COLLOIDAL BEHAVIOUR
OF RUBBER

"A STUDY OF THE COLLOIDAL BEHAVIOUR OF RUBBER"

A THESIS

by

R. S. JANE

Presented in part-fulfilment of the requirements for
the Degree of Doctor of Philosophy.

McGILL UNIVERSITY MAY, 1925.

CONTENTS

Page

SECTION I

SECTION II

THEORETICAL DISCUSSION

SECTION III

--o0o--

INTRODUCTION.

Modern colloidal chemistry is the result of the development of Graham's (1) epoch-making experiments which led to his classification of matter into the crystalloidal and colloidal states. In the development, however, Graham's classification has not been retained. The large number of facts that have been discovered since 1861 indicates that a sharp line can scarcely be drawn between the two domains. Gold, for example, in the colloidal state may be essentially crystalline. Furthermore, one and the same substance may be crystalloidal in one solvent and colloidal in another. The difficulty of classification is still a problem and even at the present time our nomenclature is in a primary stage of refinement.

Probably the best classification is due to Freundlich (2). This author used the term lyophobe to represent colloids, which when taken in bulk had no affinity for the dispersion medium, while lyophile was the term used to designate a colloid which when taken in bulk was peptized by the dispersion medium.

It is not surprising to find that with the discovery of the colloidal state of matter there followed a period of enthusiastic research in the new field. As a result, today, the applications of colloidal chemistry extend into a great many branches of science, as well as everyday life. Bancroft (3) states that "a knowledge of colloidal chemistry is essential to anybody who really wishes to understand about: cement, bricks, pottery, procelain, glass, enamels, oils, greases, soaps, candles, glue, starch and adhesives; paints, varnishes, lacquers; rubber, celluloid and other plastics; leather, paper, foundry cores, coke, asphalt; graphites, zinc, phosphorus, sodium and aluminum; contact sulphuric acid, hardened oils, etc., etc.; beer, ale and wine, cream, butter, cheese, and caseine products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal, smoke prevention, photography; wireless telegraphy; illuminants; comets; pharmacy; physiology."

For the most part, however, investigators have confined their efforts to hydrophobic and hydrophilic systems, and with few exceptions, (4) lyophilic colloids dispersed in non-aqueous media have been neglected.

The study of hydrophilic sols is rendered exceedingly difficult by at least three disturbing factors; first, hydrolysis; second, in some cases, ionization; third, the effect of the adsorption of hydrogen or hydroxyl ions, which are always present in the purest water. In consequence of this, particularly in the case of proteins, the hydrogen ion concentration must be controlled within very narrow limits. Moreover, the slightest impurity in the form of traces of electrolytes in the dispersed phase, is likely to introduce an element of uncertainty into the experimental results. In spite of this, however, it must be admitted that the masterly researches of Loeb, Robertson, Michaelis and others have done a great deal to unravel the colloidal problems presented by the proteins. But at the same time it can not be said that the problems are solved, or that all phenomena encountered in their study are entirely understood.

In view of the fact that ionization, hydrolysis, and ion adsorption are disturbing elements in the study of hydrolphilic sols, the question of the adaptability of a substance dispersed in a feebly ionizing medium as a means of studying the lyophilic system, presented itself.

In a system, such as cellulose nitrate in nitrobenzene or rubber peptized in benzene, the possibility of hydrolysis is absolutely eliminated, and the adsorption of ions due to the dissociation of the solvent is entirely out of the question. Moreover, it is inconceivable that substances, such as cellulose nitrate or the rubber hydrocarbon could be dissociated or in any way acted upon by such inert solvents as benzene and nitro benzene. Consequently, assuming that the disperse phase, in this case rubber or cellulose nitrate, is obtainable in the pure state, such a lyophilic system, is infinitely less complicated, and certainly less susceptible to solvent action than any known lyophilic system.

At the present time an investigation of a typical organophilic colloid is of the greatest theoretical importance. Especially is it true, when we consider the possibility of ascertaining the parallelisms and the difference in the behaviour of the organo and hydrophilic systems. For instance, the effect of acids, bases, and neutral substances, including inorganic salts, on the disperse phase. The effect of addition of ions of increasing valence; the possible influence of variable charge on the degree of solvation of the colloid. The nature of the action by which light of different wave lengths influences the state of aggregation of the disperse phase. A comparison of the effect of thermal and mechanical treatment in both systems and finally the influence of time or age on the physical properties of the sol.

After a consideration of these possibilities it was decided to commence a rather extensive study of the colloidal behaviour of some typical organophilic colloid. The system chosen was the rubber hydrocarbon dispersed in absolute benzene. This selection was made on account of the fact that Dr. Whitby under whose direction the work was carried on, has a detailed knowledge of the chemistry of rubber. Such a knowledge was found to be invaluable in the preparation of the substance in the pure state, and in subsequent handling of the solutions which was a considerable factor in determining the success of the investigation.

THE IMPORTANCE OF VISCOSITY IN THE STUDY OF THE COLLOIDAL STATE.

The question of the most suitable method for studying the possible changes in the colloidal state of a system now presented itself. In spite of that fact that modern colloidal chemistry affords an extraordinary variety of phenomena, the methods used for their investigation are, however, extremely special ones. Viscosity is by far the most general and universally used. The reasons for this can best be illustrated by explaining the significance of the experimental and theoretical study of viscosity as a means of advancing our knowledge of the colloidal state.

The viscosity of a true solution is completely defined by concentration and temperature. The system consists of only three variables, and therefore we may plot viscosity-concentration curves at constant temperature and viscosity-temperature curves at constant concentration.

The viscosity of colloids presents an entirely different case. A considerably greater number of variables defines the viscosity of emulsoid colloids, especially those which become emulsoid through the adsorption of the solvent followed by peptization, such as gelatin agar in aqueous medium and rubber in non-aqueous media.

In addition to the two variable factors, concentration and temperature, the following factors are already known to affect the viscosity of these systems.

(1) Degree of Dispersity.

It seems as if a maximum viscosity accompanies a medium degree of dispersion, the question being left open, whether the size of the particles influences the viscosity directly or indirectly, that is, through the variable quantity of adsorbed dispersion medium associated with it.

(2) Solvate Formation.

The viscosity is greatly influenced by the amount of solvent associated with each particle of disperse phase. The liquid associated with each particle is probably in the form of an adsorbed layer of orientated molecules. The thickness of this layer in lyophilic sols is at the present unknown, but it nevertheless must have a great deal of influence on the physical properties of the sol. This will be discussed more fully later on.

(3) Previous Thermal Treatment.

A gelatin hydrosol or a rubber organosol which has been repeatedly heated and cooled has a much lower viscosity than it had before this thermal treatment. In the case of gelatin it may be due to hydrolysis or the breaking down of some sort of structure, but in the case of rubber, it has hitherto been assumed due to depolymerization. In section II of this paper thermal treatment has been taken up in detail and will not be discussed any further at this point.

(4) Previous Mechanical Treatment.

An enormous decrease in viscosity for a definite concentration is observed in a solution of rubber, when the rubber has been previously masticated on hot rolls. An unmasticated sample of rubber in benzene of a concentration of .3% gives a solution of about five times the viscosity of that of benzene itself, while with a thoroughly masticated sample, a concentration of nearly 8% is required to give a solution of the same viscosity. The same is true in nearly all hydrophilic sols but generally to a much less extent.

(5) Time.

The time factor is one of the most striking variables of viscosity in solvated colloids. Different values are obtained according to the age of the sol. For rubber this change is always a decrease. The magnitude and the rate depends on the temperature and the method of preparation of the solution. This factor will be discussed later on in connection with the desolvation phenomenon.

(6) Addition of Electrolytes.

It is already known that additions of certain substances may raise or depress the viscosity of both organo and hydrophilic sols. These effects depend both qualitatively and quantitatively on the concentration of the added substances. They show an extremely interesting number of transitional and intermediate steps as the concentration of the added substance is increased. In the case of organophilic systems a classification of these compounds according to the nature of the effect produced is not yet on record. It is hoped, however, that the results of this investigation will throw considerable light on these, so far unexplained changes in the colloidal state of the system.

In addition to the importance of viscosity phenomena as forming an extremely varied field for investigation, a further significant factor might be considered, namely, the importance of viscosity as a "Methodie Principle" in the study of the alterations in colloidal systems, generally described as "Changes of State". If it is desired to follow quantitatively the alterations of dispersity, solvate formation, etc., in principle, any physiochemical property of the system may be used as an indication of such changes. But on examining a few properties like conductivity, optical effects, Brownian movements, etc., it is found that such properties either do not vary sufficiently during a change of state or that they are not suitable for quantitative investigation. That property of a colloid will,generally speaking, be best suited as an indicator, which shows the largest possible variation with small changes in the colloidal condition, and on the other hand permits quantitative measurements, if possible by a method not too difficult. All these requirements are admirably fulfilled by the viscosity. I think sufficient has been said to justify a study of the colloidal behaviour of rubber sols by means of their viscosity.

SECTION I

(Curves for Section I given on pages 40 to 47.)

THE PREPARATION OF MATERIALS

The rubber used for this work was of the pale crêpe variety. A 300 gram sample was cut from a large sheet and allowed to stand over P_2O_5 in a vacuum desiccator for several weeks before using. In every case the rubber used was cut from the desiccated sample. This was necessary in order to be certain that every sample had been subjected to the same previous thermal and mechanical treatment and possessed a uniform chemical composition.

It was considered advisable to reduce the amount of impurities present in the rubber to a minimum by carrying out a preliminary extraction. . The usual procedure adopted for the extraction of resins and resin acids is one in which the rubber is subjected to the action of boiling acetone in a soxtlet for about forty-eight hours. Since heat alters greatly the colloidal properties of rubber in solution this method had to be replaced by a less drastic treatment. The ordinary precipitation method from the standpoint of purification is quite satisfactory, but the fact that after a few precipitations the rubber becomes insoluble renders the procedure entirely unsuitable. Finally it was found that a mixture of anhydrous acetone and ether kept at room temperature constituted an extraction reagent almost as efficient as the hot acetone.

The theory of the cold extraction is as follows: The ether is a very efficient swelling agent and finds its way into the spaces between the rubber aggregates. The acetone being a precipitant for rubber prevents the swelling from proceeding to the stage of dispersion. Both liquids are excellent solvents for resins and resin acids, consequently conditions are quite favourable for efficient extraction. There is no doubt that after cold extraction the quantity of resins left behind in the rubber is negligible.

After the cold extraction rubber was thoroughly dried in a vacuum desiccator over P_2O_5 a suitable quantity (about 12 grams) was allowed to disperse in 2 litres of absolute benzene. The solution was allowed to stand for twenty-eight days after which it was filtered through cotton wool in a Buchner funnel. The concentration was adjusted to .496% corresponding to a relative viscosity of 5.00, and unless otherwise stated, this solution is used throughout Section I.

Under no conditions whatsoever was the solution allowed to come in contact with daylight or actinic light of any kind. All samples were contained in dark brown glass stoppered bottles, and placed in a dark room. The preparations of electrolyte solutions and all the filtrations were carried out either at night or in the day time in the presence of artificial light. Such precautions are necessary in view of the fact that ultra-violet and light of longer wave lengths lower the viscosity of rubber solutions even on short exposure.

Since, as appears below, the colloidal condition of rubber sols is highly susceptible to the presence of minute quantities of acids and bases, it was necessary to work in a laboratory free from acid and ammonia fumes. It was found that the presence of such fumes in the atmosphere when sols were being poured from one vessel to another noticeably affected the viscosity values obtained.

THE PREPARATION OF SOLUTIONS OF ELECTROLYTES IN BENZENE.

Probably one of the most difficult parts of the experimental procedure was the introduction of exceedingly minute amounts of an electrolyte into a rubber sol. Eggink (5) adopted the method of adding 25 cc of a dilute solution of electrolyte in benzene to the same volume of rubber sol. The viscosity of the resulting solution was compared with that of a similar mixture without the electrolyte. This procedure has one outstanding objection. When a rubber sol is diluted to the extent of twice its original volume it is a matter of days before the rubber particles became in equilibrium with the solvent. It was found by the author that a rubber sol diluted to the extent mentioned above, gave uncertain viscosity readings for at least two days after dilution had been performed. Also, Eggink found that he had to make a correction for the change in viscosity during the short period over which a series of experiments were carried out.

In order to eliminate these corrections, a method had to be devised by means of which unweighable quantities of substances might be added to the rubber sol, without, at the same time, introducing appreciable amounts of solvent. In the procedure finally adopted it was necessary to add, only 4 to 6 millimoles of solvent, a quantity quite insufficient to upset the equilibrium between solvent and disperse phase. An account of an actual experiment will best illustrate the method.

4.3308 grams of trichloracetic acid was weighed out in a tight fitting glass stoppered weighing bottle, and benzene added in sufficient amounts to dissolve the acid completely. Let this solution be denoted by A. From A, still more dilute solutions were obtained as follows:

(1)	1 cc of A	20 cc of benzene
(2)	1 cc of A	10 cc of benzene
(3)	2 cc of A	8 cc of benzene
(4)	2 cc of A	2 cc of benzene
(5)	1 cc of A	2 cc of benzene

Knowing the concentration of A it is a simple calculation to obtain the concentrations of solutions one to five. One drop from each of these was introduced separately from a standard pipette, into five glass stoppered bottles, each containing 10 cc. of rubber sol. In this way five electrolyte rubber solutions were obtained without the addition of an appreciable quantity of solvent. The exact amount of electrolyte added was calculated from the weight of the drop, obtained directly by weighing. A few actual figures will illustrate the accuracy of the method.

