharply upward than that with the higher;

8. a higher acid content produces a steeper slope in the refractive index plots but does not alter its values to any extent;

9. in Tests 3 and 4, differing only in their acid content, the conductivity reaches its first maximum at the same electrolyte concentration (ca. 10.9%) in both cases;

10. in Test 5 containing tricresyl phosphate and naphthenic acid and Test 6 containing ethyl ricinoleate, the first maxima or levelling-off areas and the greatest maxima in the conductivity occur at approximately the same electrolyte concentration of ca. 9 and 16% respectively;

11. in Tests 4, 5 and 6, the first main viscosity break occurs in each case at the same concentration of ca. 10%. Whether Test 3 does also is not clear. All four tests however, have another break at the same concentration of ca. 14%;

12. the refractive index curves show in Test 3 a decrease and in Test 4 an increase up to 3% electrolyte concentration, as do the viscosity curves.

c) BE₂ Oil Mixtures

The results of Test 7 are shown in figures 52, 53 and 54. The first viscosity break at about 6.2% occurs at the first and greatest maximum of the conductivity. The next break at ca. 8.2% occurs at no

particular transition point in the conductivity. At 9.3%, where occurs a maximum in the viscosity, is the conductivity's first minimum, followed in the viscosity by a break upwards at 10% to very high values which corresponds to the second conductivity maximum.

The refractive index corresponds to the conductivity this time only at 9.3% where it has a levelling-off area and the conductivity a minimum (and the viscosity a maximum).

The curves for Test 8 are seen in figures 55, 56, 57 and 58. Figure 58 is given as an example of the usual temperature dependence of the conductivity which produced similar curves in all these tests.

The first viscosity break at between 3 and 4% occurs at a levelling-off in the conductivity; the second, at 6.2%, at the first and greatest conductivity maximum; and the third, at around 8.3% (best seen at 20°C), at a further slight levelling-off in the conductivity. The viscosity maximum at 9% and the minimum at 10% occur respectively at minimum and maximum in the conductivity.

The refractive index compares only at 3% to a levelling-off in the conductivity.

Figures 59, 60, 61 and 62 show graphically the results of Test 9, figure 58 showing the refractive index-temperature graph which is representative of the linear relationship found throughout these tests.

The viscosity break between 3 and 4% corresponds to a conductivity levelling-off area; the next, at between 7 and 8%, to the greatest conductivity maximum; and the levelling-off in the viscosity between 10 and 11% to a conductivity minimum. The final upward break in the viscosity at 13% to very high values corresponds to the last conductivity maximum.

The refractive index again does not compare very favourably with the conductivity, corresponding only roughly to conductivity maxima and minima.

Using ethyl ricinoleate instead of tricresyl phosphate and naphthenic acid with unrefined BE₂ oil leads to similar electrical conductivity curves but about 37% lower in value. Ethyl ricinoleate in refined BE₂ oil leads to a conductivity of the same order as with unrefined BE₂ oil, tricresyl phosphate and naphthenic acid, but of a more irregular nature after the initial maximum between 6 and 7% is reached. Employing ethyl ricinoleate with refined BE₂ oil gives a conductivity around 65% greater in value than when used with unrefined BE₂ oil, and up to around 73% higher at 0°C.

The viscosity is similarly affected by the various combinations of these sub-

stances. The ethyl ricinoleate leads to lower viscosity values when used with the unrefined BE₂ oil than when tricresyl phosphate and naphthenic acid are used. Ethyl ricinoleate with refined BE₂ oil gives viscosity values and curves similar to those obtained when tricresyl phosphate and naphthenic acid are used with unrefined BE₂ oil.

In general, the same can be said for the refractive index as said above for the viscosity.

The above remarks concerning the BE₂ oil base mixtures can be summarized as follows:

1. regardless of the substances added or whether the BE₂ oil is refined or unrefined, the first and greatest conductivity maximum occurs at a magnesium oleate concentration of between 6 and 7%, as was the case with the CY1 oil base mixtures;
2. there is again the relation between the conductivity and viscosity. In general, the first viscosity break occurs at a levelling-off in the conductivity; the second, at the main maximum in the conductivity; and the last, at the second conductivity maximum. The viscosity maximum occurs at the first conductivity minimum;
3. the refractive index compares only roughly with the conductivity;
4. following the initial maxima, the ethyl ricinoleate in refined BE₂ oil (Test No. 8) is quite irregular in its conductivity and refractive index, whereas the other two tests (7 and 9) are regular in their conductivity curves and almost symmetrical about the vertical maximum conductivity line;
5. in refined BE₂ oil, ethyl ricinoleate gives conductivity and viscosity values of the same order as tricresyl phosphate and naphthenic acid in unrefined BE₂ oil;
6. in unrefined BE₂ oil, ethyl ricinoleate leads to lower conductivity, viscosity and refractive index values than does tricresyl phosphate and naphthenic acid;
7. in refined BE₂ oil ricinoleate gives conductivity values from 65 to 73% greater than when used with unrefined BE₂ oil.

CONCLUSIONS

The behaviour of magnesium oleate in these investigated mixtures is obviously that of a cationic colloidal electrolyte. On the basis of the previous researches on colloidal electrolytes discussed earlier ("LITERATURE SURVEY"), these anomalous variations in the properties of electrical conductivity, viscosity and refractive index can be explained by assuming various degrees and forms of micellar association of the magnesium oleate ions and molecules.

In general the conductivity and viscosity curves can be divided into four zones distinguished by the abrupt change of the effect measured with the CY1 and BE₂ oil base mixtures. The first, from 2-4% electrolyte concentration, when the conductivity begins to increase rapidly. The corresponding viscosity change in this range is only noticeable at 0°C when it passes through a minimum value, changing the sign of its slope from negative (decreasing) to positive (increasing). The second, at 5-7%, where the conductivity reaches its first maximum value and the viscosity begins to increase more strongly. The third, at 8-10%, where the conductivity levels slightly in its decreasing trend then drops sharply and passes through a minimum value, and the viscosity passes through its maximum value. The fourth, from approximately 9.5 to 11.5%, where the conductivity passes through a second maximum value and the viscosity a minimum value.

The refractive index-concentration curve variations show fair agreement with these zones of change, although not at all clearly, the best agreement being at the higher concentrations.

The D.C.-concentration curves for Test No. 1 are in good agreement with these change zones, the variations in D.C. being quite clear. The capillarity-concentration curves for Test No. 1 are only in fair agreement.

Heavier, more compact micelles forming at the lower temperatures account for the fact that greater variations in the viscosity are noted at the lower measurement temperature of 0°C than at the higher ones, and these viscosity results compare favourably with Umstätter's (see figures 10 and 11).

These sigmoid type curves found for the conductivity, and to a lesser extent, the viscosity, can be considered as composed of three main ranges with respect to micellar aggregation, as follows - the pre-critical (concentration) range, which precedes the critical concentration point from 2 to 4%. At this critical concentration we have the beginning of micelle formation - the formation of small, probably spherical, highly conducting ionic micelles. In this case, that of a non-aqueous non-polar solvent, the Lawrence or inverted McBain micelle (see figure 24), i.e. with the polar groups together, probably exists. The second range, in which the effect

measured changes quickly with concentration, is where these micelles increase rapidly in quantity, and as a consequence, their net charge also, accounting for the great increase in electrical conductivity in this range. The third range from 5-7% where the effect measured changes the algebraic sign of its slope, is the transition area where the large, poorly-conducting, McBain lamellar micelles ('neutral colloid') begin to form from the small micelles, with alternate head-to-head (polar groups) and tail-to-tail (anionic paraffin chain groups) arrangement.

That the results for conductivity and viscosity do not both show just the same values for the critical concentration is not surprising. Previous researchers have experienced similar variations of this value depending on the particular effect measured. In the results here the viscosity (at 0°C) gives a slightly higher critical concentration value than does the conductivity.

This qualitative similarity in the results for the CY1 and BE₂ oil base mixtures is not shared at the same concentrations for the hexaline naphthenate base mixtures. Here, the conductivity and viscosity curves vary much more and are difficult to analyse for corresponding areas of change. As the concentration increases as many as three maxima occur in the conductivity up to 18-20%. But, in general, abrupt changes in one property are matched or followed closely by abrupt changes in the other.

The viscosity curves in these hexaline naphthenate base mixtures are the easiest to analyse. Micelle formation probably begins between 1.5 and 4% electrolyte concentration where the conductivity begins to increase noticeably, and the viscosity changes abruptly the sign of its slope (best seen at 0°C). A change in the nature of the micelle is indicated at between 8 and 10%. Here the viscosity begins a sharp increase and the conductivity passes through a small maximum followed by a minimum in its upward trend. A third area of change occurs from 13.5 to 15.5% where the viscosity curve increases still more sharply upward and the conductivity passes through a high maximum value, indicating transition to a poorer conducting micelle form.

Following this the conductivity passes through one or two more maximum and minimum values, a maximum in the conductivity usually matching a minimum in the viscosity and vice versa. The conductivity remains high and fluctuates between rough limits. This would seem to substantiate the presence of two or more micelle types, the total charge of the better conducting one(s) being almost balanced by the total charge of the poorer conducting one(s), additional colloidal electrolyte forming approximately equal amounts of both better and poorer conducting micelles. The variation in the net charge of these mixtures at these higher concentrations may be due only to slight variations in the number of ions absorbed in the magnesium oleate salt complex during its preparation (see page 20).

As is to be expected, the conductivity, at least up to the concentrations employed here (18-20%), does not diminish to very small values, since the hexaline naphthenate has little tendency to polymerize, resulting in the gradual absorption of the micelles as soap, as is probably the case with the two lubricating oil solvents, CY1 and BE₂.

Research on colloidal electrolytes at concentrations above, say, 10%, is lacking, but what has been done is in general agreement with the results at higher concentrations obtained here (see pages 26 - 28 and 31). At these higher concentrations evidence has been found for at least some lamellar repeating arrays of long-chain electrolyte molecules in water. But other micellar forms give evidence of their probable presence and rod or plate forms have been suggested (page 27/28).

We may consider that solubilization of our lubricating oil solvents is accomplished by the lamellar micelles, which begin to form at 5-7% concentration, the oil being taken up between the alternate head and tail spacings. The oleate chain being ca 28 Å long, the overall length of one micellar combination of two long-chain electrolyte molecules with solubilized oil in their intramicellar spaces is probably from 70 to 90 Å.

X-ray data on such lamellar micelles has come from investigations of detergent-water and detergent-water-hydrocarbon mixtures. Just what would be the size and form in a detergent-hydrocarbon mixture such as ours, can as yet only be surmised.

The work and conclusions of Harkins, Mattoon and Corrin (pages 31) may quite possibly be applicable to our results at high concentrations. They consider that the soap micelles continue to act as loci in the polymerization reaction of the solvent only up to a certain polymer yield, at which time the micelles will have all disappeared, having changed into absorbed soap. This would result in a reduction of the conductivity with the disappearance of micelles such as was found in Test 1, the conductivity falling off to zero at 20%. The other tests in which CY1 and BE₂ oils form the solvent also tend toward zero conductivity at the higher concentrations from 14 to 16%. Further measurements at still higher concentrations were not made as the mixtures became so thick and viscous as to make the proper handling of the mixtures impossible.

The added substances, tricresyl phosphate, naphthenic acid and ethyl ricinoleate appear to act as peptizers (see page 31) in promoting colloidal conditions, their main effect being a quantitative one on the order of the physical property being measured. From the results with the CY1 oil and hexaline naphthenate base mixtures, ethyl ricinoleate appears to be a slightly better

peptizer than the combination of tricresyl phosphate and naphthenic acid, if we take the (critical) concentration of the beginning of micelle formation as the criterion. The extra naphthenic acid in the naphthenate (Test No. 3) also appears to have a peptizing effect. In BE₂ oil, ethyl ricinoleate and tricresyl phosphate with naphthenic acid appear to have the same amount of peptizing action for the amounts used.

Micelle formation began earlier and higher conductivities were attained in the mixtures in which the BE₂ oil was first refined, and the deterring effect on micelle formation, solubilization and polymerization, of the waxy substances first removed (Test No. 9).

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CURRICULUM VITAE

I am a Canadian citizen. Born September 6, 1924, in Calgary, Province of Alberta, (Canada), the son of William C. R. and Eva P. (née Daley) Gall. My family moved east to the Province of Ontario in 1928, and then in 1929 to Detroit, Michigan, United States of America, where I began Public (Primary) School.

My eight years public schooling were spent consecutively in Detroit (U.S.A.), East Windsor, Toronto and South Windsor, Ontario, and latterly in Chatham, Ontario, where I graduated in June, 1937, at the age of 12. Same year entered Secondary School - the Chatham Collegiate Institute, from which I graduated with honours, obtaining the Senior Matriculation Diploma in 1942 at the age of 17.

Proceeded to the University of Toronto, Toronto, Ontario, from which, after four years of study, I received the degree of Bachelor of Applied Science (B. A. Sc.) in Chemical Engineering on June 6th, 1946, at the age of 21.

During both my Secondary and University schooling I was active in numerous student athletic and social organizations. While attending University I worked during the holiday periods for the Canadian Pacific Railway (1943); the Goodyear Tire and Rubber Co. of Canada, Ltd. (1944). Following my third University year (1945), I transferred from the "Reserve" to the "Active Canadian Army", and underwent training as an Officer Cadet in the Royal Canadian Engineers. At the cessation of hostilities later that year I returned to my final University year.

Shortly after graduation I entered the employ of the Canada and Dominion Sugar Co. Ltd., Chatham, Ontario, as Assistant Chemist, in which position I remained until proceeding to Europe in March, 1947. In May of that year, Professor Dr. F. Fischer, Director of the Institute for Technical Physics at the Swiss Federal Institute of Technology, Zurich, Switzerland, agreed to give me space and equipment in the Section for Industrial Research (Afif) of his Institute, to carry out physical-chemical investigations on non-aqueous semi-conducting hydrocarbon oil systems.