Drops	Total Weight	Weight of one drop
1	.01380	.01380
5	.0692	.01385
10	.1382	.01382
20	.2766	.01383

The experimental error is well below one percent.

It must be admitted, however, that this is a somewhat tedious procedure and therefore cannot be recommended as a rapid method for preparing solutions. Nevertheless, the regularity of the viscosities and the close agreement of consecutive readings were extremely gratifying. No correction was necessary for the change of viscosity during the period over which the experiment was performed.

The question of obtaining solutions of inorganic salts which are only very slightly soluble in benzene presented another difficulty. Fortunately, however, it was found that a considerable number of inorganic salts were extremely soluble in absolute alcohol and consequently could be introduced into the rubber sol in the form of a drop, as described above, the only difference being that a correction for the effect of the alcohol was necessary. The method proved to be very convenient and gave satisfactory results.

ANHYDROUS BENZENE

Kruyt and Eggink(6) have suggested that the influence of electrolytes on the viscosity of rubber solutions may be due to the ionization of the electrolytes in water present in the benzene. In view of this, especial precautions were observed in the preparation of the anhydrous benzene. About four litres of Kahlbaum's molecular weight, thiophene free benzene was allowed to stand for ten days over finely divided fused calcium chloride. Frequent shaking kept the fine grains of drying agent in suspension most of the time, thus exposing a tremendous drying surface. This was decanted into a pyrex flask and a very large amount of sodium wire was added from sodium press. The flask was allowed to stand for a considerable period, again, with frequent shaking and with the occasional addition of fresh wire. Finally the benzene was distilled from the sodium through a continuous glass apparatus into a glass stoppered bottle.

PREPARATION OF ANHYDROUS, ETHER, ACETONE AND ALCOHOL.

The ether and acetone employed in the cold extraction process was prepared in the anhydrous form. The ether was first washed with water to remove alcohol, followed by a preliminary drying with fused calcium chloride. After standing for a few days, the liquid was decanted from the solid and sodium wire was added in sufficient quantities to remove all traces of water. The ether was finally distilled through a dry apparatus into a carefully dried glass stoppered bottle.

About three litres of acetone was allowed to stand for three weeks in contact with a large quantity (Ca. 300 gms.) of finely powdered anhydrous sodium carbonate. During this time the liquid was frequently shaken in order to expose a large drying surface. The acetone was finally filtered and distilled through a dry apparatus.

The alcohol used for dissolving the inorganic salts (mentioned below) was prepared absolute. Two litres of commercial alcohol (95%) was refluxed over lime for fifty-six hours in a large pyrex flask. Without transferring the alcohol to another container, distillation was carried out directly from the lime, thus eliminating the possibility of obtaining moisture from the air. The distillation was performed as described for acetone and ether.

THE PREPARATION OF ANHYDROUS ELECTROLYTES.

Since all care was taken to obtain both rubber and benzene in the anhydrous condition, the same precautions were necessary in the preparation of the electrolytes. Salts, such as cupric, ferric and zinc chlorides, which either contain water of crystallization or are very hydroscopic were dried in an electric oven at 160°C. until they had reached a constant weight. They were then immediately transferred to a vacuum desiccator containing $P_2 O_5$ where they were kept until removed for the purpose of preparing the solutions. Salts, such as thorium and aluminium oleates, which are not appreciably hydroscopic were dried to constand weight in the vacuum desiccator. The other electrolytes employed were Kahlbaum chemicals, and consequently, in most cases, a preliminary purification was unnecessary.

EXPERIMENTAL METHOD FOR THE DETERMINATION OF VISCOSITY.

All viscosity measurements were made in a viscosimeter of the Ostwald capillary type. The size of the capillary and the volume of the bulb were so chosen that a suitable time of flow was obtained. It was one minute and six seconds in the case of the pure solvent and about five minutes for the rubber sols. The viscosimeter was adjusted in a vertical position by means of a plumb line. The temperature was held constant at 25°± .01°C. in an electrically controlled thermostat. All care was taken to remove traces of rubber from the capillary after each determination. In order to achieve this, the instrument was washed through with pure benzene, ten to twelve times, and after each series of observations, the capillary was carefully freed from solution, dried and left to stand overnight in cleaning solution. From time to time during a series of readings the benzene constant of the instrument was redetermined to assure that the capillary was clean.

A fixed volume of solution was always introduced into the viscosimeter from a 5 cc pipette and after being raised to the upper mark by suction, was allowed to run through the capillary to the lower mark. The time was registered by an accurate stop watch.

The density of the sols was measured in a specific gravity bottle. It was found, however, that the density of the sols used in this investigation was practically the same as the pure solvent. This is not surprising since rubber and benzene have nearly the same specific gravity.

The relative viscosity was calculated from the formula:

$$\frac{N_s}{N_b} = \frac{t_s \, d_s}{t_b \, d_b}$$

Where N_s – relative viscosity of the sol.
N_b – taken as unity - absolute viscosity of benzene.
t_s – time of flow of the sol.
d_s – density of the sol.
t_b – time of flow of pure benzene
d_b – density of benzene

but $d_s = d_b$ (see above)

$$N_s = \frac{t_s}{t_b}$$

(The electrolytes added had no effect on the time of flow of the pure solvent.)

The possibility of employing viscosity for the evaluation of raw rubber lead many investigators into this field. Schidrowitz and Goldsbrough (7) occupied themselves with the technique, and the details associated with viscosity measurements of rubber sols. Fol (8), van Heurn (9) van Rossem (10) Gorter (11) and de Vries (12) have also contributed much to our knowledge of viscosity of rubber sols. Van Rossem (13) and de Vries (14) have made extensive surveys of the relation between viscosity and vulcanizing properties. There is, however, every likelihood that such a relation does not exist, and that viscosity is not a sufficiently reliable index for the evaluation of raw rubber. Kirchhof (15) and van Rossem (16) have examined the viscosity of rubber in a number of solvents and over a range of concentrations.

The investigation was undertaken with the intention of showing the applicability of Hatschek's emulsoid equation (17). Although, very important in describing the mechanism of the rapid rise in viscosity with increasing concentration of rubber, this work is hardly within the scope of the present investigation. Le Blanc and Krüger (18) have studied the viscosity of rubber sols on addition of a great many compounds including a number of accelerators of vulcanization. Their results were such that they were unable to make any generalizations or to submit a satisfactory classification of the added substances according to their effect on the viscosity.

Studies of the influence of small amounts of electrolytes have been hitherto confined almost entirely to hydrophilic sols, such as agar-agar, starch caseine and gelatin . It is true that Kruyt and Eggink (19) have examined the effect of a few electrolytes, as hydrogen sulphide, sulphur dioxide, benzoic acid, but the investigation was not sufficiently extensive to enable them to state definitely whether the changes in viscosity were due to electrical or chemical phenomena. In the present work, however, a very much more complete compilation of data has been obtained. The substances added to the rubber sols have been extended to nearly every type of organic and inorganic compound, including alcohols, ketones, hydrocarbons, mustard oils, nitro compounds, organic acids and bases, ethers, esters, halogens and inorganic acids, bases and salts. The results obtained made it possible to arrive at certain definite conclusions and also permitted several generalizations to be made.

EXPERIMENTAL RESULTS

It was found that the effect of very small additions to benzene rubber sols could be classified according to four types of added substances, namely:

(a) Diluents
(b) Precipitants
(c) Reactants
(d) Electrolytes

Each type is essentially different in the manner by which it influences the viscosity of the rubber sol. A reference to some experimental results will illustrate this fact very clearly.

Diluents. By diluents is meant non-electrolytes which like benzene itself are peptizing agents and will not precipitate rubber from its solutions. Minute quantities of such substances of the order of 1-2 millimoles per litre do not alter the viscosity to an extent that can be detected experimentally. A curve in Fig. (I) shows the hardly appreciable effect of small amounts of anisole on the viscosity of a rubber benzene sol. The compounds listed in Table (I) may be taken as typical of such substances. Even when added in very much larger proportions of the order of ten millimoles per litre the effect is still only slight; see Table (II) below.

TABLE I

INFLUENCE OF DILUENTS ON THE VISCOSITY OF A BENZENE RUBBER SOL

(Protein and resin free rubber used. Concentration.32%,see Sec.II.)

Substance added.	Concentration in Millimoles per Litre of sols.	Relative Viscosity
None		5.06
Carbon Disulphide	1.6	5.09
Chloroform	1.02	5.09
Amyl Acetate	1.0	5.06
Methyl Acetate	1.0	5.06
Ethyl Ether	2.0	5.05
Anisole	1.1	5.02
Benzyl Benzoate	.09	5.09
Phenyl Mustard Oil	1.2	5.15
Pentane	2.0	5.06
Tetrahydronaphthalene	1.6	5.05
Phenetole	1.5	5.06
Ethyl Phthalate	1.0	5.05

TABLE II

INFLUENCE OF A FEW DILUENTS AT HIGHER CONCENTRATIONS ON A RUBBER SOL.

(.323% unextracted rubber solution used.)

Substance added	Concentration in Millimoles per Litre of Sol.	Relative Viscosity
None		4.86
Phenetole	11.5	4.89
Benzylethyl Ether	7.8	4.77
Isoamylether	6.9	4.69
Anisole	11.7	4.56
Ethyl Mustard Oil	11.1	4.90
Allyl Mustard Oil	13.9	5.11

None of these substances were subjected to purification and possibly the results in Table II, particularly, are influenced by the presence of impurities. In later experiments the anisole after being shaken with water and redistilled had practically no effect on the viscosity of the sol.

The data given above is probably sufficient to illustrate the fact that substances falling in the class called diluents do not influence the viscosity when introduced into the sol in small amounts.

Precipitants. The number of liquids capable of precipitating rubber from its solutions is very limited. Ethyl alcohol is one of the best known of such liquids. The curve for alcohol in Fig. I shows that when added in very small proportions, alcohol has only a small depressing effect on the viscosity. The curve was constructed from data given in Table III.

TABLE III

INFLUENCE OF ALCOHOL ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.85
.11	4.85
.22	4.84
.86	4.84
1.5	4.84
2.2	4.83

When a precipitant such as alcohol is added in larger quantities, for example 30 millimoles per litre, the immediate reduction of viscosity is appreciable, but on allowing the sol to stand for several hours, the viscosity gradually rises and reaches finally a constant value not a great deal below that of the original sol. The initial fall is presumably due to local desolvation produced at the point of entry of the alcohol; and on standing the portion of the disperse phase which has thus fallen in its degree of solvation, swells again, and consequently the viscosity rises. In Table IV, below, this phenomena is represented numerically.

TABLE IV

Times In Hours	Relative Viscosity
0	4.840
0.25	4.560
2.0	4.550
4.5	4.550
12.0	4.640
24.0	4.710
29.5	4.710

Reactants - - - Electrolytes. The influence on the viscosity of rubber sols of, on the one hand, substances which undergo chemical reaction with the caoutchouc and on the other hand electrolytes, appears to be definitely distinguishable by examination (a) the change of viscosity with time; (b) the change of viscosity with increasing amount of the added substance.

Organic acids and organic bases produce their effect on the viscosity practically at once, as is shown by the time curves for piperidine and for dichloracetic acid given in Fig. II and III respectively. The effect on the viscosity of substances which react chemically with caoutchouc is not thus immediate but instead of coming sharply to an end, continues over a long period of time, as the progressive fall in viscosity produced by iodine and by bromine (shown in Fig. (IV)) demonstrates. The curves representing the influence of increasing amounts of substances in the two classes, viz. reactants and electrolytes are similarly contrasted. The curves for acids, organic bases and salts flatten out, addition of these substances beyond a certain small amount producing but little additional effect. This is shown by curves in Fig. I and VI. The curves for reactants on the other hand, do not flatten out in this way. Whereas an electrolyte is capable of reducing the viscosity only to a certain extent no matter how much is added, increasing amounts of iodine and bromine produce progressively increasing reductions in viscosity. Fig. I enables a comparison to be made of an electrolyte, piperidine and a reactant, iodine.

The proportion of a reactant such as iodine, which is capable of reducing the viscosity is surprisingly small and would indicate that the effect is not ascribable merely or directly to the formation of an addition compound, such as $(C_5 H_8 I_2)n$. For example, as may be seen from Fig.I, 1.7 millimoles of iodine per litre of sol containing 4.96 gms. of rubber reduced the viscosity from 4.30 to 4.27; and this amount of iodine corresponds to only 0.12 percent. of the theoretical amount required to convert the caoutchouc present into $(C_5 H_8 I_2)n$. In some further experiments an amount of iodine corresponding to only 3.24 percent. of the amount required to saturate the caoutchouc present reduced the viscosity from 4.35 to 2.94. It may further be remarked that with sols to which iodine or bromine have been added it is difficult to get concordant results in repeat measurements. It was observed for example that the time of flow of a sol initially about five minutes, might change as much as ten seconds when the sol was run through the viscosimeter a second time. With sols to which electrolytes had been added no such difficulty was encountered.

Another reagent, presumably, a reactant which brings about a great fall in viscosity is tetranitromethane, one drop added to 10 cc. of a sol with an initial relative viscosity of 4.35 reduced the viscosity to 1.70 . Hydriodic acid also brings about a similar reduction.

Table V, below, gives the data from which the iodine curve in Fig. I has been constructed.

TABLE V

SHOWING THE EFFECT OF IODINE ON THE VISCOSITY OF A BENZENE RUBBER SOL.

Concentration of Iodine in Millimoles per Litre	Relative Viscosity
Blank	4.800
.021	4.70
.043	4.58
.086	4.49
.172	4.27
.344	4.080

Tables VI, VII, VIII and IX represent data corresponding to the curves in Fig. II, III and IV.

TABLE VI

THE VARIATION OF VISCOSITY WITH TIME AFTER THE ADDITION OF 14.1 MILLIMOLES OF PIPERIDINE PER LITRE OF RUBBER SOL.

Time In Hours	Relative Viscosity
0	4.86
0.25	4.07
5.0	4.01
17.0	4.00
24.	3.97

TABLE VII

THE VARIATION OF VISCOSITY WITH TIME AFTER THE ADDITION OF 10 MILLIMOLES OF DICHLORACETIC ACID PER LITRE OF RUBBER SOL.

Time In Hours	Relative Viscosity
0	4.82
.166	3.92
2.5	3.88
5.5	3.86
10.5	3.85
24.0	3.84

TABLE VIII

THE VARIATION OF VISCOSITY WITH TIME AFTER THE ADDITION OF 3.9 MILLIMOLES OF IODINE PER LITRE OF RUBBER SOL.

Time in Hours	Relative Viscosity
0	4.85
.5	3.60
3.0	3.51
6.5	3.30
10.5	3.00
25.0	2.3
43.0	2.727 (not plotted)

TABLE IX

THE VARIATION OF VISCOSITY WITH TIME AFTER THE ADDITION OF 6.2 MILLIMOLES OF BROMINE PER LITRE OF RUBBER SOL.

Time in Hours	Relative Viscosity
0	4.85
.25	3.33
2.0	3.0
5.75	2.8
10.25	2.7
23.5	2.5

By far the most interesting class of chemical reagents affecting the viscosity of rubber sols is electrolytes. These are best discussed under the subdivisions, organic acids, organic bases and salts.

Acids. The magnitudes of the reduction of viscosity, caused by the addition of small amounts of acetic acid and its three chlorine derivatives form a very interesting series. A comparison of the effects of acetic, monochloracetic, dichloracetic, and trichloracetic acids is shown in Fig. V. The order of the effectiveness of these acids in reducing the viscosity of a benzene rubber sol is the same as that of their dissociation constants (shown below) determined in water.

	Dissociation Constant in Water
Acetic Acid	1.8×10^{-6}
Monochloracetic	1.55×10^{-3}
Dichloracetic	$5. \times 10^{-2}$
Trichloracetic	$3. \times 10^{-1}$

The results drawn graphically in Fig. V are collected in Tables X, XI, XII, XIII.

TABLE X

INFLUENCE OF THE ADDITION OF ACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles Per Litre	Relative Viscosity	
Blank	4.86	
.07	4.85	
.12	4.81	
.24	4.79	
.60	4.78	
1.16	4.72	
2.16	4.62)	not plotted
4.47	4.53)	

TABLE XI

INFLUENCE OF THE ADDITION OF MONOCHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles Per Litre	Relative Viscosity
Blank	4.86
.03	4.77
.07	4.73
.12	4.68
.33	4.58
.55	4.53
? .11	4.48

TABLE XII

INFLUENCE OF THE ADDITION OF DICHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles Per Litre	Relative Viscosity
Blank	4.86
.02	4.72
.07	4.53
.15	4.39
.29	4.29
.43	4.23
.85	4.19

TABLE XIII

INFLUENCE OF THE ADDITION OF TRICHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles Per Litre	Relative Viscosity
Blank	4.86
.01	4.75
.03	4.58
.09	4.45
.19	4.29
.32	4.19
.67	4.10

In view of the fact that fatty acids (heveic, oleic and linolic) occur naturally in rubber, it is of interest to enquire whether such acids appreciably affect the viscosity of the rubber sols. The following Table shows some results obtained with a number of fatty acids, the rubber used being unextracted.

TABLE XIV

INFLUENCE OF SOME FATTY ACIDS ON THE VISCOSITY OF BENZENE SOLS OF UNEXTRACTED RUBBER.

Caprylic Acid

Concentration in Millimoles per Litre of Rubber Sol.	Relative Viscosity
0	4.86
10.4	4.14

Stearic Acid

Concentration in Millimoles per Litre of Rubber Sol.	Relative Viscosity
0	4.85
.71	4.63
2.91	4.35

Heveic Acid

Concentration in Grams per 100 cc. of Rubber Sol.	Relative Viscosity
0	6.24
2	5.93
7	5.83
30	5.72
50	5.67

Oleic Acid

Concentration in Millimoles per Litre of Rubber Sol.	Relative Viscosity
0	6.325
12.8	6.07
20.1	5.88

The total amount of fatty acid naturally present in rubber is of the order of 1.7 millimoles per litre of sols such as those used. The above data make it clear that additions to the naturally present acid reduce the viscosity. It has been frequently proposed to use measurements of the viscosity of benzene sols of different samples of raw rubber as a means of estimating the vulcanization quality of the samples. The influence of the natural acid content of rubber (which varies in different samples) on the viscosity has, however been overlooked. It would appear then that such determinations are not reliable for the evaluation of rubber.

BASES

It was found that not only organic acids but also organic bases reduce the viscosity of benzene rubber sols. As in the case of strong organic acids, the effective amounts of strong bases are extremely small; an increase beyond a certain point of the amount of reagent added has little additional effect. An examination of the curves for piperidine and diethylamine in Fig. I and VI, and also the data in Tables XV and XVI below, show that only a fraction of a millimole of the base per litre of rubber sol is necessary to bring about substantially the maximal reduction in viscosity. For example in the case of piperidine, Fig. I, using a sol with an initial viscosity of 5.00, a concentration of the base of the order of .07 millimoles per litre of sol was sufficient to reduce the viscosity from 4.86 to 4.36 . Increasing the concentration of piperidine from .07 to 1.5 millimoles per litre, causes only a small additional lowering of .16 units. The curve for diethylamine, Fig. VI, provides a similar example. The addition of .5 millimoles per litre of rubber sol reduces the viscosity from 6.25 to 5.00 while an increase of 3 millimoles per litre has the slight additional effect of 0.1 units.

TABLE XV

INFLUENCE OF PIPERIDINE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	5.00
.024	4.52
.048	4.38
.079	4.36
.16	4.34
.40	4.31
.79	4.24
1.58	4.20 (not plotted)

TABLE XVI

INFLUENCE OF DIETHYLAMINE ON THE VISCOSITY OF A RUBBER SOL.

(Unextracted rubber)

Concentration in Millimoles per Litre	Relative Viscosity
Blank	6.25
.092	5.37
.451	5.04
1.03	5.00
2.00	4.92

The following table shows the effect of a number of bases whose strengths are known from their dissociation constants determined in aqueous solution. It is seen that the amounts added vary considerably, but are all comparatively large, that is to say: amounts falling, at least, on the flat portion of the curves connecting viscosity and concentration of the bases.

TABLE XVII

INFLUENCE OF BASES ON THE VISCOSITY OF A BENZENE SOL OF UNEXTRACTED RUBBER.

Base	Dissociation Constant	Concentration of Base in Milli-moles per Litre of Sol.	Relative Viscosity
None			4.86
Piperidine	1.6 x 10^{-3} (25°)	14.0	3.73
Diethylamine	1.26 x 10^{-3} (")	16.0	3.84
Dipropylamine	1.02 x 10^{-3} (")	9.5	3.77
Di-isobutylamine	4.8 x 10^{-4} (")	8.3	3.91
Isobutylamine	3.1 x 10^{-4} (")	15.6	3.88
Benzylamine	2.4 x 10^{-5} (")	17.0	4.04
Dibenzylamine		8.7	4.04
Quinine	2.2 x 10^{-7} (")	2.9	4.47
Methylaniline	7.4 x 10^{-9} (")	16.0	4.77
Pyridine	2.4 x 10^{-10} (13°)	21.0	4.45
Aniline	1.7 x 10^{-10} (")	20.	4.86

With the exception of pyridine the effectiveness of these bases in reducing the viscosity of rubber sols closely follows the order in which they fall when ranged according to their dissociation constants in water. That pyridine is an exception is not surprising in view of the fact that this compound is exceedingly difficult to obtain free from impurities. From what has been already observed regarding acetic acid and its chlor-derivatives and now from the data in Table XVII above, it would appear that the reduction of viscosity on addition of organic acids and bases is intimately connected with their degree of dissociation.

SALTS

The effect of salts of both organic and inorganic acids presents a very interesting type of phenomena. It has been found that in some cases the type of effect on addition of the salts to a benzene rubber sol is analogous to that already described in connection with acids and bases. On the other hand, however, there were several salts examined that showed very striking differences. A consideration of the curves for mercuric chloride and cupric chloride, Fig. VII reveals that on progressive increase in the concentration of salt, the change of viscosity is similar to that observed for acids and bases, but the curves for zinc chloride and ferric chloride, Fig. VII, aluminium oleate and thorium oleate, Fig. VIII, show that at exceedingly minute concentrations of salt, there is an initial rise, followed by a sudden depression in viscosity. The portion of the curves following the maximum point is substantially the same as the curves in which no initial rise was observed. A further examination of Fig. VII and VIII shows that there is no obvious relationship between the valence of the ions present, either cation or anion, and their effectiveness in reducing the viscosity of the rubber sol. Also it may be observed that the degree of ionization of the salt and the magnitude of the reduction of viscosity do not vary progressively as was the case with the acids and bases.

The data from which the curves in Fig. VII and VIII are constructed, are given below in Tables.

TABLEXVIII

INFLUENCE OF MERCURIC CHLORIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.85
.013	4.82
.052	4.80
.104	4.79
.390	4.74
1.50	4.60
3.16	4.52 (not plotted)

TABLE XIX

INFLUENCE OF CUPRIC CHLORIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.78
.0110	4.52
.029	4.41
.066	4.16
.126	4.05
.179	3.83
.454	3.82
.955	3.82

TABLE XX

INFLUENCE OF ZINC CHLORIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.80
.010	4.85
.038	4.86
.080	4.79
.093	4.74
.243	4.47
.404	4.26
1.250	4.08

TABLE XXI

INFLUENCE OF FERRIC CHLORIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.78
.009	4.85
.042	4.55
.081	3.35
.179	3.14
.450	3.03
.880	3.00

TABLE XXII

INFLUENCE OF ALUMINIUM OLEATE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	5.00
.003	5.35
.006	5.39
.016	5.12
.032	4.90
.063	4.71
.121	4.55
.222	4.47
.667	4.46 (not plotted)

TABLE XXIII

INFLUENCE OF THORIUM OLEATE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	5.00
.005	5.26
.012	5.17
.027	4.86
.058	4.73
.117	4.61
.206	4.55