In August, 1947, I was accepted as the first Canadian exchange student (to the Swiss Federal Institute of Technology) in the newly arranged Swiss-Canadian Student Exchange, for the school year 1947/48, and later, also for 1948/49. In July, 1948, I accepted the position of Scientific Co-Worker in the Institute for Technical Physics, then, and now, under the directorship of Professor E. Baumann, who succeeded Professor Dr. Fischer following his death in December, 1947. This thesis was completed in October, 1949.

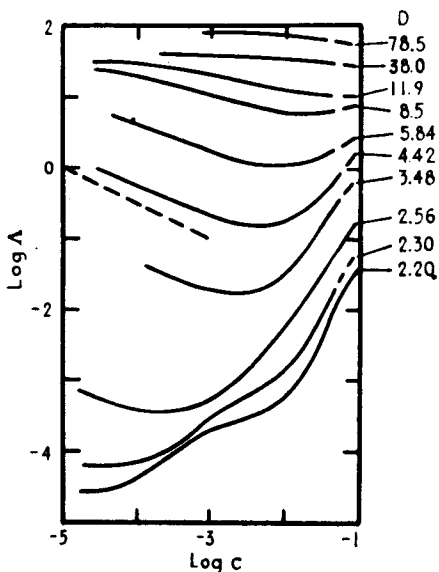


Fig. 1 The influence of D.C. on the variation of conductance with concentration. Tetraisoamylammonium nitrate in dioxane-water mixtures at 25°C. D.C. indicated at the right hand margin (Experimental curves after Fuoss and Kraus)

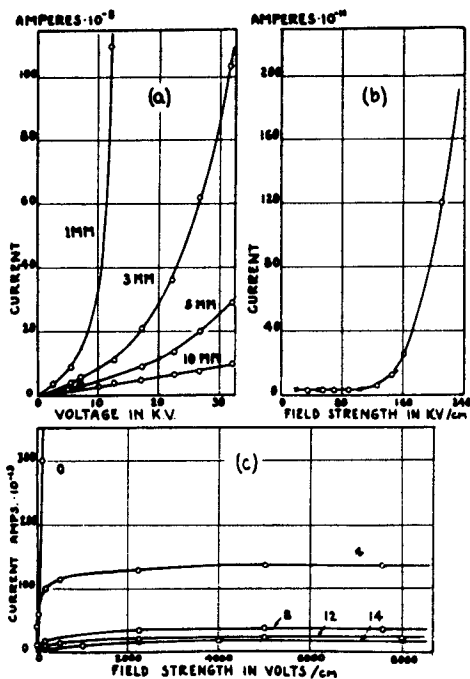


Fig. 2 Current-voltage curves in insulating oils. (a) commercial insulating oils; (b) further purified; (c) successive distillation

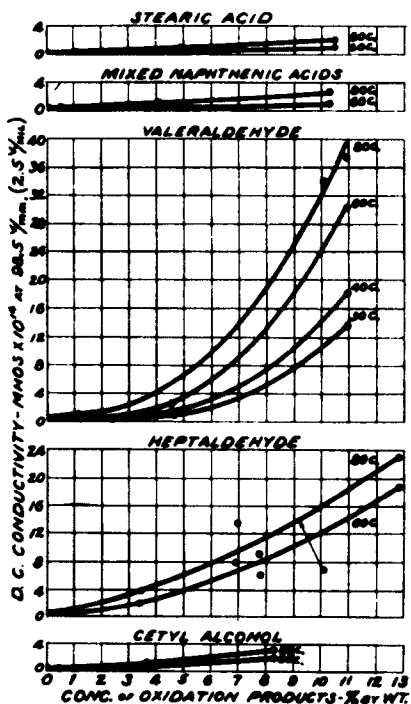


Fig. 3 Effect of Soluble Oxidation Products on the Conductivity of Liquid Paraffin

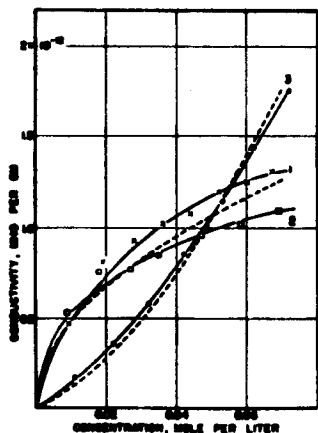


Fig. 4 Conductivity vs. Concentration of Solutions in Hydrocarbon Oil
 Curve 1: Tributylamine varying; oleic acid 0.05N; o-cresol 0.05N
 Curve 2: Tributylamine 0.05N; oleic acid varying; o-cresol 0.05N
 Curve 3: Tributylamine 0.05N; oleic acid 0.05N; o-cresol varying
 (Conductivity data reduced to a D.C. of 2.35)
 x o and solid lines - experimental data
 Dotted lines - calculated

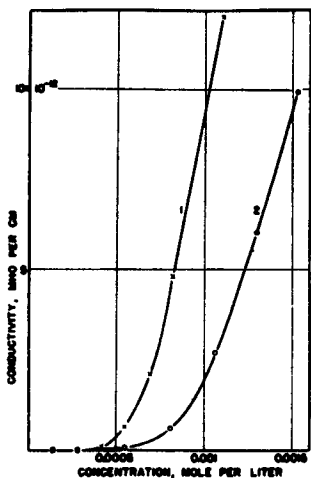


Fig. 5 Conductivity vs. Concentration of Solutions in Hydrocarbon Oil

Curve 1: Triethanolamine varying; oleic acid 0.06N
 Curve 2: Triethanolamine varying; oleic acid 0.03N

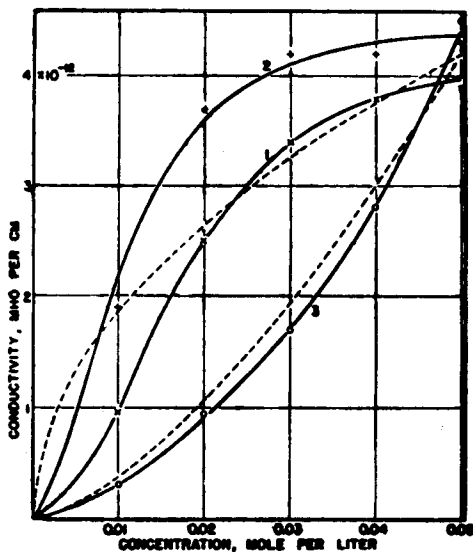


Fig. 6 Conductivity vs. Concentration in Hydrocarbon Oil

Curve 1: Tributylamine varying; myristic acid 0.05N

α -naphthol 0.05N

Curve 2: Tributylamine 0.05N; myristic acid varying;

α -naphthol 0.05N

Curve 3: Tributylamine 0.05N; myristic acid 0.05N;

α -naphthol varying

(Conductivity data reduced to a D.C. of 2.35)

x + o and solid lines - experimental data

Dotted lines - calculated

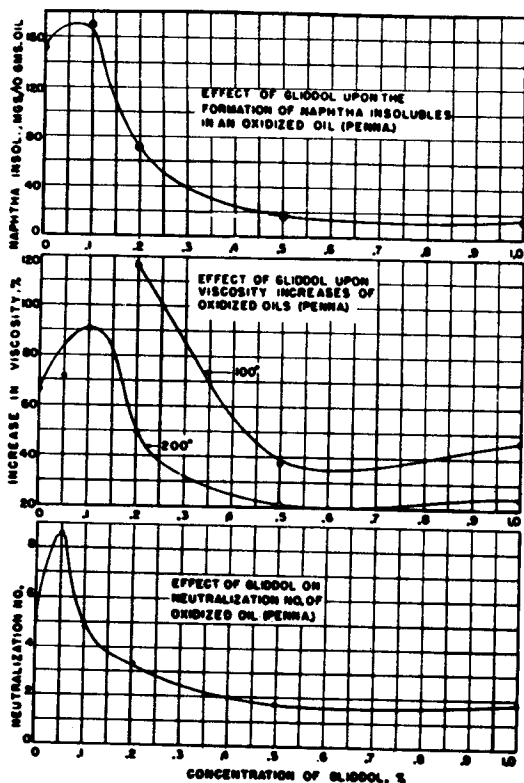


Fig. 7
Effect of Gliddol Concentration on Deterioration of High Viscosity Index Oil

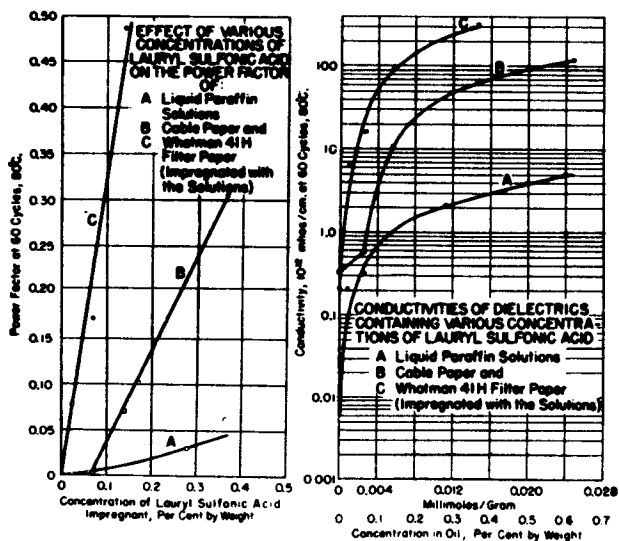
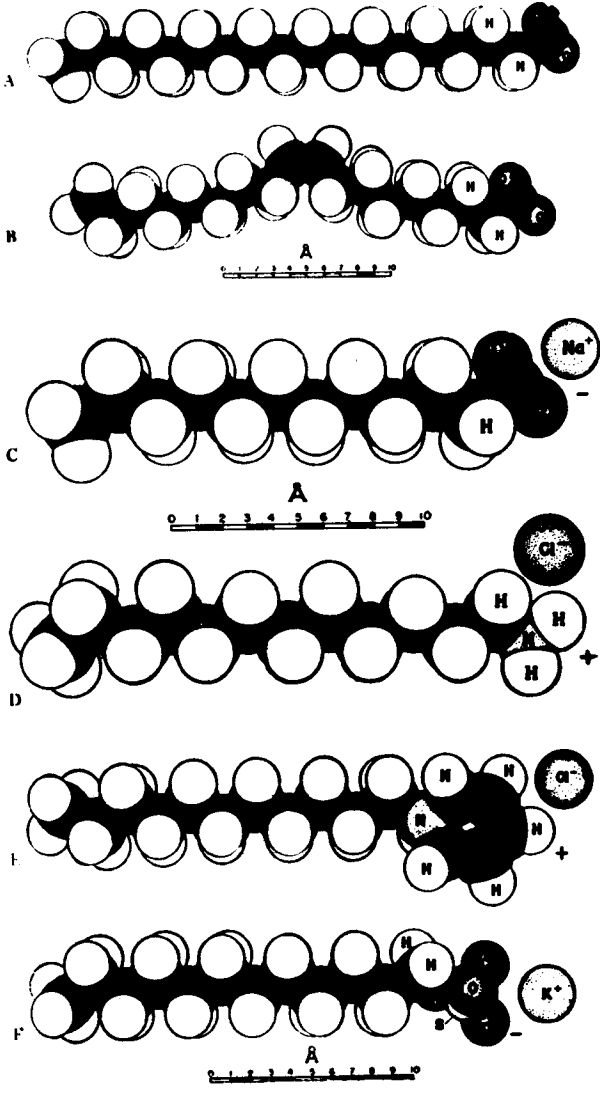


Fig. 8
Effect of Lauryl Sulphonic Acid on the Power Factor and Conductivity of Various Dielectrics

Fig. 9 Models of Colloidal Electrolyte Ions
 A Stearate, B Oleate, C Sodium laurate, D Lauryl ammonium chloride, E Lauryl pyridinium chloride, F Potassium lauryl sulphate



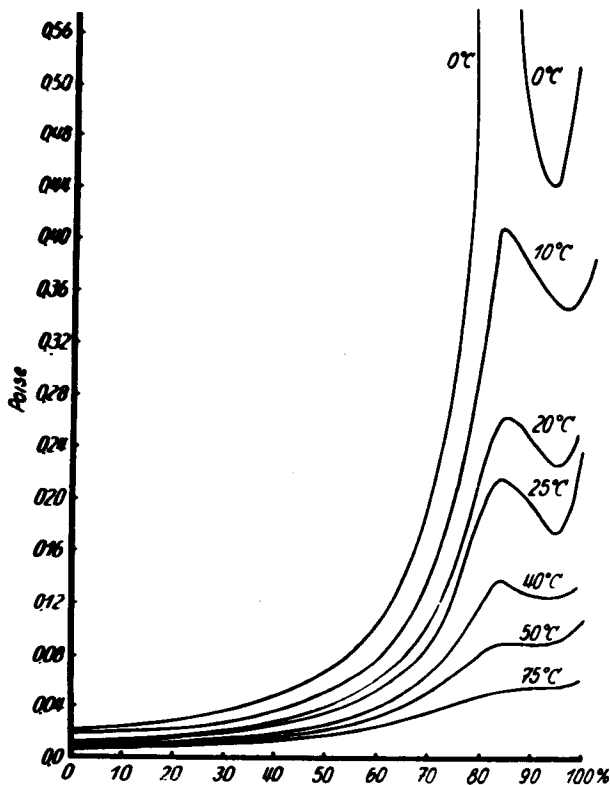


Fig. 10 Viscosity of Sulphuric acid-Water Mixtures

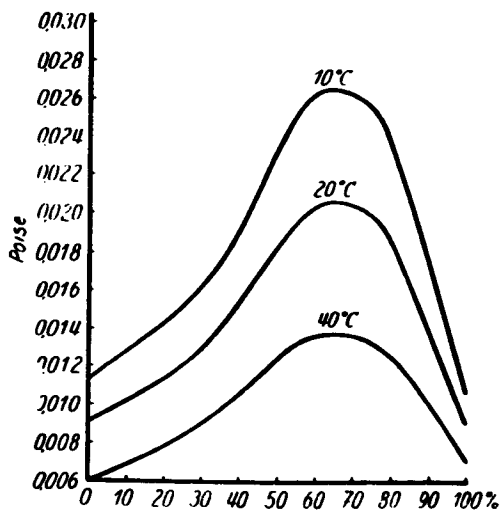


Fig. 11 Viscosity of Nitric acid-Water Mixtures

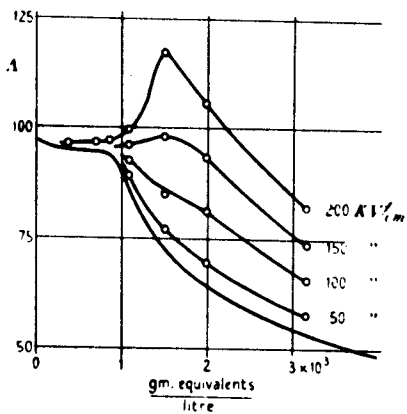


Fig. 12 Equivalent Conductivity of Cetyl Pyridinium Chloride at different Field Strengths at 25°C