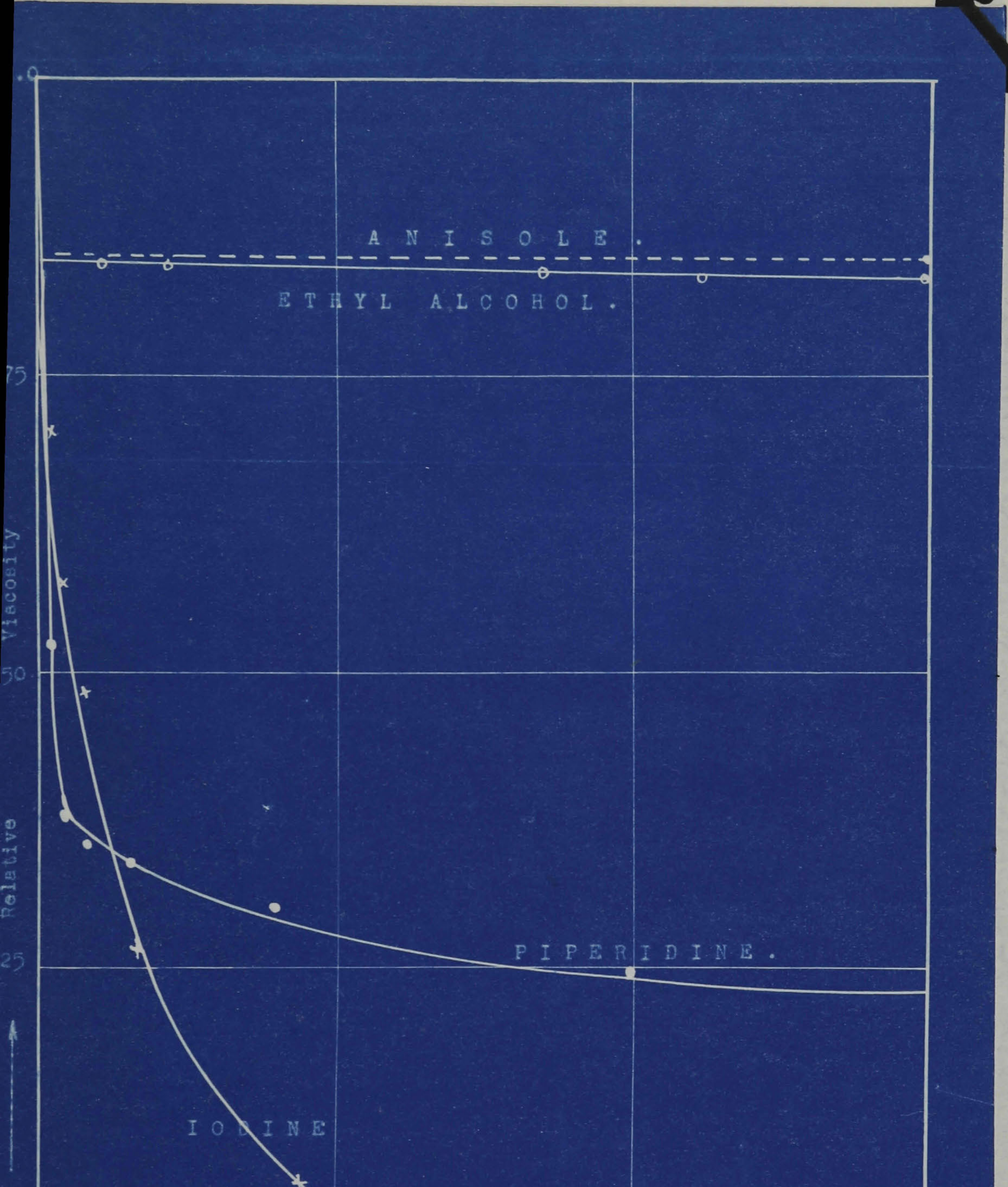
Potassium Hydroxide. That the addition of ammonia to benzene rubber sols, increases the viscosity has been shown by Eggink (20). The present author has examined the effect of small quantities of potassium hydroxide and has found that a very considerable initial rise takes place, followed by a sudden decrease, extending well below the original viscosity of the sol. This behaviour is very markedly different from the effect of organic bases, but is somewhat analogous to the behaviour of the salts already alluded to in Fig. VII and VIII. The analogy, however, must not be carried too far as the initial rise in the case of the potassium hydroxide as shown in Fig. IX, extends over a greater range of concentration and also rises to a much higher maximum than was observed in the curves for salts. The data for the potassium hydroxide curves are collected in Table XXIV below.

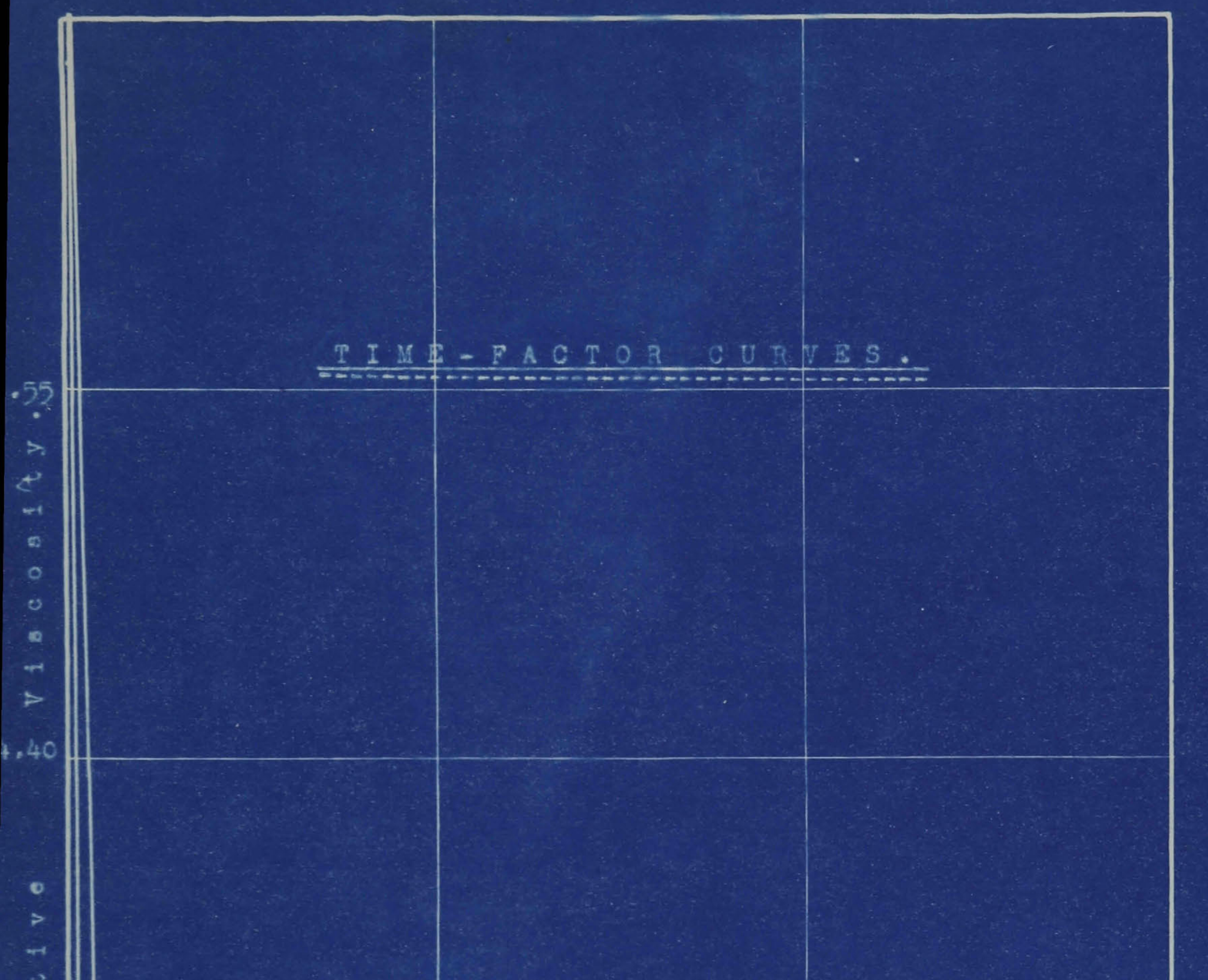
TABLE XXIV

EFFECT OF POTASSIUM HYDROXIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.83
.089	5.00
.179	5.32
.321	5.37
.538	5.41
.805	5.56
1.077	5.58
1.605	5.67
1.820	5.00
2.156	4.39
2.680	4.32
3.210	4.32

FIGURE I


.0
75
50
25
4.0
Relative Viscosity
A N I S O L E .
E T H Y L A L C O H O L .
P I P E R I D I N E .
I O D I N E
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution.
Z(Cold - extracted rubber used)



(Cold-extracted rubber used)

FIGURE IV

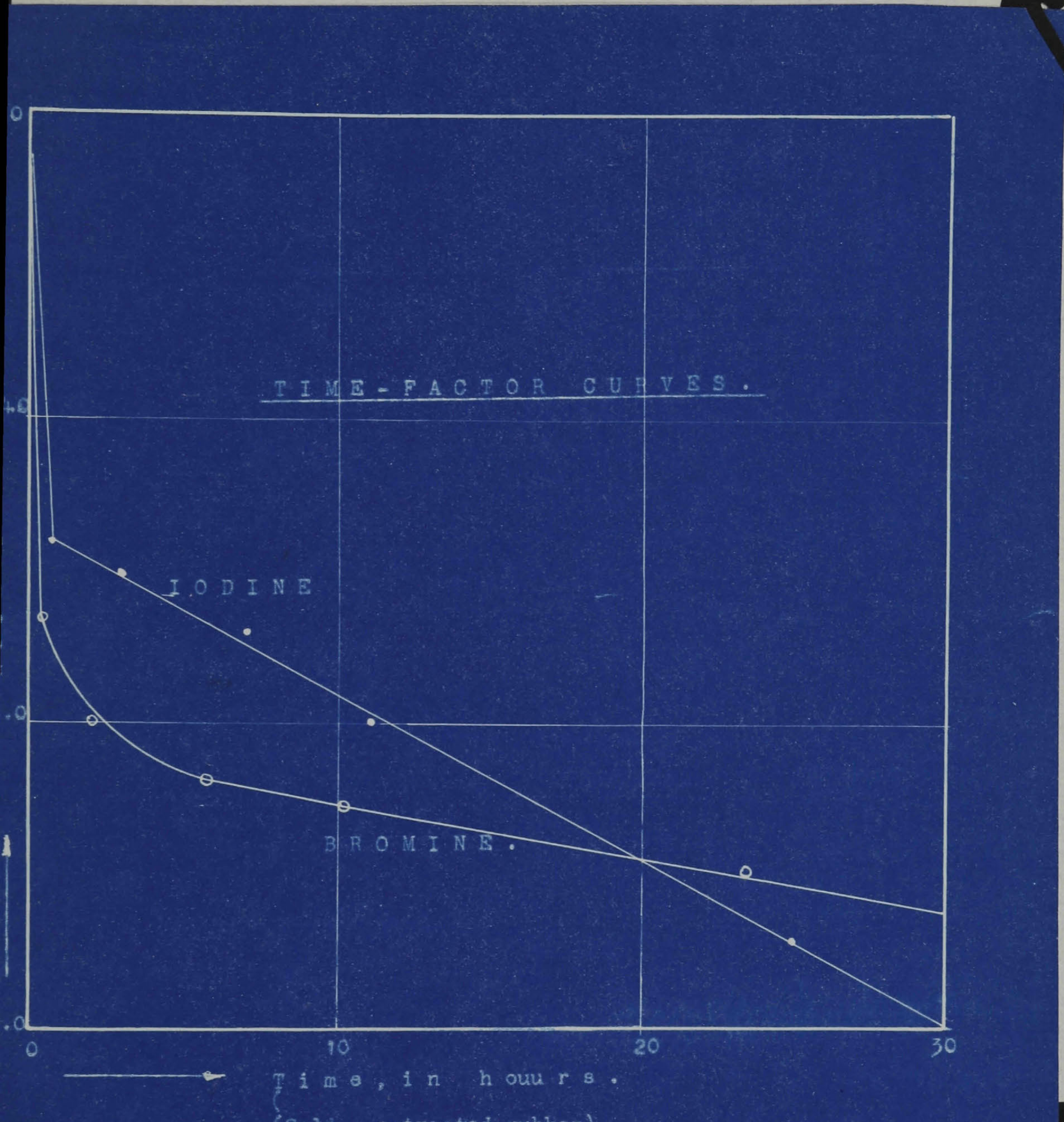

TIME-FACTOR CURVES.
IODINE
BROMINE.
4.0
.0
.0
0
10
20
30
Time, in houurs.
(Cold - extracted rubber)

FIGURE V

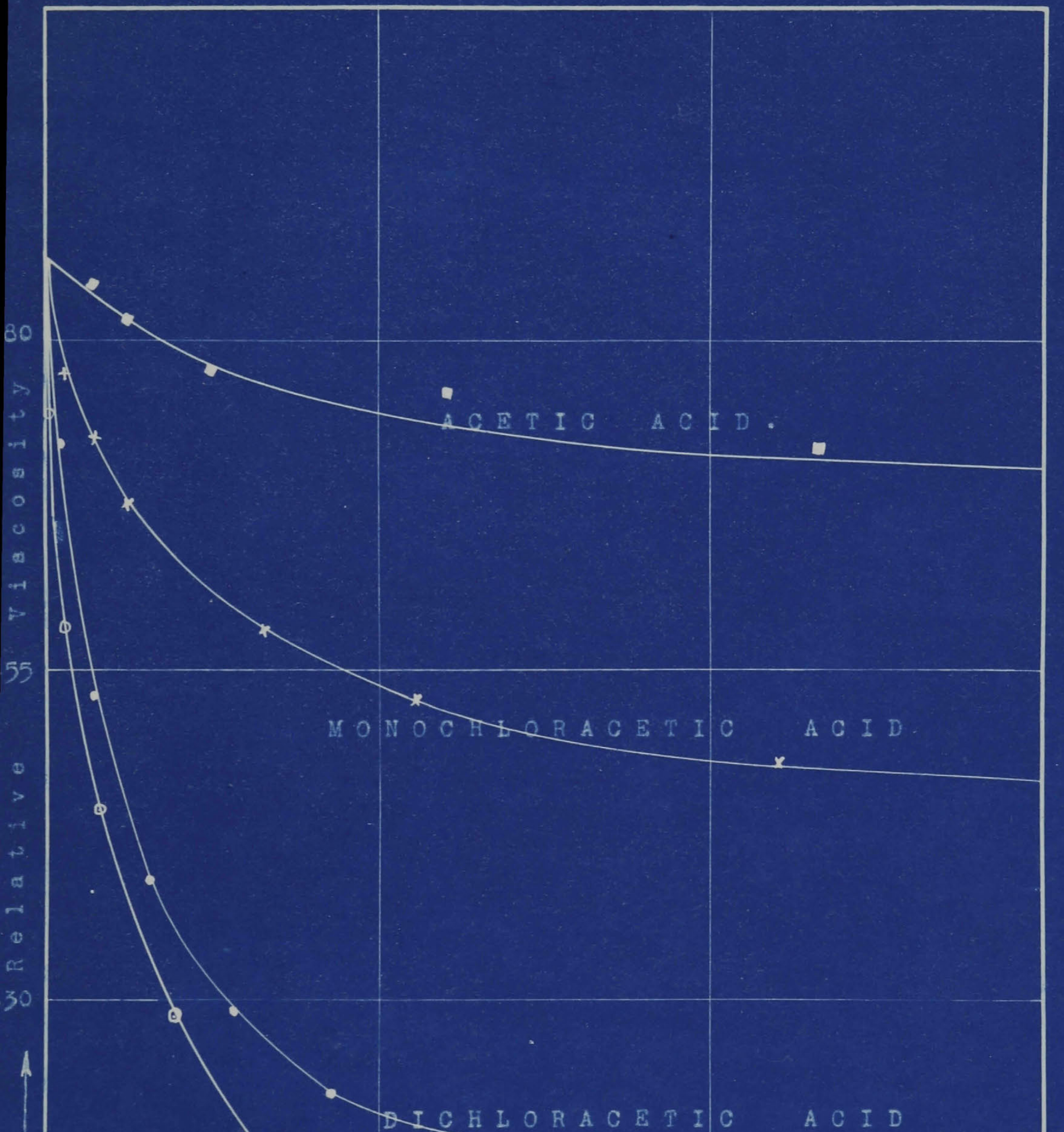

80
55
30
Relative Viscosity
ACETIC ACID.
MONOCHLORACETIC ACID
DICHLORACETIC ACID
TRICHLORACETIC ACID.
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution
(Cold - extracted rubber)

FIGURE VI

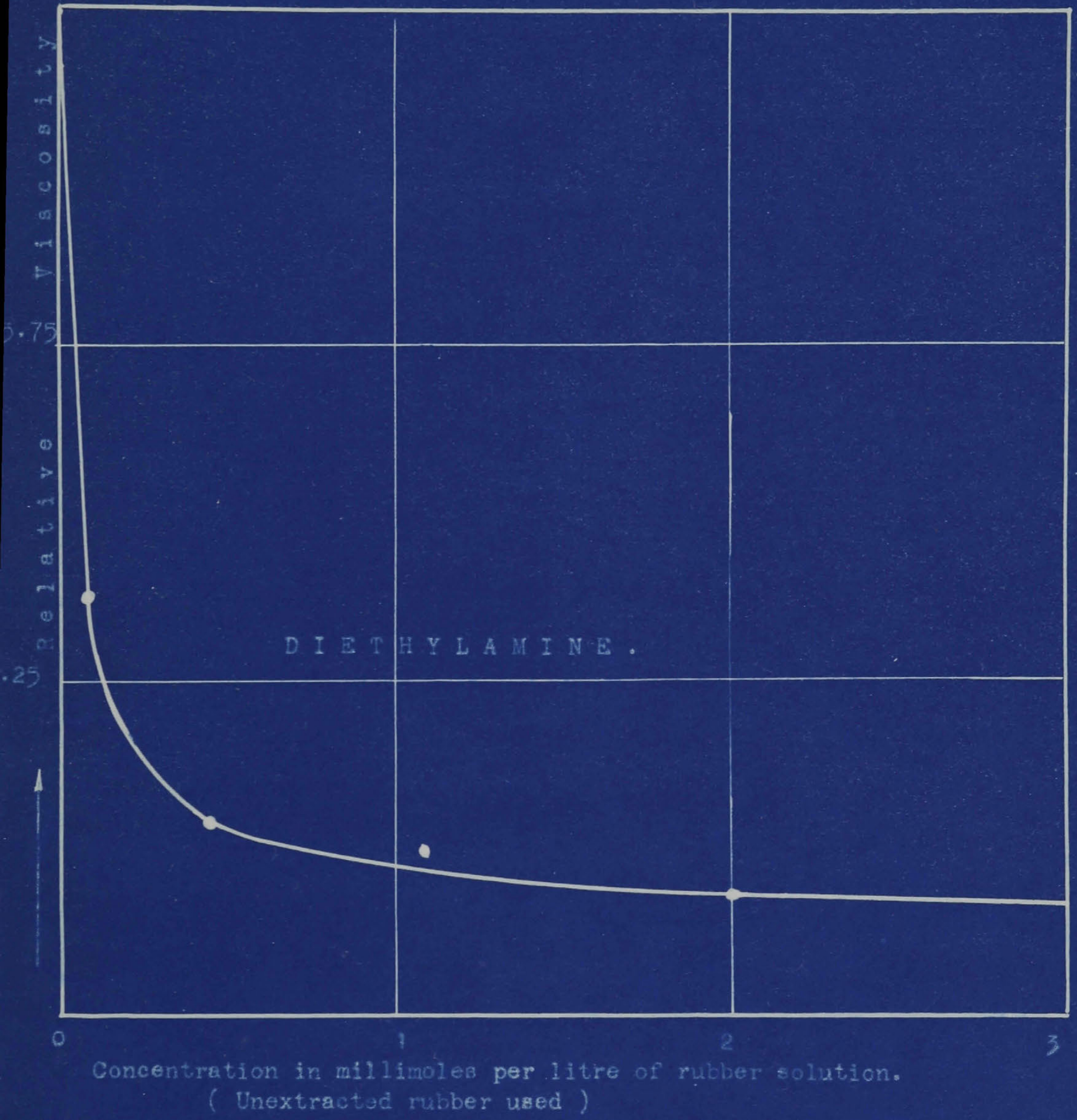

Relative Viscosity
5.75
.25
DIETHYLAMINE.
0
1
2
3
Concentration in millimoles per litre of rubber solution.
(Unextracted rubber used)

FIGURE VII

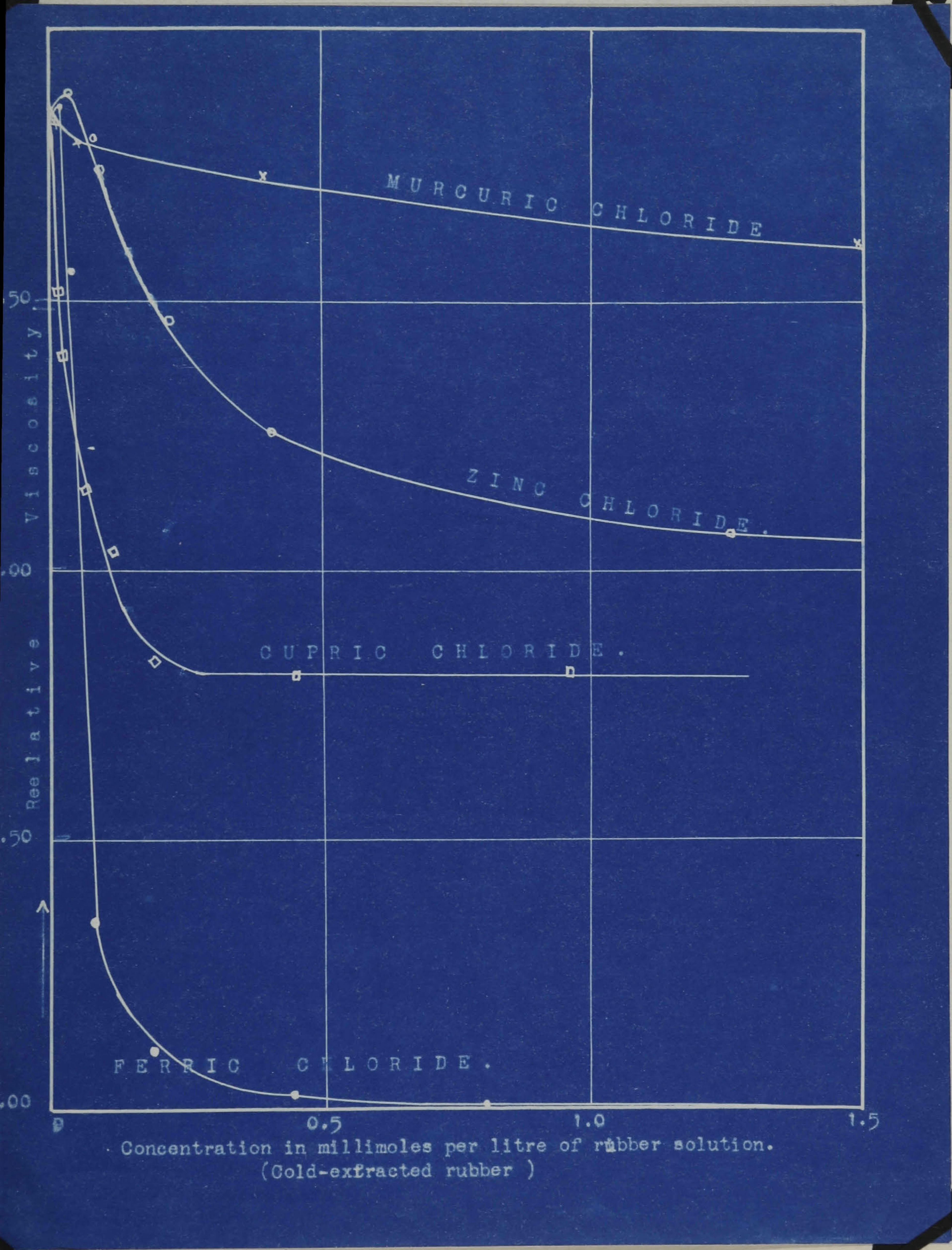

MURCURIC CHLORIDE
ZINC CHLORIDE.
CUPRIC CHLORIDE.
FERRIC CHLORIDE.
.50
.00
.50
.00
Reelative Viscosity.
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution.
(Cold-extracted rubber)