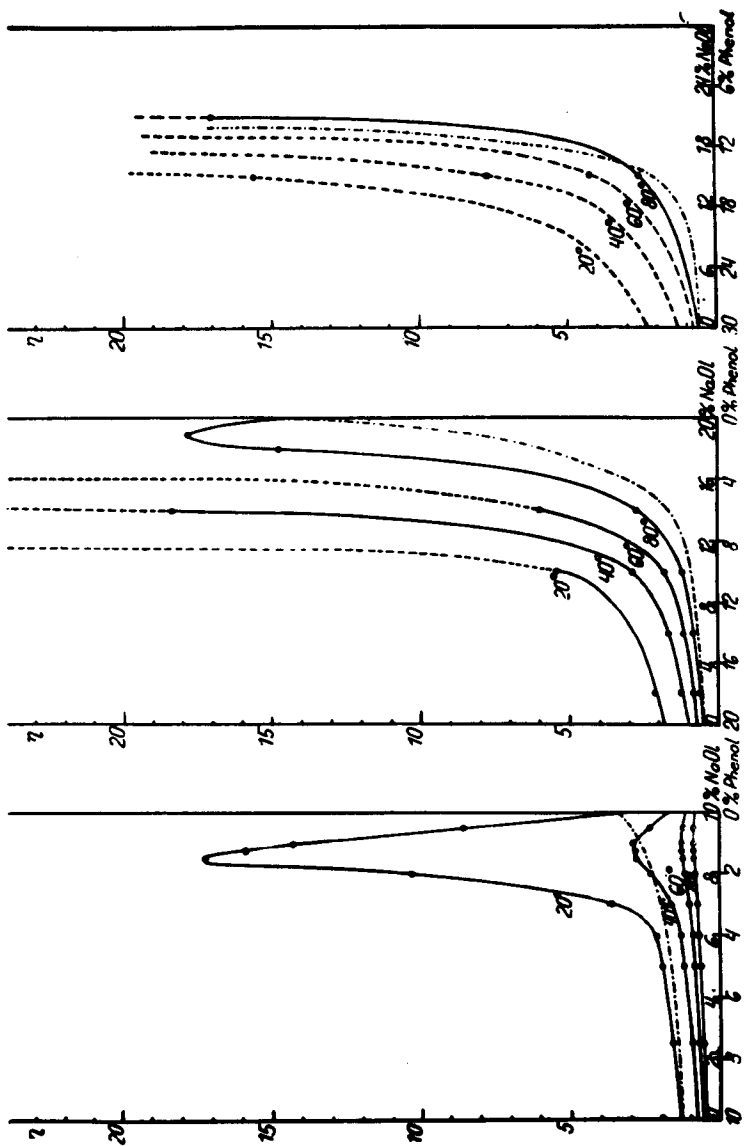


Fig. 13 Viscosity Isotherm for Sodium Oleate-Phenol-Water Mixtures
 From left to right 90, 80 and 70% water content respectively

Viscosity Isotherms at 30° C for Aqueous Sodium Oleate and Phenols (% by weight)

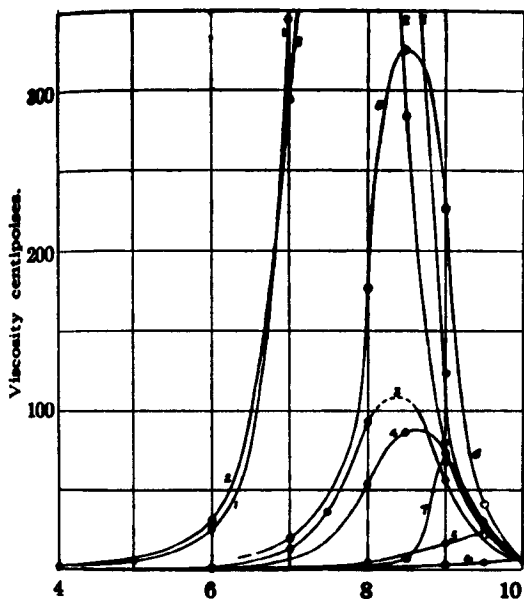


Fig. 14 Water content 90%

1. p-cresol
2. creosol
3. guaiacol
4. phenol
5. resorcinol
6. vanillyl alcohol
7. o-bromophenol
8. catechol

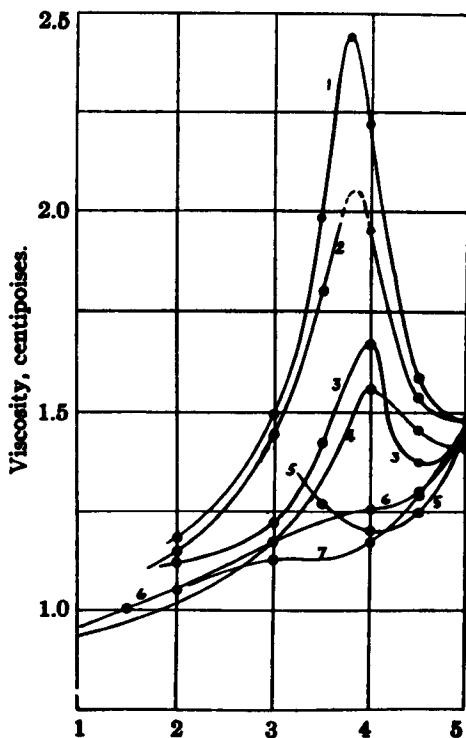


Fig. 15 Water content 95%

1. p-cresol
2. creosol
3. guaiacol
4. phenol
5. catechol
6. vanillyl alcohol
7. resorcinol

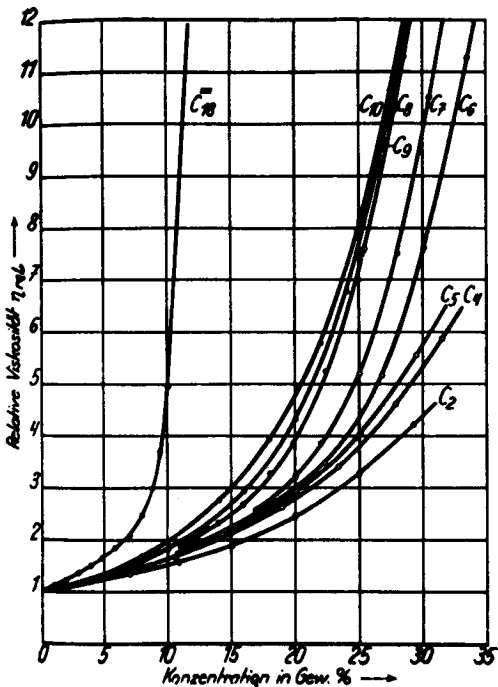


Fig. 16
Viscosity-Concentration
Curves for Homologous
Sodium Soaps at 20°C in
Water

C₂ acetate, C₄ butyrate,
C₅ valeriate
C₆ capronate
C₇ heptylate
C₈ caprylate
C₉ nonylate
C₁₀ caprinat
C₁₈ oleate

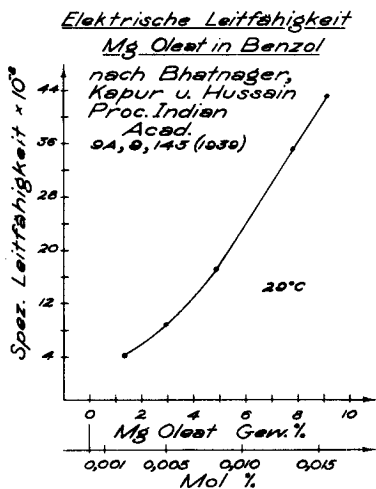


Fig. 17
Electrical conduc-
tivity of Magnesium
Oleate in Benzene
at 29°C

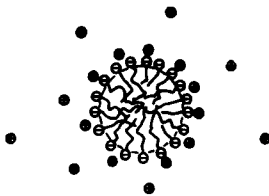


Fig. 18 Spherical Micelle in Dilute Soap Solution showing Fos. Gegenions

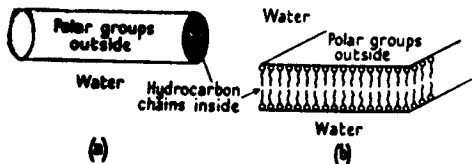


Fig. 20 Structure of Rod-like and Plate-like Micelles

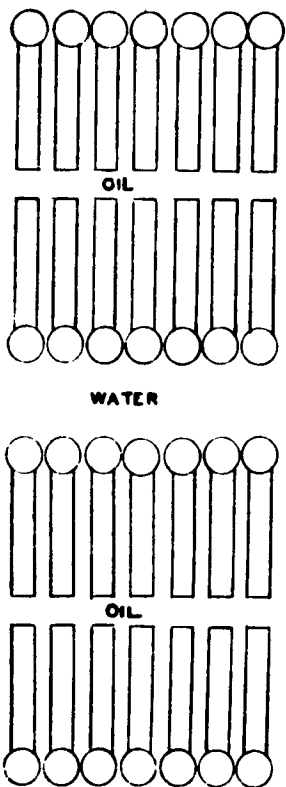


Fig. 21 Idealized Hess Lamellar Micelle made of two McBain Lamellar Micelles or "Sandwiches"

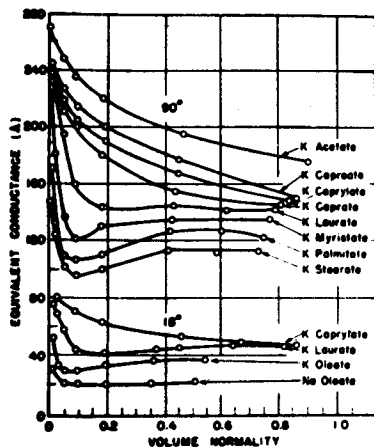


Fig. 19 Equivalent Conductances of Soap Solutions at 18 and 90° C

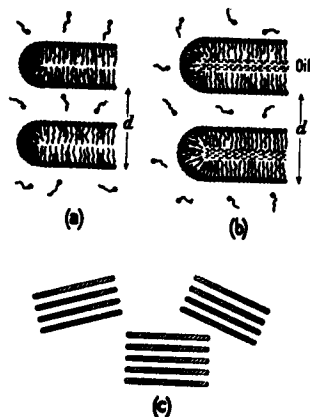


Fig. 22 Suggested Structure of Lamellar Micelles in Aqueous Solution:
 (a) alone
 (b) containing solubilized oil;
 (c) laminated 'bundles' (two-dimensional)