FIGURE VIII

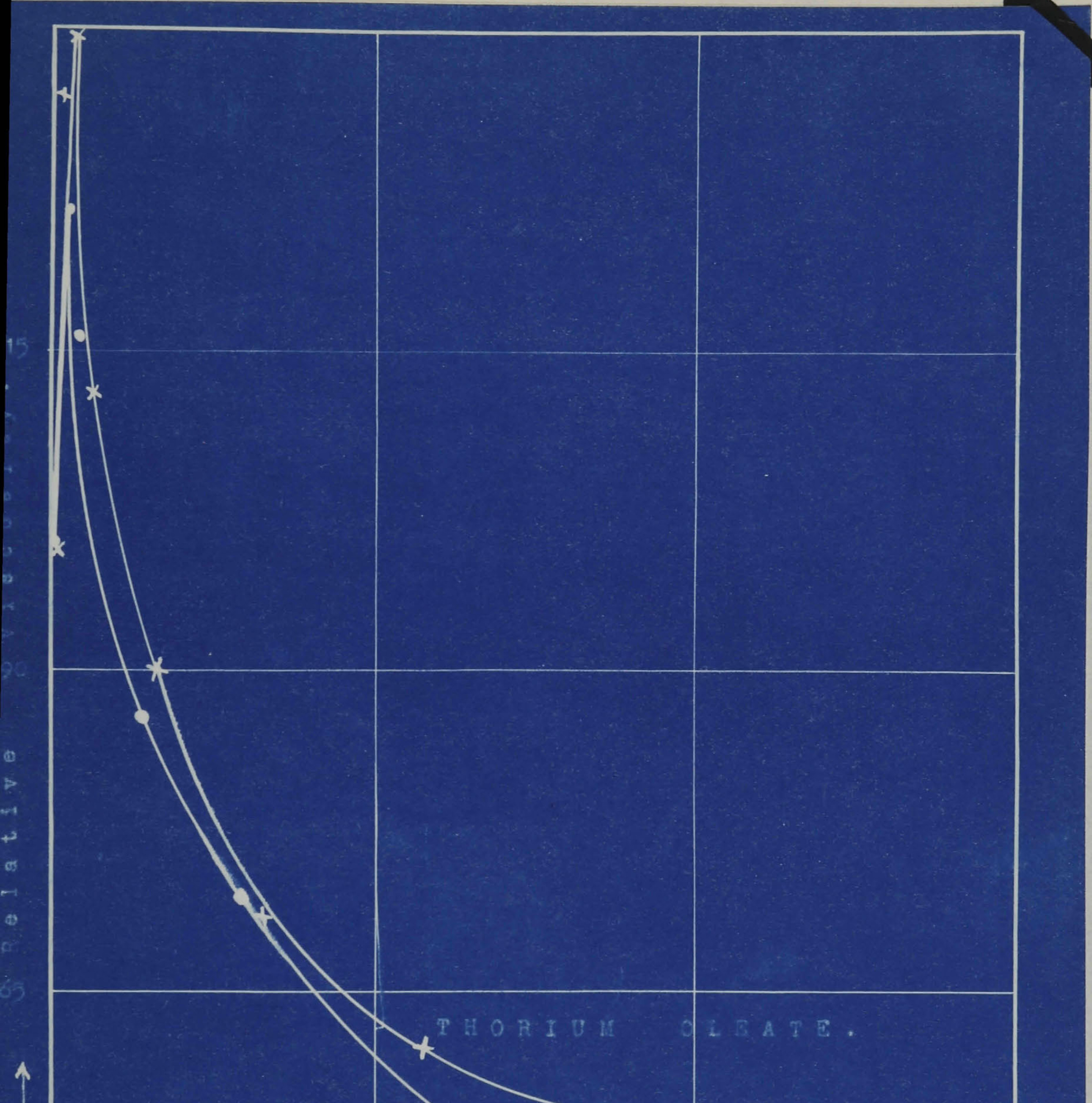
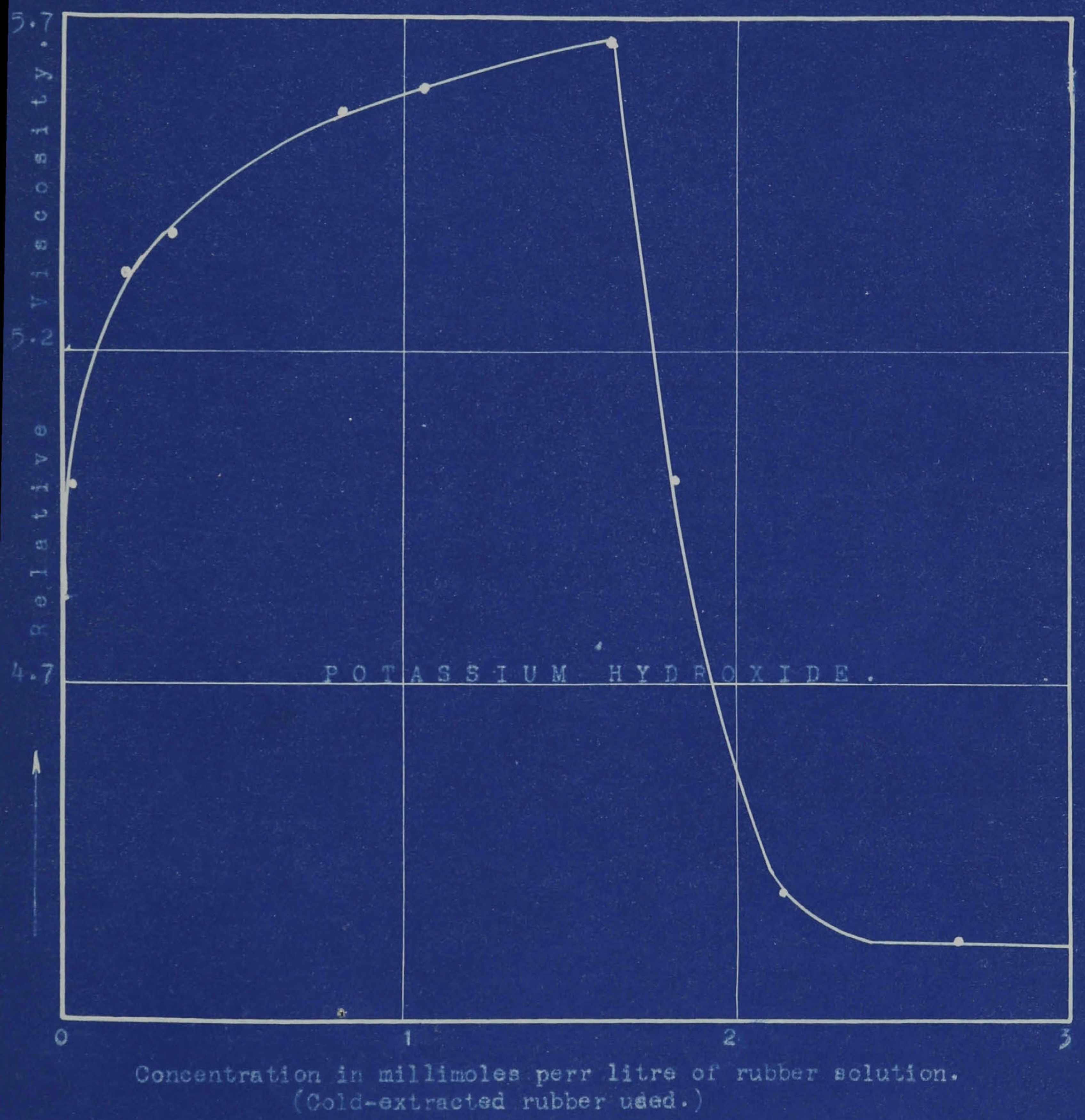

Relative viscosity
15
10
05
THORIUM OLEATE.
ALUMINIUM OLEATE
0
0.1
0.2
0.3
Concentration in millimoles per litre of rubber solution
(Cold-extracted rubber.)

FIGURE IX


5.7
5.2
4.7
Relative Viscosity.
POTASSIUM HYDROXIDE.
0
1
2
3
Concentration in millimoles perr litre of rubber solution.
(Cold-extracted rubber used.)

SECTION II

(Curves for Section II given on pages 72 to 76.)

The rubber used in the experiments described in Section I was practically free from resin acids but still contained appreciable quantities of nitrogenous material. In order to eliminate the possibility that the effect of chemical reagents on the viscosity of rubber sols may be due, indirectly to the presence of some impurity, it was thought advisable to repeat a few of the experiments on a sample of rubber that consisted entirely of the caoutchouc hydrocarbon.

Up to the present, there is on record no suitable method for obtaining raw rubber free from nitrogenous impurities. It is true that fairly satisfactory samples have been prepared by repeatedly precipitating and redissolving the rubber. Such a procedure, however, is not free from objection. After a few precipitations the rubber becomes increasingly insoluble, due, apparently, to oxidation. For the sake of comparison with the work already described it would appear necessary to eliminate entirely any factor in the preparation of the pure rubber which would in any way alter the colloidal state of the system. Obviously, then, any process involving oxidation is not to be considered.

In order to appreciate the method finally adopted, it is first necessary to be acquainted with the nature of the impurities and the mechanism by which they became associated with the caoutchouc.

It is rather a striking fact that natural rubber should make its first appearance in a condition which is typically colloidal. The rubber used in the present investigation was obtained from the milk or latex of hevea brasiliensis, a white fluid very similar to cows' milk or cream. Under the ultra microscope such latex is seen to consist of particles suspended in an aqueous serum and engaged in active Brownian movement. This aqueous serum or dispersion medium, although not directly connected with the present work is of utmost importance at this point. The serum of hevea brasiliensis is known to contain, in various proportions, resins, proteins, metallic salts, etc. If these substances were confined to the dispersion medium alone they would not be mentioned here, but unfortunately for the rubber chemist, the suspended caoutchouc particles adsorbed on their surfaces, the majority of these compounds in appreciable quantities.. Consequently, when coagulation is brought about by acetic acid (as was the case with the samples used) the product is obviously not pure hydrocarbon but a very intimate mixture of rubber, protein, resin, etc., with some acetic acid. In factory practice the wet coagulum, usually after being left in the serum overnight, is converted into thin sheets on a series of rolls, rotating in opposite directions. A current of water is allowed to flow over them continuously after which the sheets are hung up to dry. Such a treatment is, of course, hopelessly inadequate to remove even a fraction of the impurities. A typical analysis of a rubber prepared in this way gives an idea of the percentage of foreign material.

	Loss on Washing.	Ash	Resin	Pretein	Caoutchouc
Mean of eight samples.	0.57	0.256	3.00	2.28	94.44

From a consideration of what has just been said, it is clear, that raw rubber consists of a mass of caoutchouc globules, each surrounded by adsorbed resin and nitrogenous material. The resins can be very efficiently extracted by the cold extraction method outlined in Section I, but the removal of the protein which is insoluble in all ordinary organic solvents, presents an entirely different problem. It would appear, however, that if some liquid could be obtained which would peptize a portion of the caoutchouc without dispersing the whole mass of rubber and in any way disturbing the protein, the problem would be immediately solved. It was finally discovered that low boiling (20° - 35°C) petroleum ether, if allowed to stand in contact with acid free rubber, peptized a portion of the caoutchouc which was (according to the analysis given below) free from any detectable quantity of foreign material.

Preparation of Pure Caoutchouc. About 50 grams of pale crèpe was extracted at room temperature with a 1 - 1 mixture of acetone and petroleum ether, (B.Pt. 20°- 35°C.) The extractant was renewed every 24 hours or so, for a period of eight days and was collected in bulk for subsequent analysis. (The theory of cold extraction was discussed in Section I). The rubber was then thoroughly dried in a vacuum dessicator until it had reached a constant weight. 19.190 grams was cut from the dried sample and extracted for 51 hours in a soxhlet apparatus with boiling acetone. The acetone was evaporated to dryness and the residue redissolved in absolute neutral ethyl alcohol. The acid number (i.e. mgr. of K o H necessary to neutralize the acid in 100 grams of rubber) of the alcoholic solution was determined by titration with .01035 N alcoholic potassium hydroxide. The acid number of the original unextracted pale crêpe, as well as the acid number of the extractant, was determined in a similar manner and at the same time. Table XXV below records the results of the analysis.

TABLE XXV

Sample	Acid Number
Unextracted pale crepe	283
Cold extracted	29
Extractant	249

From the Table above it is apparent that there is a small quantity of acid left which is insoluble in the petroleum ether-acetone mixture.

A large quantity of the cold extracted pale crepe (acid No.29) was allowed to stand in contact with petroleum ether (B.Pt. 20°- 35°) for three weeks. In that time the liquid had become quite viscous, showing that a considerable quantity of caoutchouc had passed into solution. The viscous liquid was carefully decanted, filtered through cotton wool three times and subsequently evaporated to dryness under reduced pressure at room temperature. A portion of this sample was analysed both qualitatively and quantitatively for nitrogen and in each case the result was negative. An acid number determination carried out according to the method outlined above also gave negative results. A determination of the ash content by burning a sample of the rubber in a porcelain crucible revealed the fact that there was no metallic salts present. It seems reasonably certain from the analysis given above that rubber prepared by a petroleum ether peptization is an exceedingly pure hydrocarbon.

About eight grams of the freshly prepared rubber was dissolved in a litre of absolute benzene. After complete dispersion had taken place the concentration was adjusted to give a solution of a viscosity of about five, corresponding to a concentration of .328% by weight of rubber. The solution was used to obtain the experimental results recorded below.

For the purpose of comparing the effect of chemical agencies on the viscosity of natural rubber sols with that of artificial rubber sols, a small sample of the synthetic product was prepared. Use was made of the well-known method of Harries(21) by which isoprene is polymerized by means of sodium wire, heated in a sealed tube at 80°C for eight hours. The rubbery mass formed was dissolved in benzene, precipitated by absolute alcohol, redissolved and precipitated three times, after which the material was dissolved in benzene and diluted to give a sol of a suitable viscosity.

A second sample of synthetic rubber was prepared by means of the polymerization of 20 cc of isoprene in a sealed tube in contact with 1/2 cc of glacial acetic acid. In order to bring about complete polymerization it was necessary to extend the heating process over a period of twelve days at a temperature of 100°C. On cooling the viscous material in the tube solidified to a rubbery or plastic mass. The method employed for obtaining a solution of the material in benzene was similar to that described for the sodium rubber. There is every likelihood that the rubber retains a trace of acetic acid even after several precipitations and consequently the resulting benzene sol will contain small amounts of acetic acid in solution.

The isoprene was obtained from dipentene by passing the vapours over an electrically heated platinum wire according to the principle of the Harries Isoprene Lamp (22). The crude isoprene was freed from amylene by allowing it to stand over barium dioxide for several days. The liquid was decanted, dried over fused calcium chloride, fractionally distilled, dried over sodium wire and finally redistilled through a long fractionating column.

(The preparation of electrolyte solutions and the procedure for the determination of the viscosity described in Section I was duplicated in Section II.)

Experimental Results. It was found that the influence of electrolytes on the viscosity of rubber sols, free from protein was essentially the same as the effect described in Section I where rubber containing nitrogenous material was employed. A comparison of the diagrams in Fig. V, VI, VII, VIII, IX, Section I with those in Fig. X, XI, XII, XIII, XIV respectively brings out the similarity very clearly. The curves Fig. X, for dichloracetic acid and monochloracetic acid show that the magnitude of the effect is still proportional to the strength of the acids as determined by their dissociation constant in water. Also extremely small amounts of the strong electrolytes are effective in lowering the viscosity to a minimum, beyond which a further addition has little increased effect. The parallel extends to the action of salts, for example, ferric chloride, Fig. XII, aluminium and thorium oleates, Fig. XIII, and also to the alkalis represented by the diagram in Fig. XIV. The curves show that the oleates still cause an initial rise in viscosity, followed by a sudden lowering effect. The curve for potassium hydroxide is strikingly similar to the alkali curve already represented in Fig. IX, Section I.

The general parallel that is observed in the viscosity-concentration curves for rubber sols with and without protein, proves beyond a doubt that the effects observed on the addition of chemical reagents to rubber sols are not due to the non-caoutchouc constituents of the rubber, but are direct influences on the disperse phase of the system.

The numerical data from which the curves are obtained are given below in Tables.

TABLE XXVI

INFLUENCE OF STEARIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.94
.056	4.90
.172	4.78
.336	4.70
.617	4.70
.709	4.70

TABLE XXVII

INFLUENCE OF OLEIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.96
.132	4.88
.266	4.72
.533	4.65
1.060	4.65
1.600	4.65

N.B. Oleic acid occurs naturally in rubber. Table XXVII shows the effect of very small quantities of this acid on the viscosity of the solution.

TABLE XXVIII

INFLUENCE OF MONOCHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.96
.051	4.71
.111	4.53
.274	4.45
.547	4.39
1.095	4.32

TABLE XXIX

INFLUENCE OF DICHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.95
.044	4.28
.073	4.24
.147	4.20
.366	4.14
.732	4.05
1.470	4.00

TABLE XXX

INFLUENCE OF POTASSIUM HYDROXIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.80
.134	5.11
.212	5.24
.492	5.37
.737	5.18
.986	4.65
1.480	4.35

TABLE XXXI

INFLUENCE OF FERRIC CHLORIDE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.95
.019	3.98
.081	3.62
.179	3.51
.449	3.41
.881	3.37

TABLE XXXII

INFLUENCE OF PIPERIDINE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.96
.055	4.71
.092	4.58
.183	4.52
.457	4.46
.916	4.41
1.50	4.38
5.80	4.33 (not plotted)

TABLE XXXIII

INFLUENCE OF DIETHYLAMINE ON THE VISCOSITY OF A RUBBER SOL.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	4.96
.041	4.74
.068	4.63
.135	4.56
.338	4.53
.677	4.48
1.350	4.46

A comparison of the curves in Fig. I and VI, Section I, and Fig. I, Section II, shows that the amines have a slightly greater effect on the rubber containing traces of the non-caoutchouc constituents than they have on the pure rubber. This suggests the possibility that the effect of these amines may be due to an undetectable quantity of resin acid in the rubber, which with the amine forms a salt; the salt being responsible for the lowering of the viscosity. The amount of the acid being less in the pure rubber sample would naturally give rise to a smaller quantity of salt and therefore the effect on the viscosity would be proportionately reduced. Conversely, if resin acid, were added to the pure rubber sol the influence of the amine should be proportionately increased if the effect of the amine is actually due to salt formation. The results in Table XXXIV below show that the capacity of piperidine for reducing the viscosity of a pure rubber sol is unaltered by the presence of added resin acids.

TABLE XXXIV

THE EFFECT OF PIPERIDINE ON THE VISCOSITY OF A RUBBER SOL IN THE PRESENCE OF RESIN ACID.

Substance	Concentration in Millimoles per Litre.	Relative Viscosity
	Blank	5.00
Piperidine	.018	4.68
Heveic Acid	.023	4.97
Piperidine & Heveic	(.018 + .02)	4.68
	Blank	5.00
Piperidine	.055	4.59
Stearic	.057	4.97
Stearic & Piperidine	(.055 + .057)	4.54

It would appear from the results in Table XXXIV that an explanation of the action of amines on the viscosity of rubber sols must be sought elsewhere than in the direction of a salt formation.

Table XXXV below shows that the presence of small amounts of resin acid does not alter the capacity of a strong acid for lowering the viscosity of a pure rubber sol.

TABLE XXXV

THE INFLUENCE OF DICHLORACETIC ACID ON THE VISCOSITY OF A RUBBER SOL IN THE PRESENCE OF STEARIC ACID.

Substance	Concentration in Millimoles per Litre	Relative Viscosity
	Blank	5.00
Dichloracetic	.044	4.66
Stearic	.055	4.97
Dichloracetic & Stearic	(.044+.055)	4.62

Additional evidence in favour of the opinion that the influence of electrolytes on the viscosity of a rubber sol is not in any way controlled by the non-caoutchouc constituents of the rubber is given by a few results obtained, using synthetic hydrocarbon. Unfortunately artificial rubber does not reach the same degree of solvation as found in the natural samples, consequently the concentration had to be increased to 1.87% in order to give a relative viscosity comparable to that used in the natural rubber sols.

TABLE XXXVI

INFLUENCE OF ELECTROLYTES ON AN ARTIFICIAL RUBBER SOL.
(A - Polymerized by Sodium)

Substance	Concentration in Millimoles per Litre	Relative Viscosity
	Blank	4.70
Diethylamine	1.2	4.37
Piperidine	1.3	4.24
Dichloracetic Acid	—	3.70

TABLE XXXVI (Cont'd.)

(B - Polymerized by Acetic Acid.

Substance	Concentration in Millimoles per Litre	Relative Viscosity
	Blank	4.70
Piperidine	1.2	4.32
Dichloracetic Acid	1.3	4.33

The influence of electrolytes on the viscosity is slightly less in the sols of rubber prepared by acetic acid polymerization. This is due to a small preliminary reduction of the viscosity caused by the presence of a trace of acetic acid carried over from the polymerization process.

SOLS OF RUBBER IN PETROLEUM ETHER

The effect of chemical reagents on the viscosity of rubber dispersed in various organic media is a field of investigation that the results of the present work at once suggests. Although it is hardly within the scope of this paper it was considered advisable for the purpose of comparison to ascertain the effect of a few electrolytes in at least one other dispersion medium.

For this purpose a small quantity of protein and acid free rubber was dispersed in petroleum ether (B.Pt.80-90°C.) and subsequently diluted to a concentration of .448% corresponding to a viscosity of 6.19. The preparation of the electrolyte solutions and the method used for the determination of the viscosity have already been described in Section I.

The results in Table XXXVII below show that both acids and bases bring about a very considerable reduction in viscosity. The effect, while a little greater than was observed in the benzene sols is nevertheless of the same order of magnitude. The magnitude of the effect in any solvent must depend on the degree of ionization of the electrolyte in the solvent and the degree of solvation, of the rubber. Apparently in petroleum ether sols the extent of the ionization of the electrolyte and the degree of solvation are slightly greater than in benzene sols.

TABLE XXXVII

INFLUENCE OF CHEMICAL REAGENTS ON THE VISCOSITY OF A PETROLEUM ETHER RUBBER SOL.

Substance		Concentration in Millimoles per Litre	Relative Viscosity
Blank			6.19
Ether	Diluents	10.0	6.10
Amylacetate		10.0	6.12
Piperidine	Electrolytes	15.0	4.07
Dichloracetate Acid		14.0	4.09

ACTION OF LIGHT AND HEAT

Fol (23) and later Kirchhof (24) observed that viscosity measurement on rubber solutions gave values which decreased rapidly with time. The explanation of this was found by Van Heurn to lie in the influence of light on the viscosity. If the experiments were carried out in the dark there was no difference in successive readings. Porritt (25) has carried out a very extensive investigation on the effect of exposure to ultra-violet light and mastication on the viscosity of rubber sols. He found that both ultra-violet light and mastication brought about enormous reductions in the viscosity of the sol.

In view of the fact that physical and chemical agencies are somewhat analogous in their effect on the viscosity of rubber sols, it was considered of interest to investigate the subject further and ascertain whether or not a relation existed between the mechanisms by which these agencies bring about the same result.

A concentrated benzene rubber sol was refluxed for 108 hours in an atmosphere of carbon dioxide. In that time the sol was reduced from a very heavy gel to a mobile liquid. The viscosity was reduced to such an extent that it was necessary to remove some of the benzene by evaporation in order to obtain a solution of the required viscosity, the viscosity of the sol then being 5.2% .

It was found (as the results below show) that the addition of electrolytes to this sol produce little or no effect on the viscosity.

TABLE XXXVIII

Substance	Millimoles per Litre of Electrolyte	Relative Viscosity
	Blank	3.97
Dichloracetic Acid	1.0	4.01
Piperidine	1.5	3.86

(For comparison; an abstract from Table XV, Section I; 1.58 millimoles of piperidine reduce the viscosity of a benzene rubber sol from 5.20 to 4.20)

A solution of pale crêpe in benzene exposed to sunlight for 3 weeks showed a behaviour similar to that of the boiled sample. No change of viscosity on addition of electrolytes could be detected. On exposing a benzene rubber sol in a quartz tube to an ultra-violet radiation for 30 minutes the time of flow was reduced from 5 minutes to 2 minutes, 28 seconds. Again, electrolytes were found to be incapable of bringing about a further reduction of viscosity.

Although these results do not reveal the mechanism by which a reduction in the viscosity of a rubber sol is brought about, they do suggest that the process is a physical and not a chemical one, and also that the means by which the viscosity is altered by physical and chemical agencies are intimately associated. (A detailed discussion of this point is given in a later portion of this paper.)

ULTRA-MICROSCOPIC OBSERVATIONS.

Ultra-microscopic observations on lyophilic sols are always exceedingly difficult,if not altogether impossible. Each particle is associated with many times its own volume of the solvent, consequently the refractive index of the swollen gel is very little different from that of the pure solvent. Rubber sols do not constitute an exception to this rule: in fact, they form an exceptionally difficult class with which to deal from a ultra-microscopical point of view. Rubber has a refractive index of 1.520 and the refractive indices of ordinary rubber solvents range from 1.400 to 1.650, allowing very little margin for the scattering of the light. When a beam is passed through the sol the light is not diffused by the particles unless there is considerable difference between the refractive indices of the disperse phase and the dispersion medium. This is evident from Lord Rayleigh's (26) formula for the intensity of the light diffused from a particle which is small in all dimensions in comparison with a wave length of light.

$$I = \left(\frac{U_1^2}{U^2} - 1 \right)^2$$

Where I = intensity of diffused light.
U_1 and U are the indices of refraction of the particle and the medium respectively.

Several solvents of relatively high index of refraction were examined and it was found that amylacetate gave a rubber sol which, after standing for a week, was distinctly resolvable under the ultra-microscope. The particles were seen to have a very slow trembling motion, like the surface of a jelly, in vibration. Phenyl mustard oil sols became resolvable after standing some time, but the disperse phase was much less distinct than in the amyl-acetate sol.

Klein and Stamberger (27) have recently observed that an overmilled sample of rubber gave sols in benzene which when examined under the ultra-microscope were seen to consist of luminous little discs engaged in rapid Brownian movement. The writer has found that a dilute benzene rubber sol after exposure to sunlight for a few weeks, or after refluxing, as described above, becomes distinctly resolvable under the ultra-microscope. The particles, although mere pin points of light, are quite distinct, rapidly darting about in active Brownian movement.

From the standpoint of this investigation the most noteworthy observation was the effect of electrolytes on the optical properties of the sol. It was found that a rubber sol whose particles were resolvable only with very great difficulty in the ultra-microscope, became distinctly visible on the addition of small amounts of a strong electrolyte, the slow trembling motion changing to a rather mobile type of Brownian movement. The very indistinct flashes of scattered light were transformed to more luminous sub-microscopic particles.

In general the effect of the electrolytes is parallel to the action of light, mechanical and thermal treatment. This observation is an exceedingly important factor in the theoretical explanation of the colloidal behaviour of rubber towards electrolytes in solution.

CELLULOSE NITRATE SOLS

While examining the effect of chemical reagents on the viscosity of rubber sols, it was decided for the purpose of comparison to extend the investigation into another organophilic system, viz. cellulose nitrate sols.

Sols were prepared in two dispersion media, (a) amylacetate, (b) nitro benzene. A small amount of cellulose nitrate (Brandram Henderson 70-second cotton) was allowed to stand in contact with the dispersion media for two days, after which it was thoroughly filtered and diluted to give a sol of suitable viscosity. The preparation of the electrolyte solutions and the viscosity determinations were carried out by the methods described in Section I of this paper.

The effect of several typical substances are recorded in Table XXXIX. It is at once seen that the effect of Strong acids are not quite so pronounced as that observed for the same reagents in benzene rubber sols. On the other hand, the influence of traces of potassium hydroxide in the cellulose nitrate sols is a little more effective than the same quantity when introduced into a rubber benzene sol. Also it will be noticed that the potassium hydroxide initially has the effect of increasing the viscosity of the sol followed at higher concentrations of alkali, by a reduction in viscosity, in a parallel manner to that already described for the rubber benzene sols. In general the nature of the effects of chemical reagents on the viscosity of rubber and cellulose nitrate sols are quite comparable.

In cellulose nitrate sols, amines or organic bases are no longer electrolytes but reactants. It was found that the addition of a few cc's of diethylamine to a small quantity of cellulose nitrate was accompanied by the liberation of a very considerable quantity of heat followed by the separation of a heavy oil. When the amine was added quickly sufficient heat was evolved to ignite the cellulose nitrate, resulting in a rather violent explosion. This reaction was not investigated further, as there was little doubt that amines are energetic reactants towards cellulose nitrate.

Tables XL and XLI represent data connecting viscosity with concentration of acid. The effective amounts are extremely small, an increase beyond a certain point of the amount of reagent added, has little additional effect. The magnitude of the effect is less than one would expect from these relatively strong acids. Another noteworthy feature is that trichloracetic and dichloracetic acids, with different dissociation constants, have practically the same capacity for reducing the viscosity of sols of cellulose nitrate in nitrobenzene. On the other hand the effectiveness of the same acids in reducing the viscosity of sols of cellulose nitrate in amylacetate is directly proportional to the strengths of the acids. Although the viscosity phenomena exhibited by rubber and by cellulose nitrate sols are essentially analogous, it cannot be denied that the latter possesses a much more complicated character than the former.

TABLE XXXIX

INFLUENCE OF CHEMICAL REAGENTS ON THE VISCOSITY OF
(A) CELLULOSE NITRATE IN AMYLACETATE.