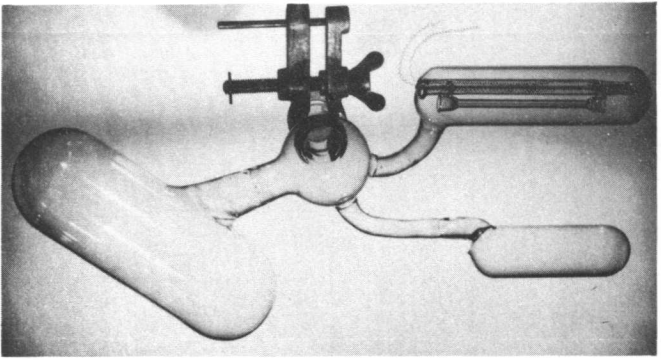


Fig. 26
Measuring
Apparatus
No. 3

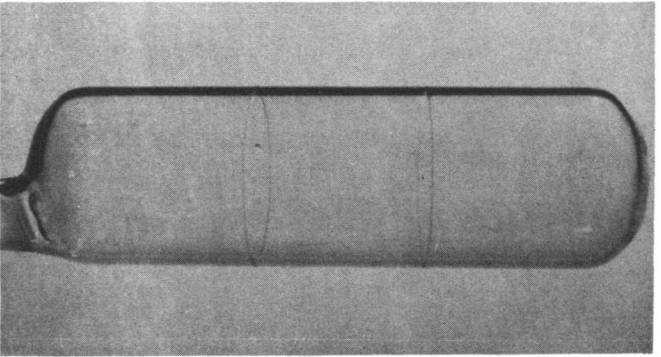


Fig. 30
Viscosity
Measuring
Arm

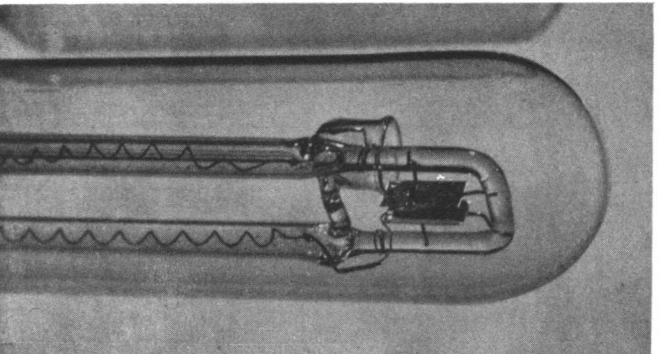


Fig. 28
Conductivity
Cell-Electrode
Arrangement

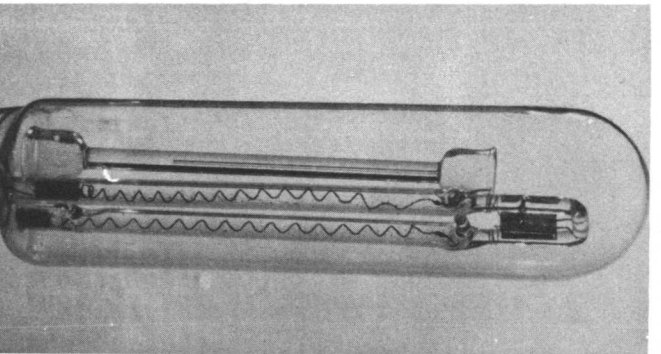


Fig. 27
Conductivity
Measuring Cell

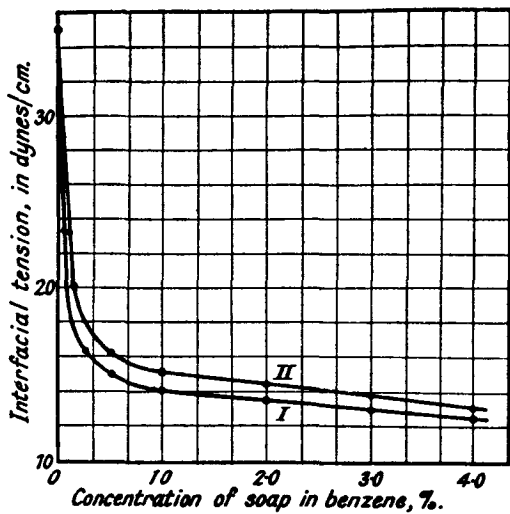


Fig. 23 Interfacial Tension of Magnesium Oleate I and Calcium Oleate II Soaps in Benzene



Fig. 24 Soap Micelle in Plastic and Gel State Lawrence or Inverted McBain Micelle

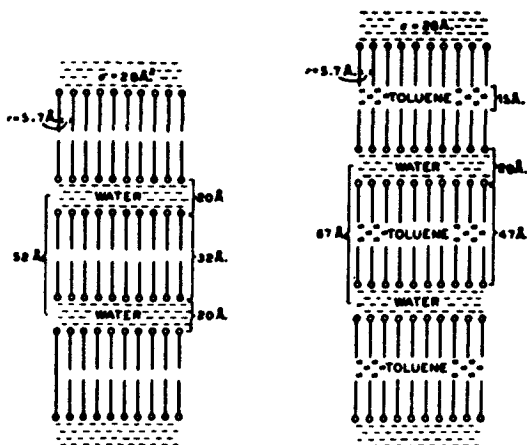


Fig. 25 Idealized Cross Section through a Soap-Water System (left) and a Soap-Water-Hydrocarbon System (right)

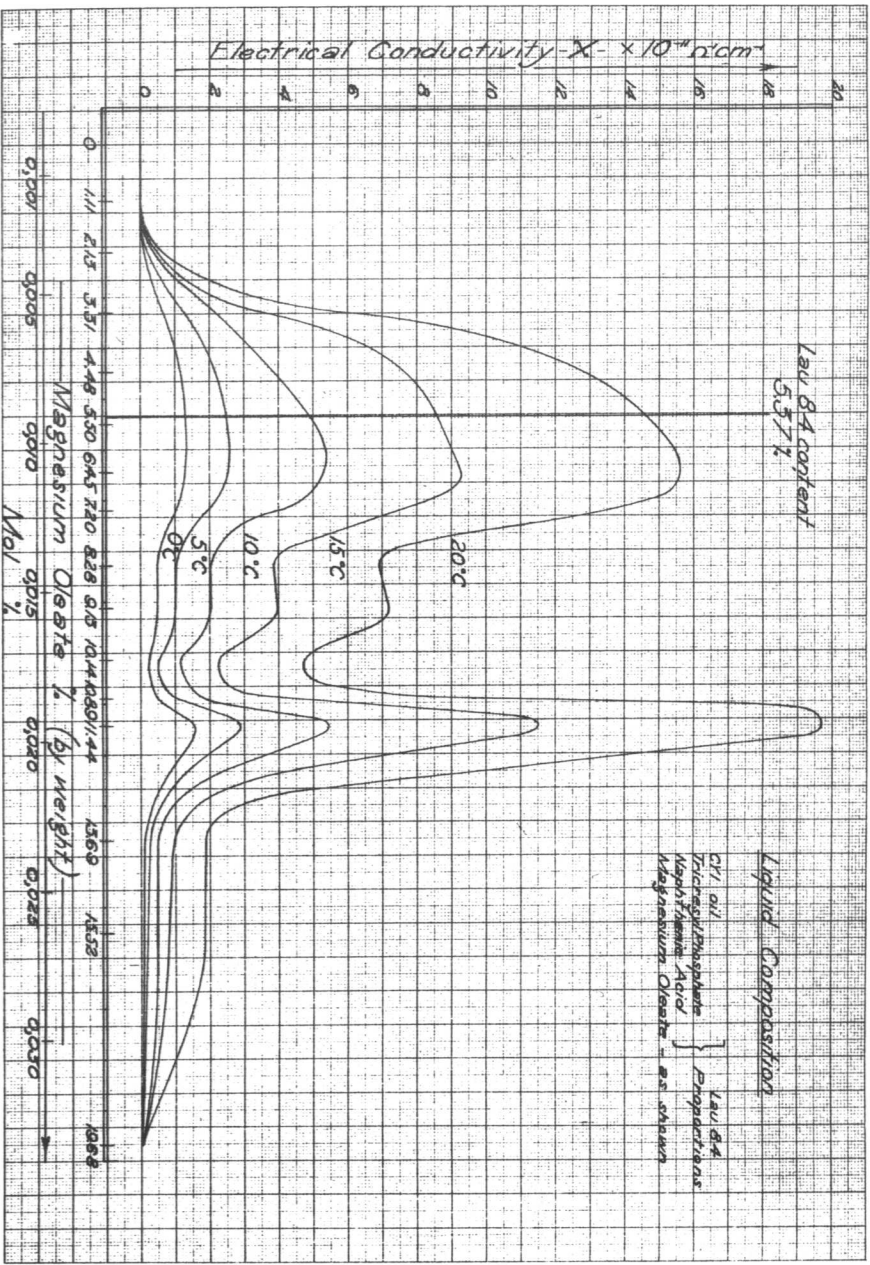
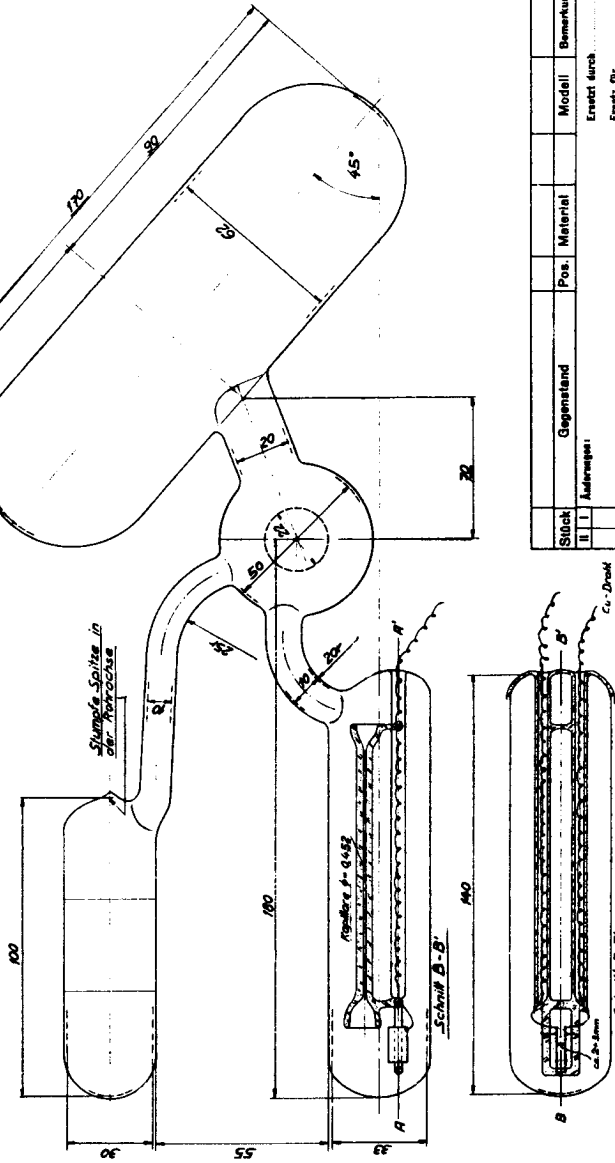


Fig. 31 Conductivity vs. Magnesium oleate Content CY1 oil 98.26%;
 Tricresyl phosphate 1.00%; Naphthenic acid 0.74%; Magnesium oleate
 varying (Test No. 1)

Fig. 29 Full Scale Working
Drawing of Measuring Apparatus
No. 3



Stück	Gegenstand	Pos.	Material	Modell	Bemerkung
II	Aufmesser				
Erstellt durch:					
Messzahl					
Zahl 28.744					
Gezeichnet von					
1/1					
Gezeichnet					
Institut f. techn. Physik der ETH Zürich					

R15040

Bei beiden Schnitten nur innere Teile im Schnitt.

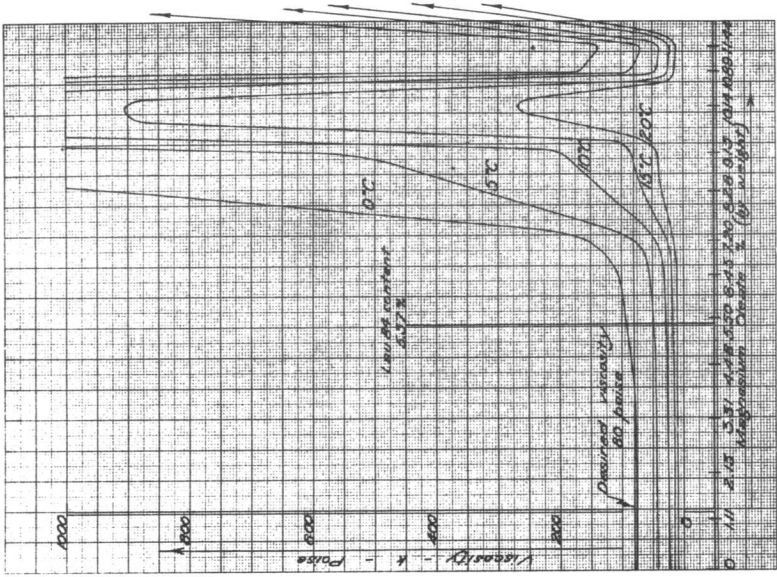


Fig. 32 Viscosity vs. Magnesium oleate Content (Test No. 1)

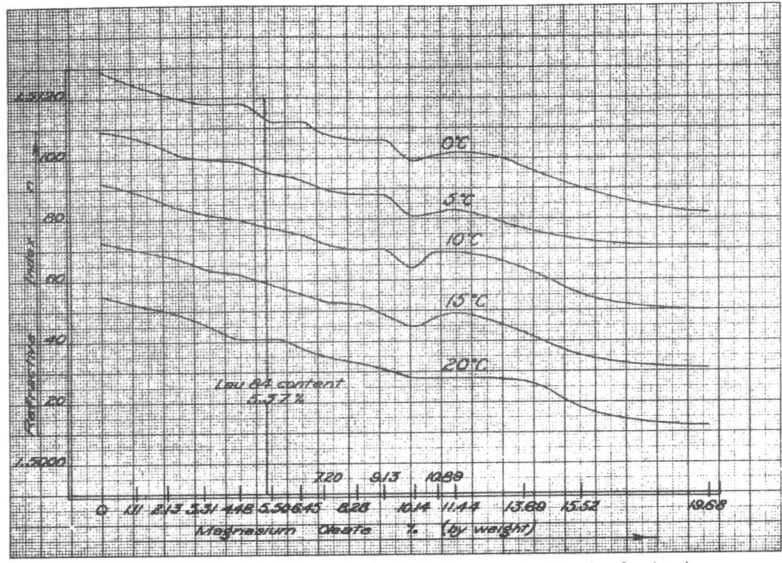


Fig. 33 Refractive index vs. Magnesium oleate Content (Test No. 1)

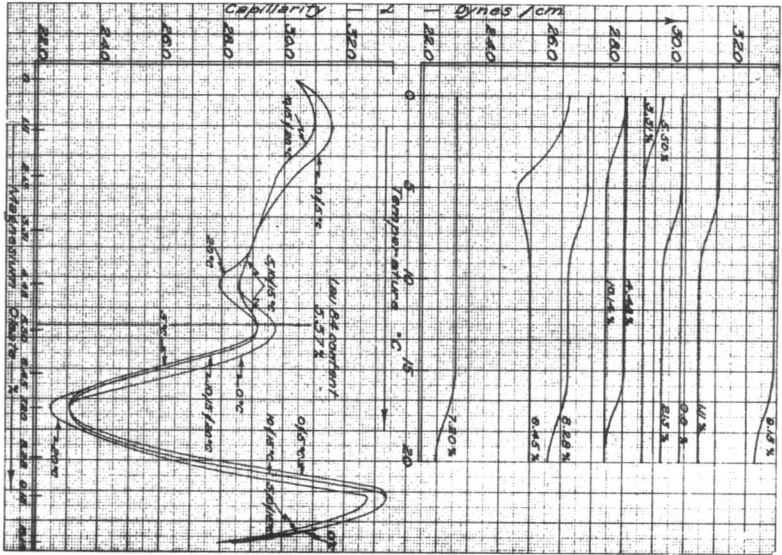


Fig. 35 Capillarity vs. Magnesium oleate Content (below) and Temperature (above) (Test No. 1)

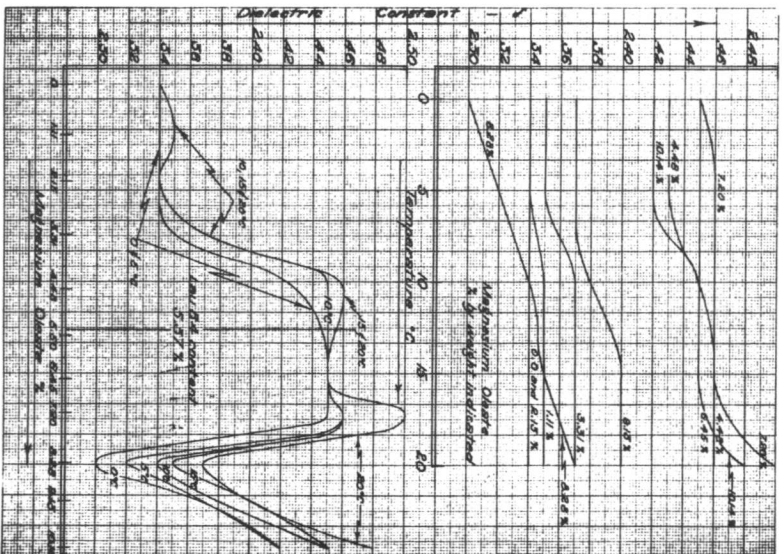


Fig. 34 Dielectric Constant vs. Magnesium oleate Content (below) and Temperature (above) (Test No. 1)

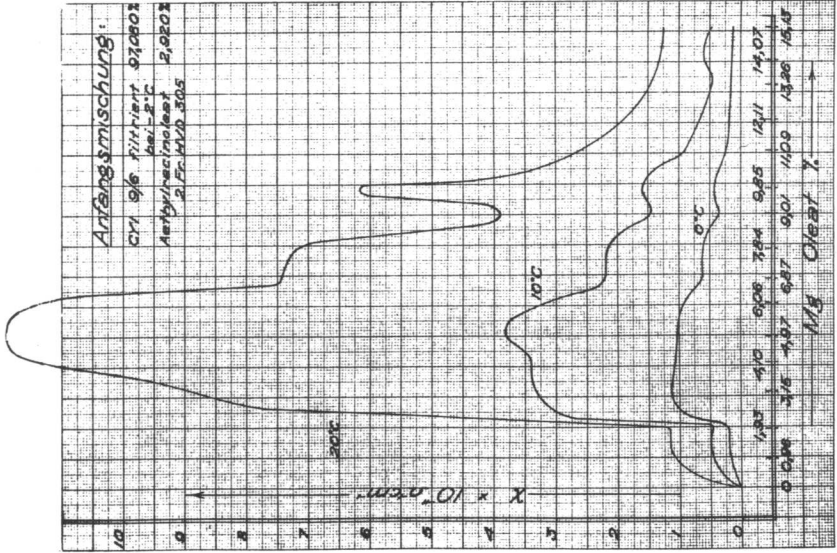


Fig. 36 Conductivity vs.
 Magnesium oleate Content CYI
 oil 97.080%; Ethyl ricinoleate
 2.920%; Magnesium oleate
 varying (Test No. 2)

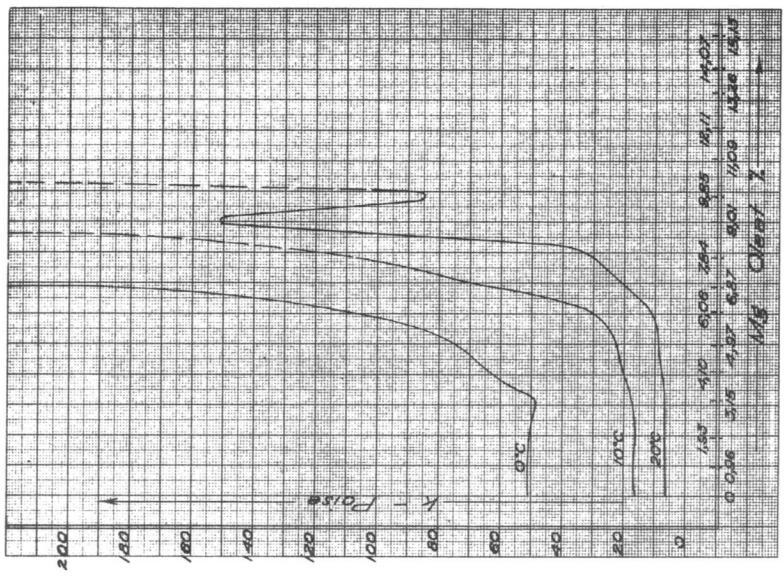


Fig. 37 Viscosity vs.
 Magnesium oleate Content
 (Test No. 2)

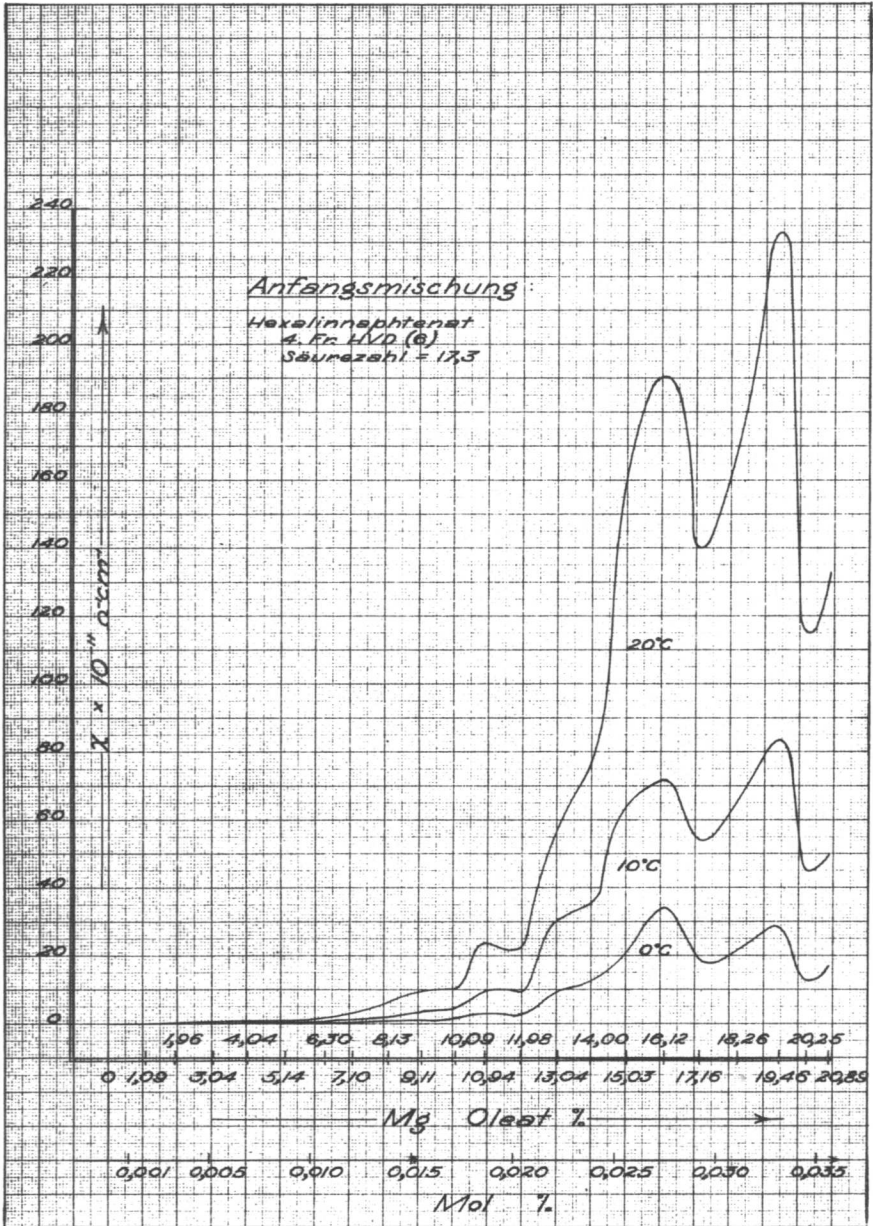


Fig. 39 Conductivity vs. Magnesium oleate Content (Test No. 3)
Hexaline naphthenate, acid no. = 17.3, 100.00%; Magnesium oleate
varying

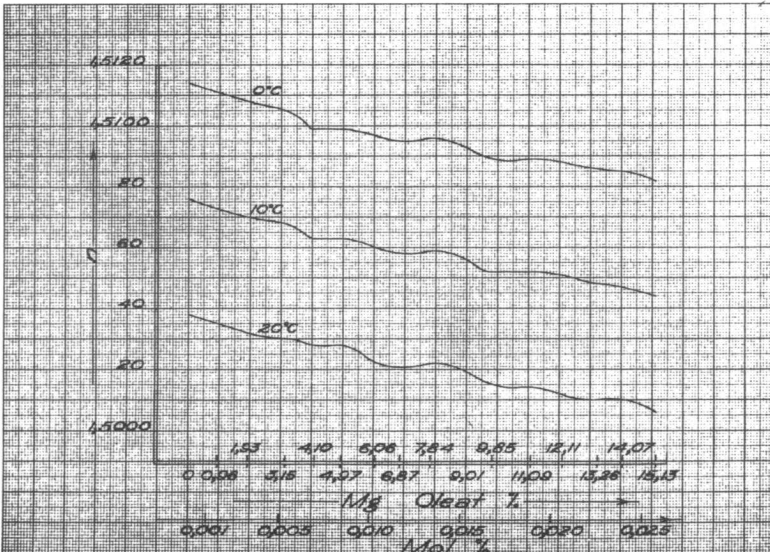


Fig. 38 Refractive index vs. Magnesium oleate Content (Test No. 2)

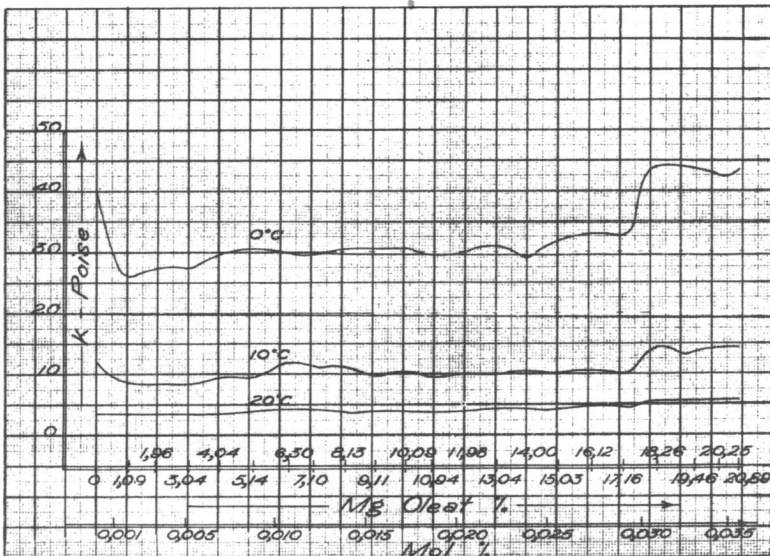


Fig. 40 Viscosity vs. Magnesium oleate Content (Test No. 3)

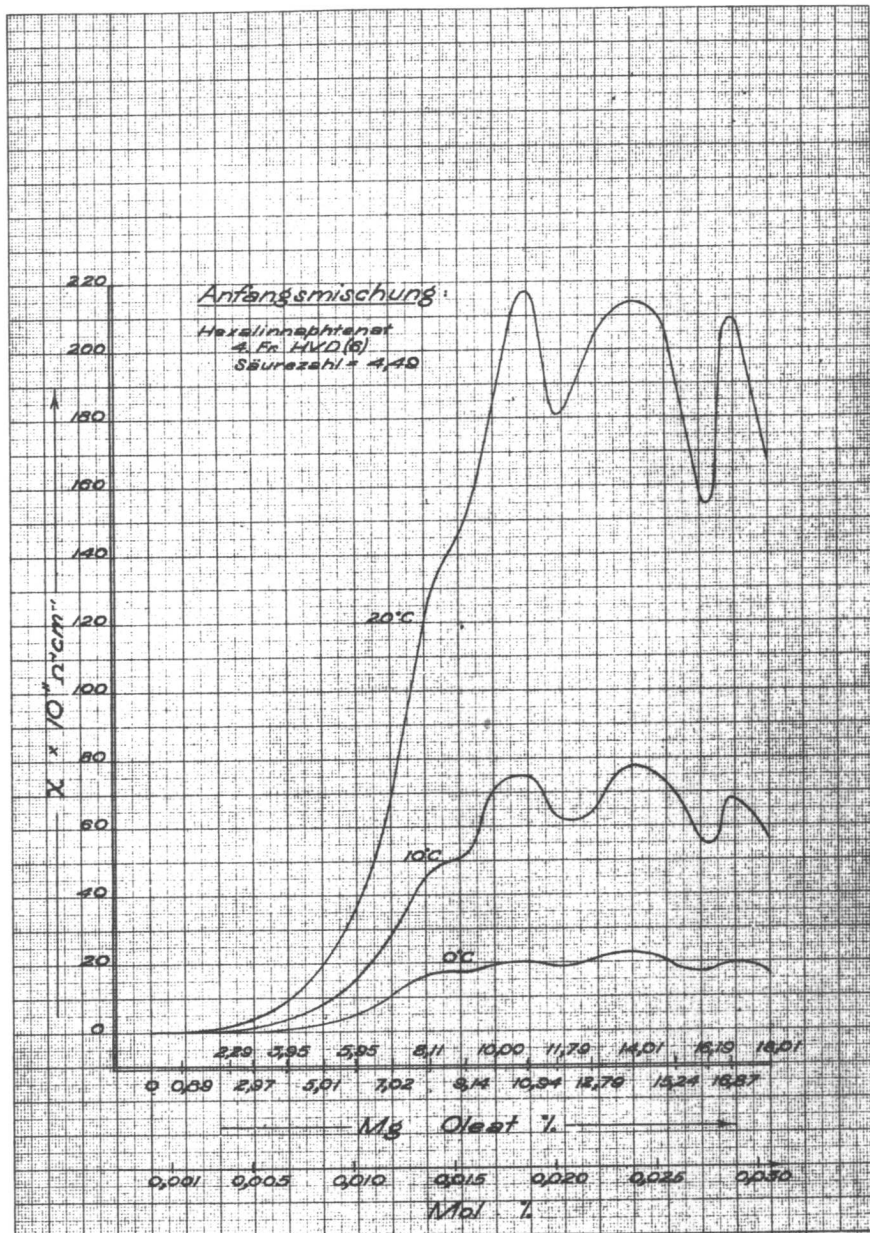


Fig. 42 Conductivity vs. Magnesium oleate Content (Test No. 4)
Hexaline naphthenate, acid no. = 4.49, 100.00%; Magnesium oleate
varying

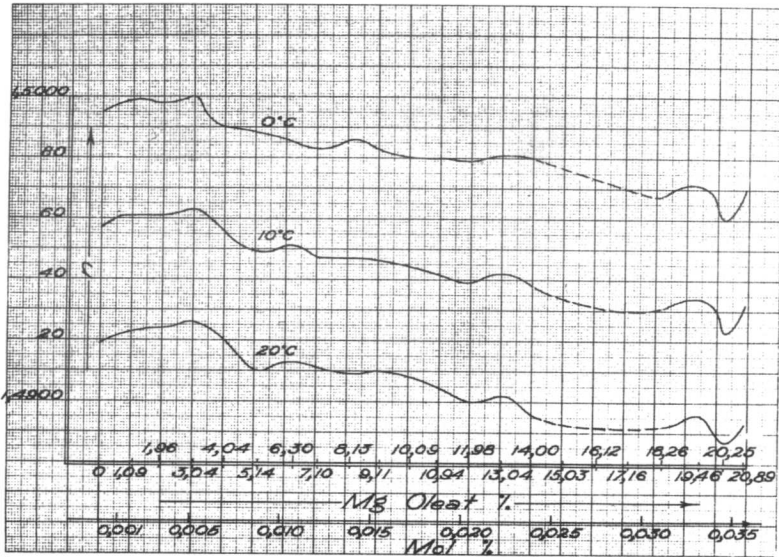


Fig. 41 Refractive index vs. Magnesium oleate Content (Test No. 3)

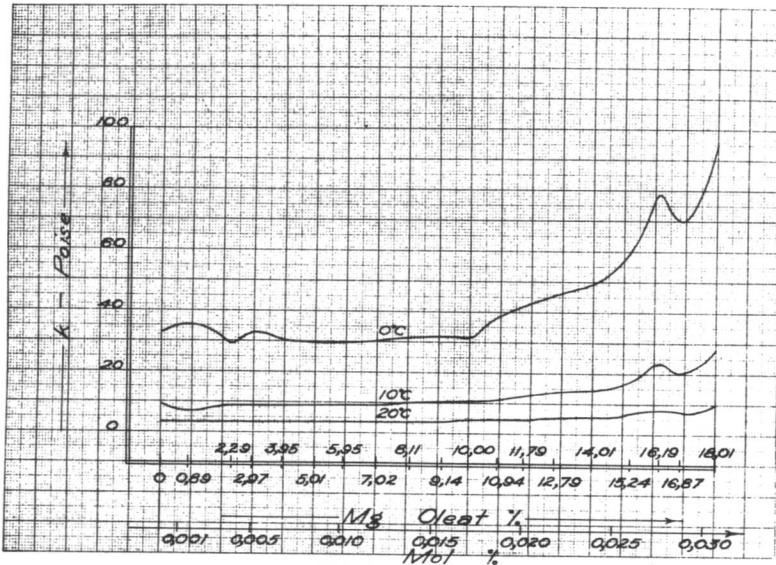


Fig. 43 Viscosity vs. Magnesium oleate Content (Test No. 4)

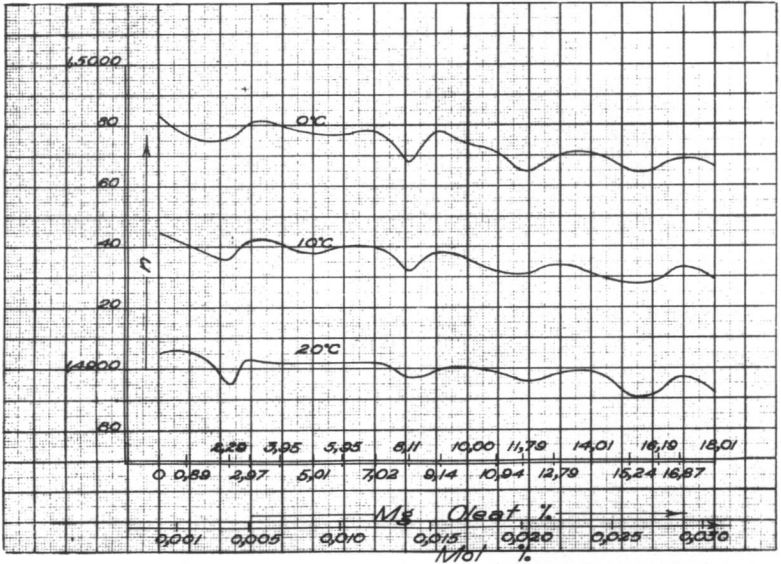


Fig. 44 Refractive index vs. Magnesium oleate Content (Test No. 4)

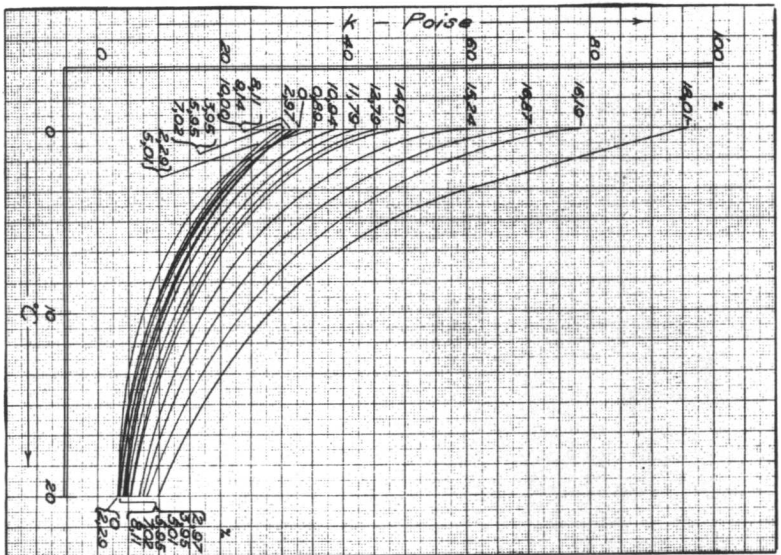


Fig. 45 Viscosity vs. Temperature (Test No. 4)

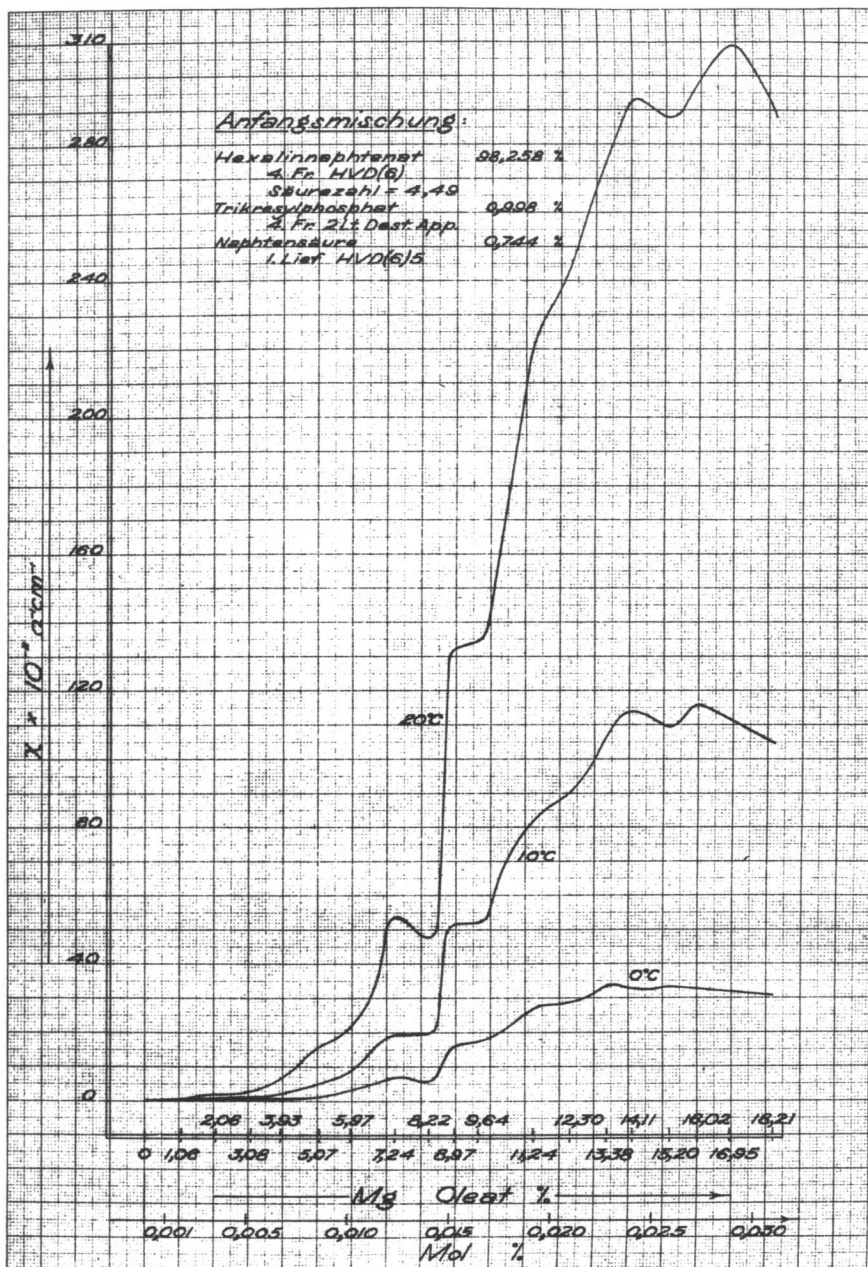


Fig. 46 Conductivity vs. Magnesium oleate Content (Test No. 5)
 Hexaline naphthenate, acid no. = 4.49, 98.258% Tricresyl phosphate
 0.998%; Naphthenic acid 0.744%

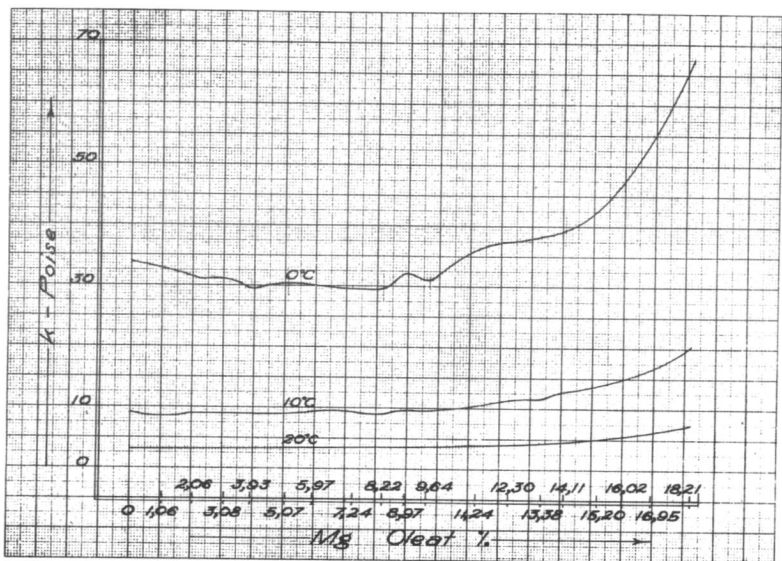


Fig. 47 Viscosity vs. Magnesium oleate Content (Test No. 5)

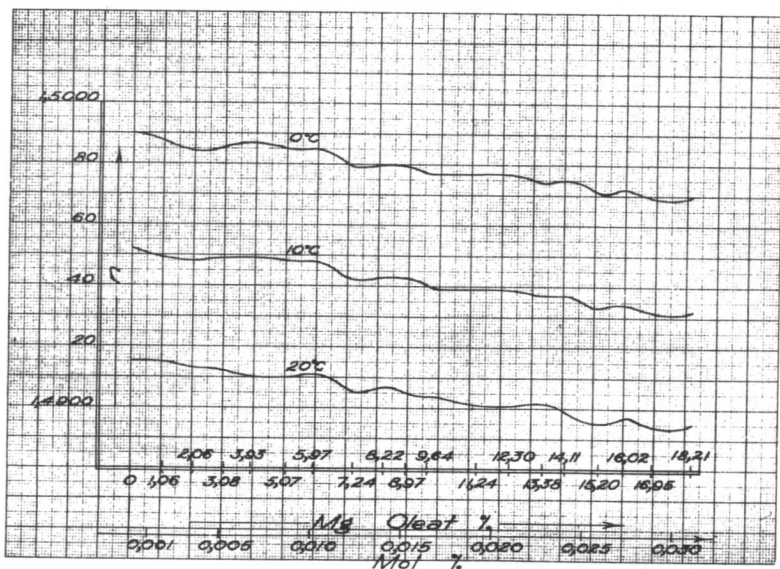


Fig. 48 Refractive index vs. Magnesium oleate Content (Test No. 5)

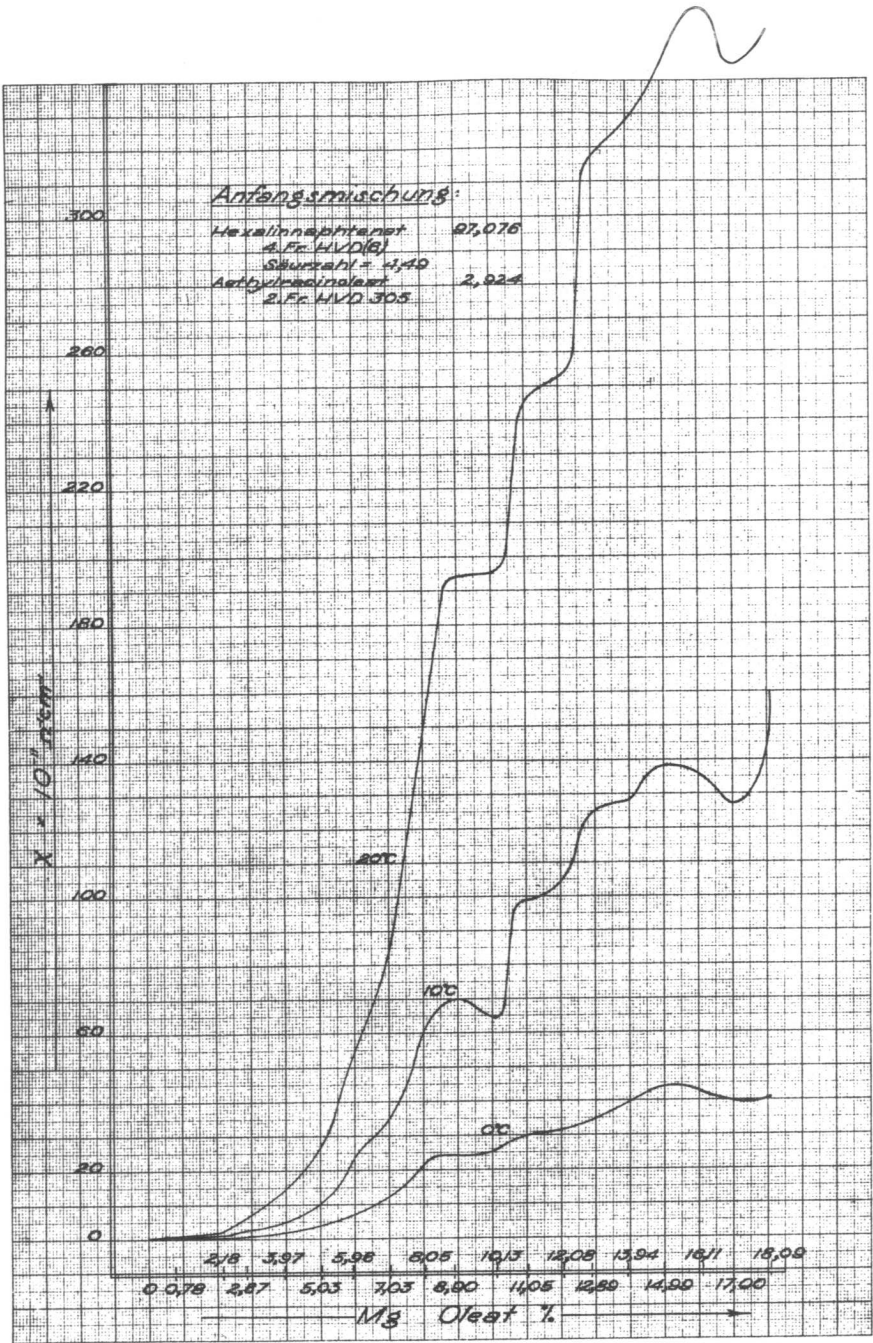


Fig. 49 Conductivity vs. Magnesium oleate Content (Test No. 6)
 Hexaline naphthenate, acid no. = 4.49, 97.076%; Ethyl ricinoleate
 2.924%; Magnesium oleate varying

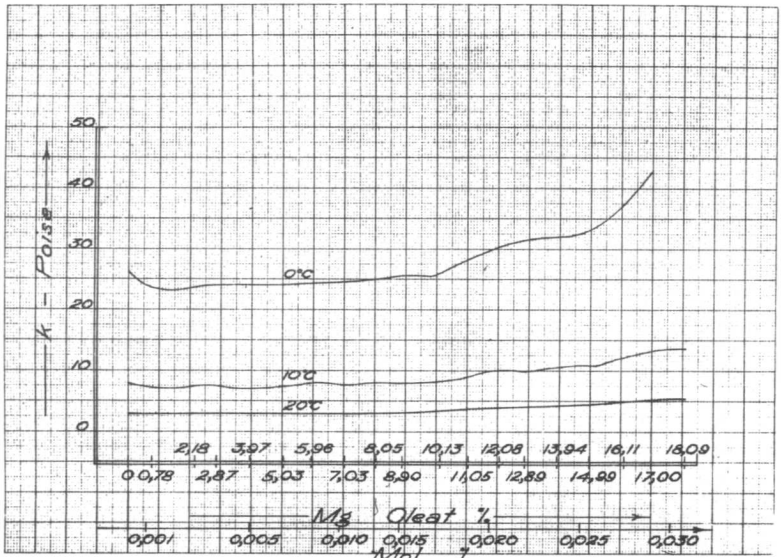


Fig. 50 Viscosity vs. Magnesium oleate Content (Test No. 6)

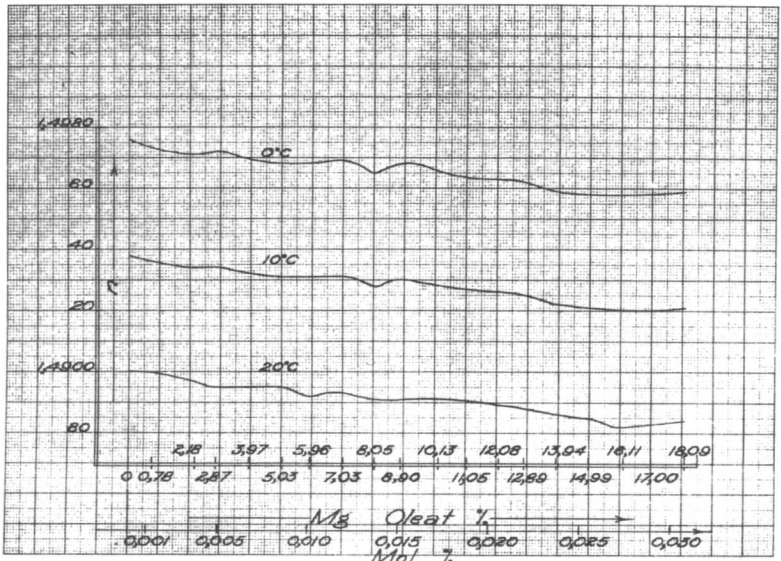


Fig. 51 Refractive index vs. Magnesium oleate Content (Test No. 6)

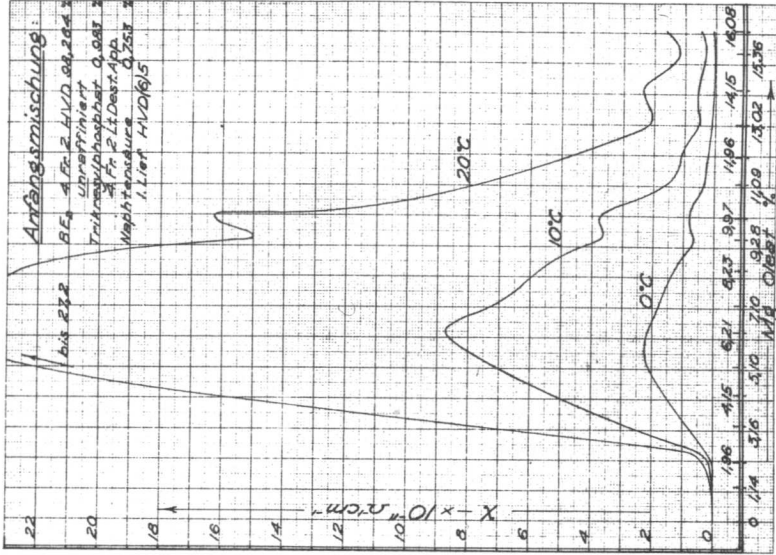


Fig. 52 Conductivity vs.
 Magnesium oleate Content
 (Test No. 7) BE₂ oil 98.264%;
 Tricresyl phosphate 0.983%;
 Naphthenic acid 0.753%;
 Magnesium oleate varying

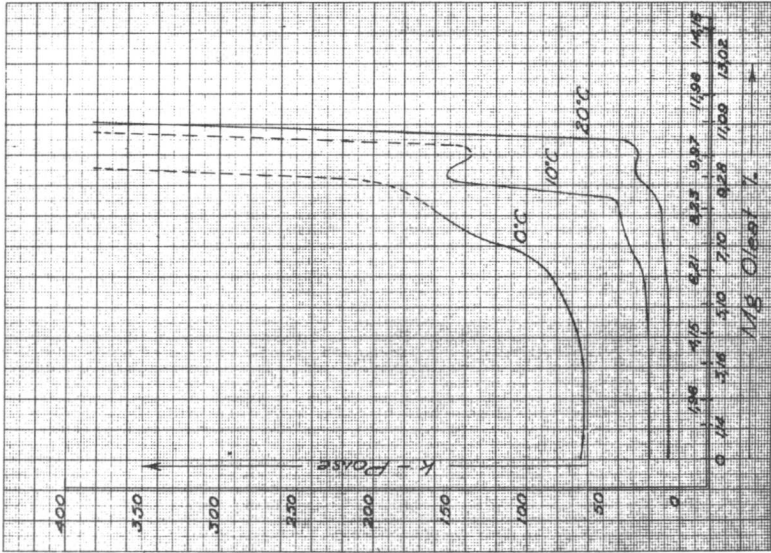


Fig. 53 Viscosity vs.
 Magnesium oleate Content
 (Test No. 7)

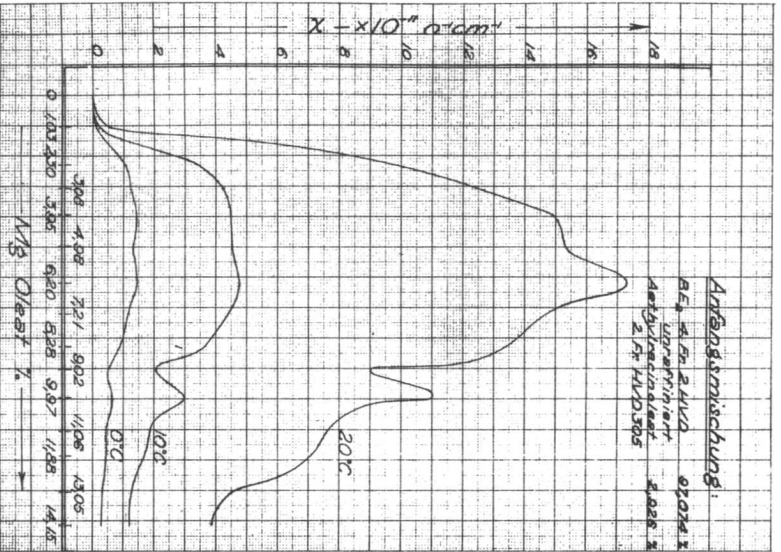


Fig. 55 Conductivity vs.
 Magnesium oleate Content
 (Test No. 8) BE₂ 0.1 97.074%
 Ethyl ricinoleate 2.926%
 Magnesium oleate varying

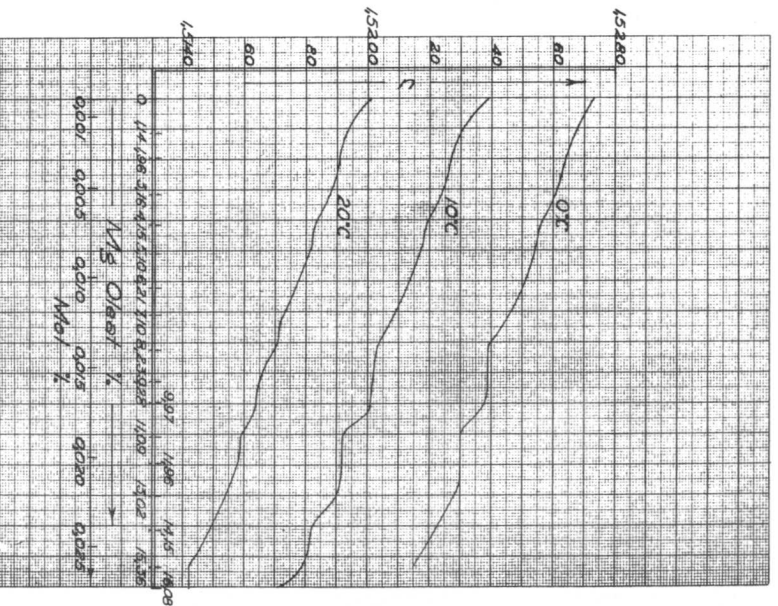


Fig. 54 Refractive index
 vs. Magnesium oleate Content
 (Test No. 7)

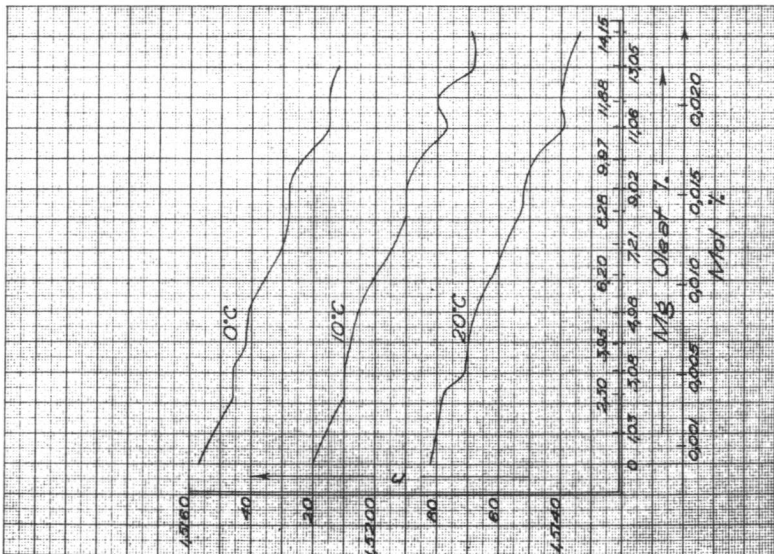


Fig. 57 Refractive index vs. Magnesium oleate Content (Test No. 8)

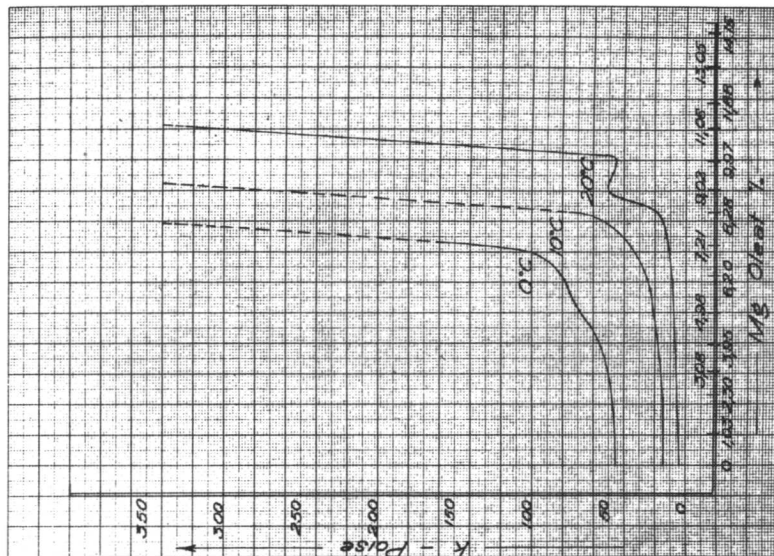


Fig. 56 Viscosity vs. Magnesium oleate Content (Test No. 8)

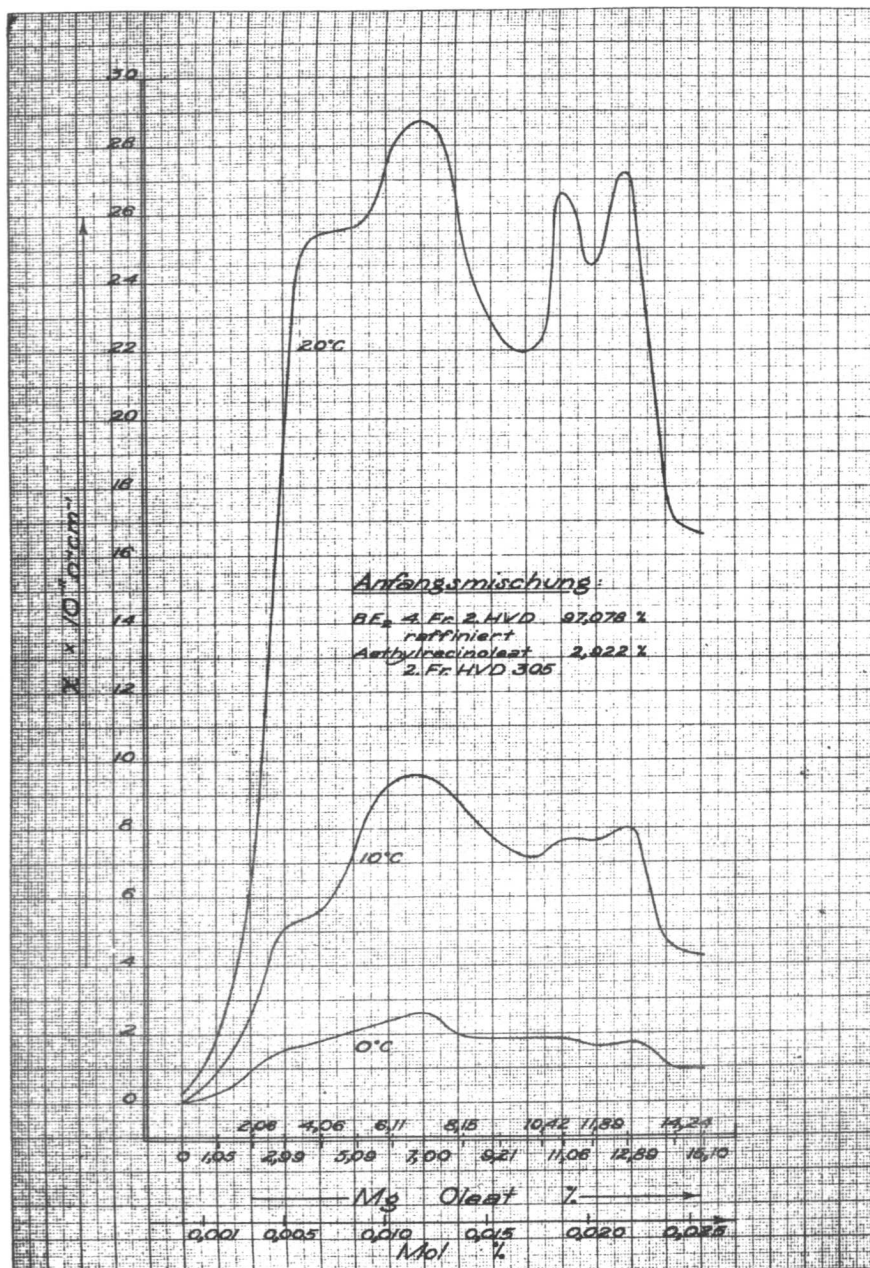


Fig. 59 Conductivity vs. Magnesium oleate Content (Test No. 9)
 BE₂ oil 97.078%; Ethyl ricinoleate 2.922%; Magnesium oleate varying

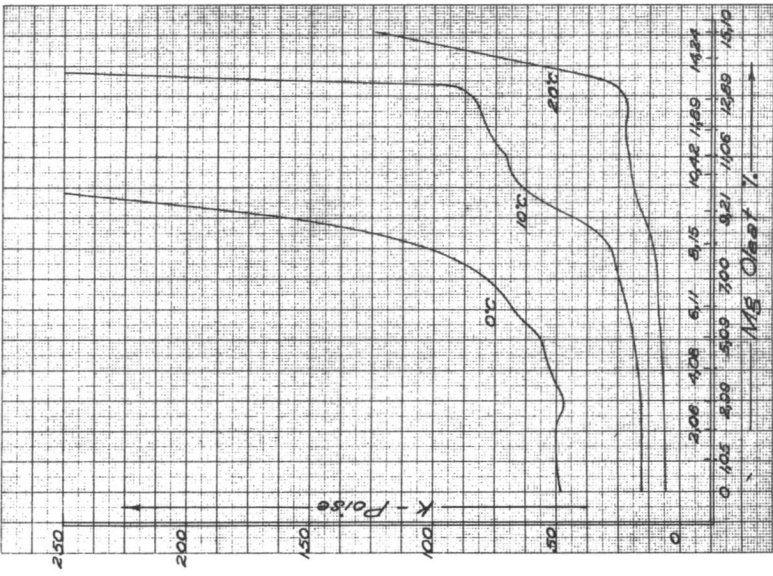


Fig. 60 Viscosity vs. Magnesium oleate Content (Test No. 9)

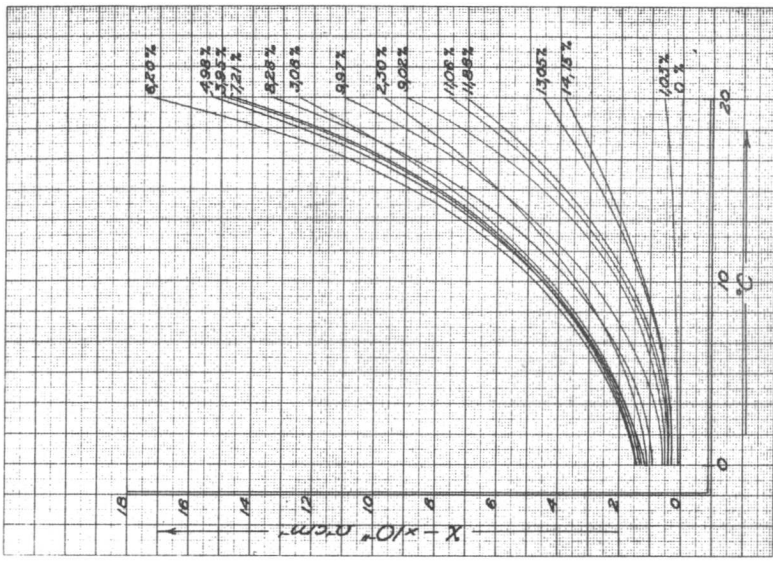


Fig. 58 Conductivity vs. Temperature (Test No. 8)

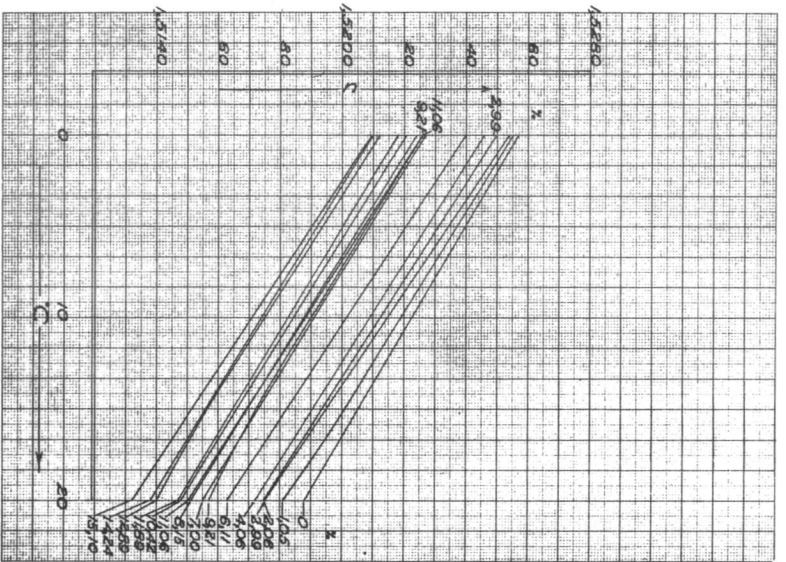


Fig. 62 Refractive index vs. Temperature (Test No. 9)

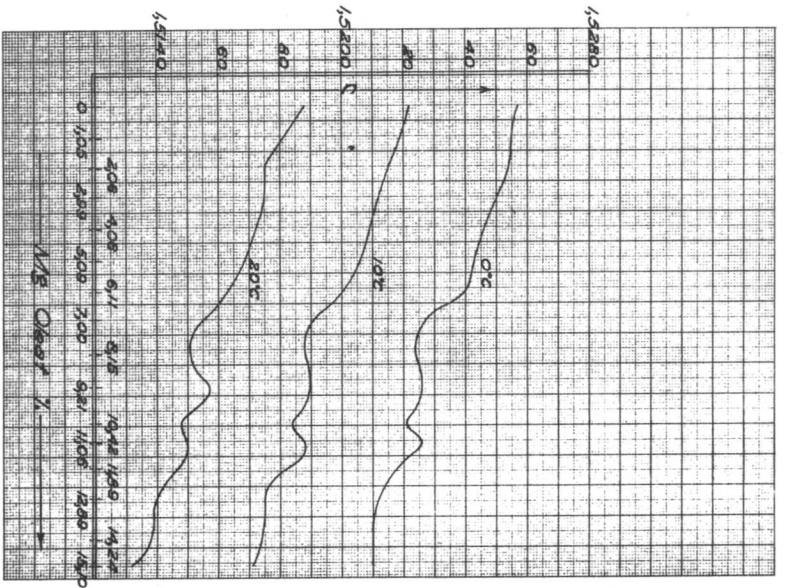


Fig. 61 Refractive index vs. Magnesium oleate Content (Test No. 9)