Substance	Concentration in Millimols per Litre	Relative Viscosity
Blank		5.37
Trichloracetic Acid	0.61	5.00
Dichloracetic Acid	9.2	5.21
Diethylamine)	0.44	4.81
")Reactants	13.7	1.67
Piperidine)	14.0	1.15
Potassium Hydroxide	0.15	5.47
" "	0.80	6.48
Ferric Chloride	0.082	5.07
Alcohol) Diluent	24.0	5.35

(B) CELLULOSE NITRATE IN NITROBENZENE

Substance	Concentration in Millimols per Litre	Relative Viscosity
Blank		3.12
Dichloracetic	9.20	2.66
Ferric Chloride	0.03	3.06
Potassium Hydroxide	0.11	3.17
" "	1.07	3.02
Diethylamine (Reactant	12.00	1.08
Blank		2.92
Trichloracetic Acid	6.1	2.58
Hydrochloric Acid	(Trace)	2.48
Ammonia	"	3.01
Potassium Hydroxide	2.5	2.83

TABLE XL

INFLUENCE OF TRICHLORACETIC ACID ON THE VISCOSITY OF NITROBENZENE-CELLULOSE NITRATE SOLS.

Concentration in Millimoles per Litre .	Relative Viscosity
Blank	3.08
.032	3.03
.073	2.93
.358	2.80
.595	2.78
1.80	2.72
9.17	2.71

TABLE XLI

INFLUENCE OF DICHLORACETIC ACID ON THE VISCOSITY OF NITROBENZENE-CELLULOSE NITRATE SOLS.

Concentration in Millimoles per Litre	Relative Viscosity
Blank	3.09
.108	2.88
.436	2.79
.970	2.73
9.6	2.71

FIGURE X

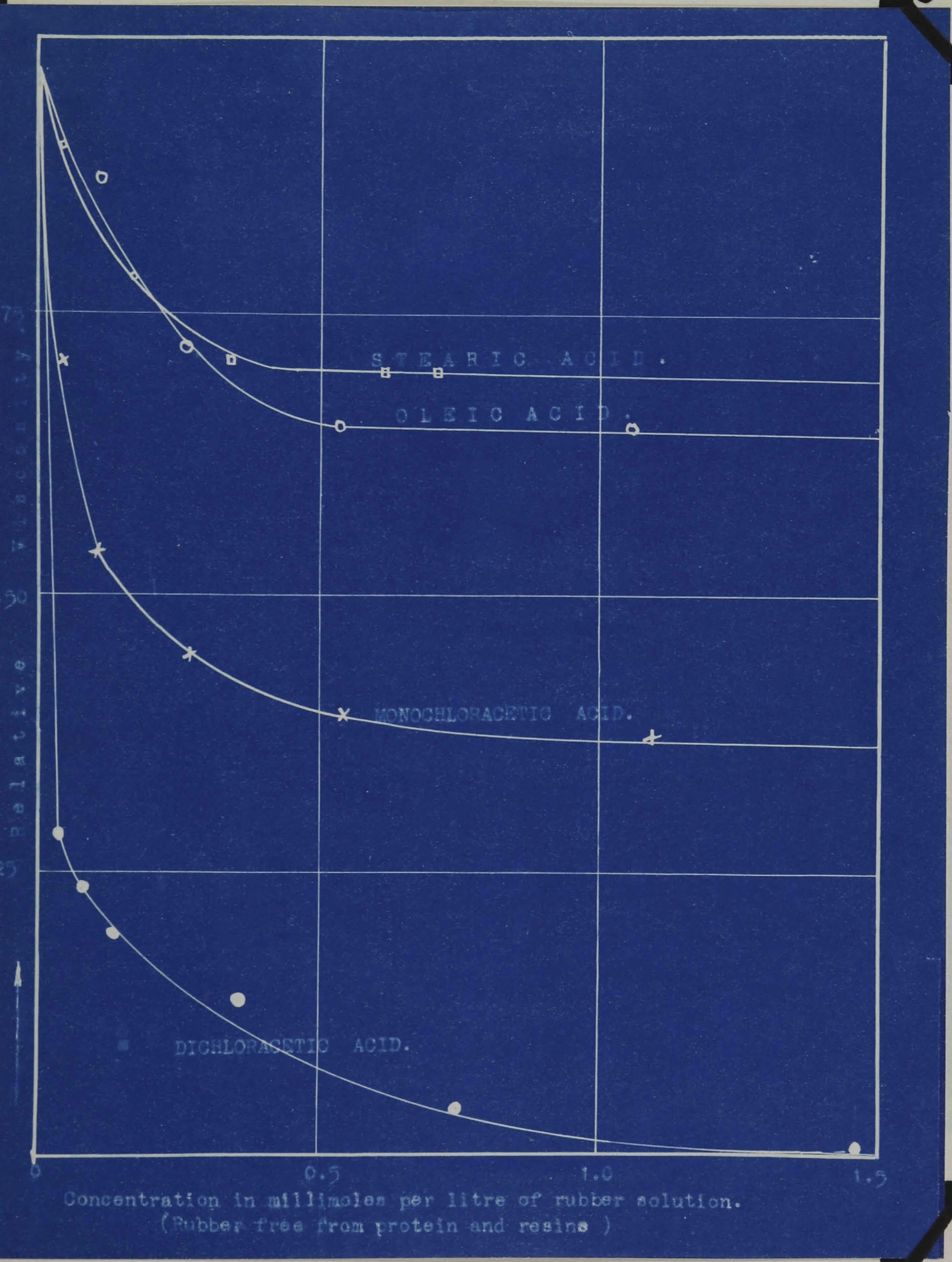

75
50
25
Relative viscosity.
STEARIC ACID.
OLEIC ACID.
MONOCHLORACETIC ACID.
DICHLORACETIC ACID.
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution.
(Rubber free from protein and resins)

FIGURE XI

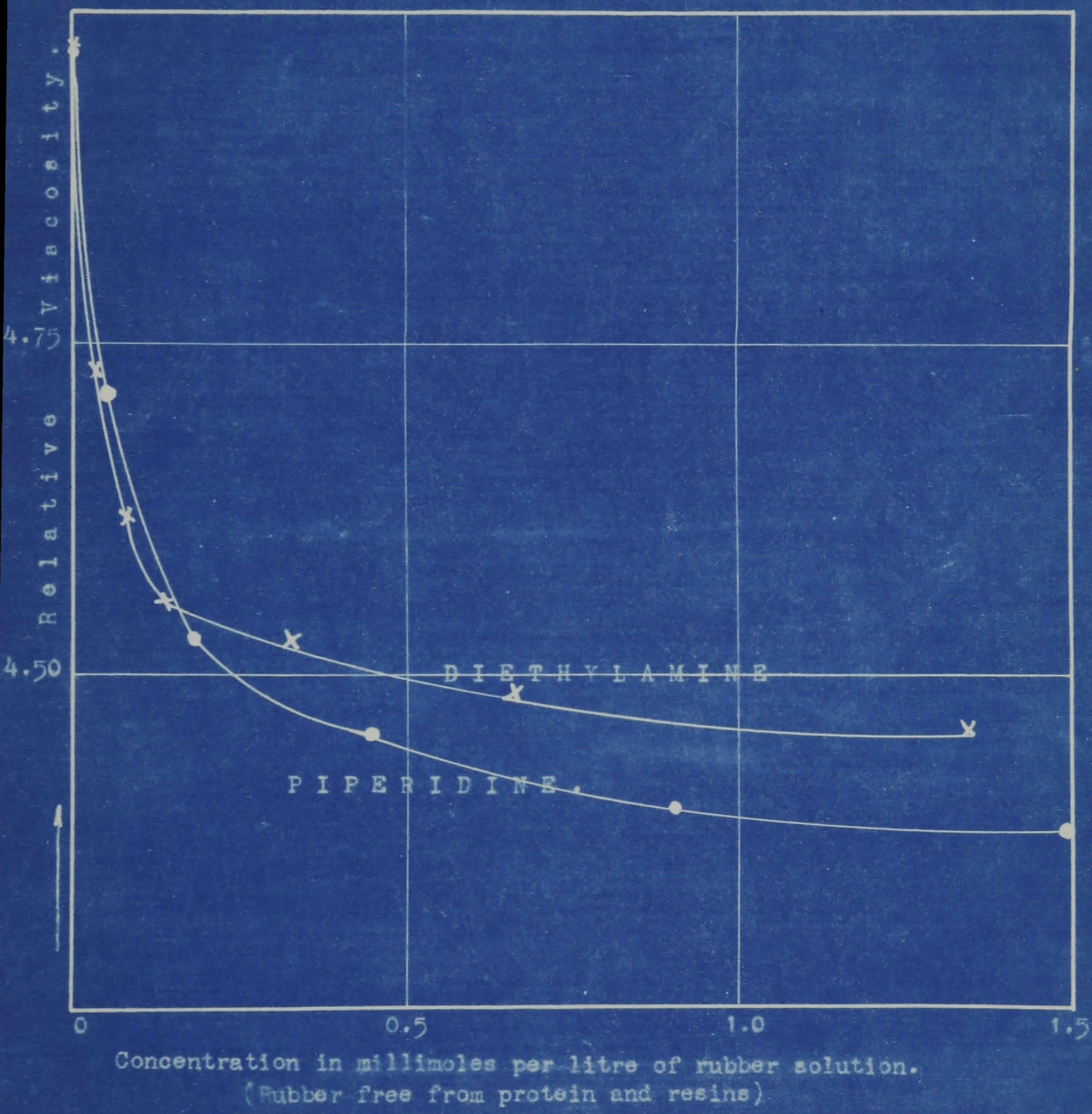

Relative Viscosity.
4.75
4.50
DIETHYLAMINE
PIPERIDINE.
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution.
(Rubber free from protein and resins)

FIGURE XII


Relative Viscosity.
FERRIC CHLORIDE
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution
(Rubber free from protein and resins)

FIGURE XIII

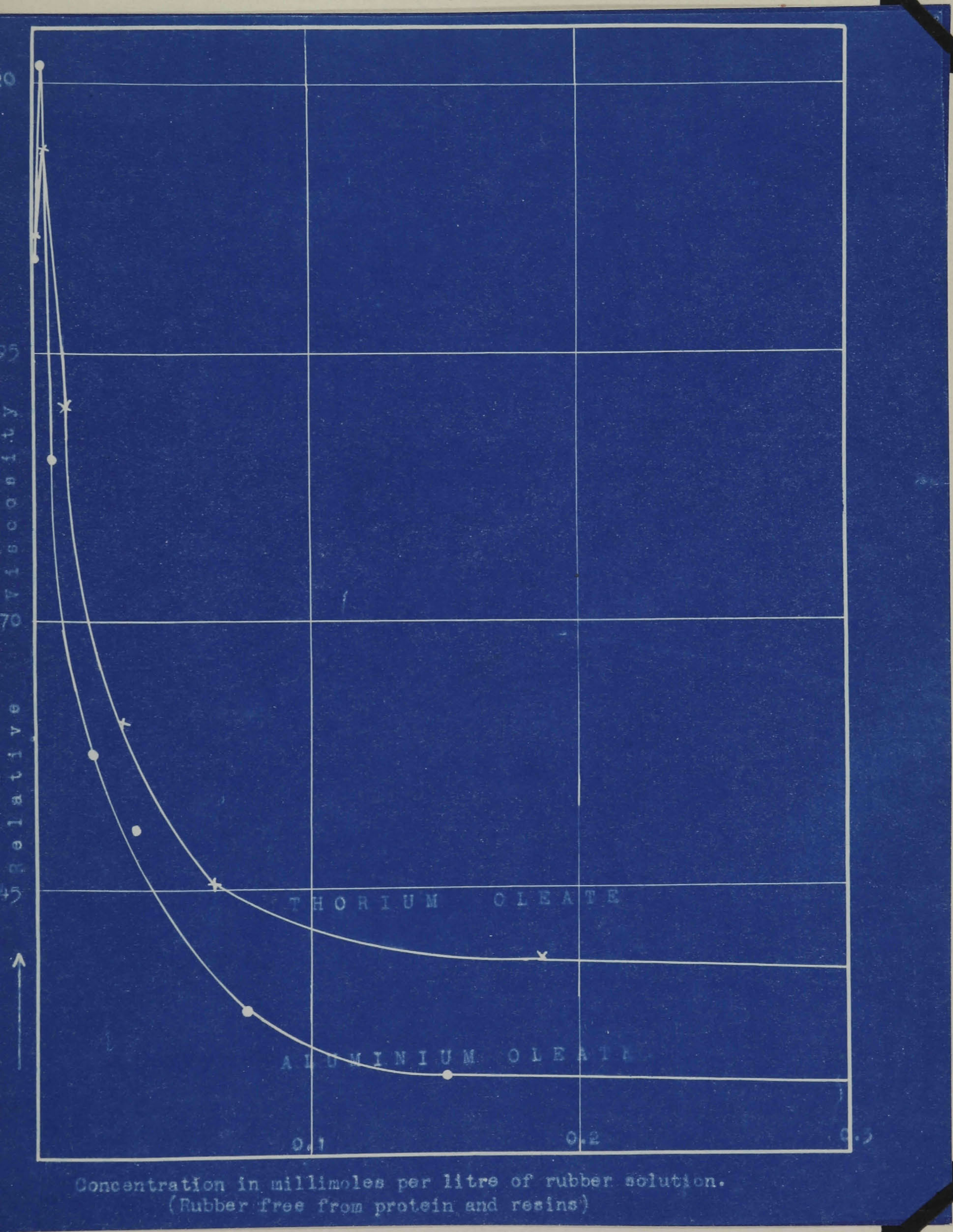
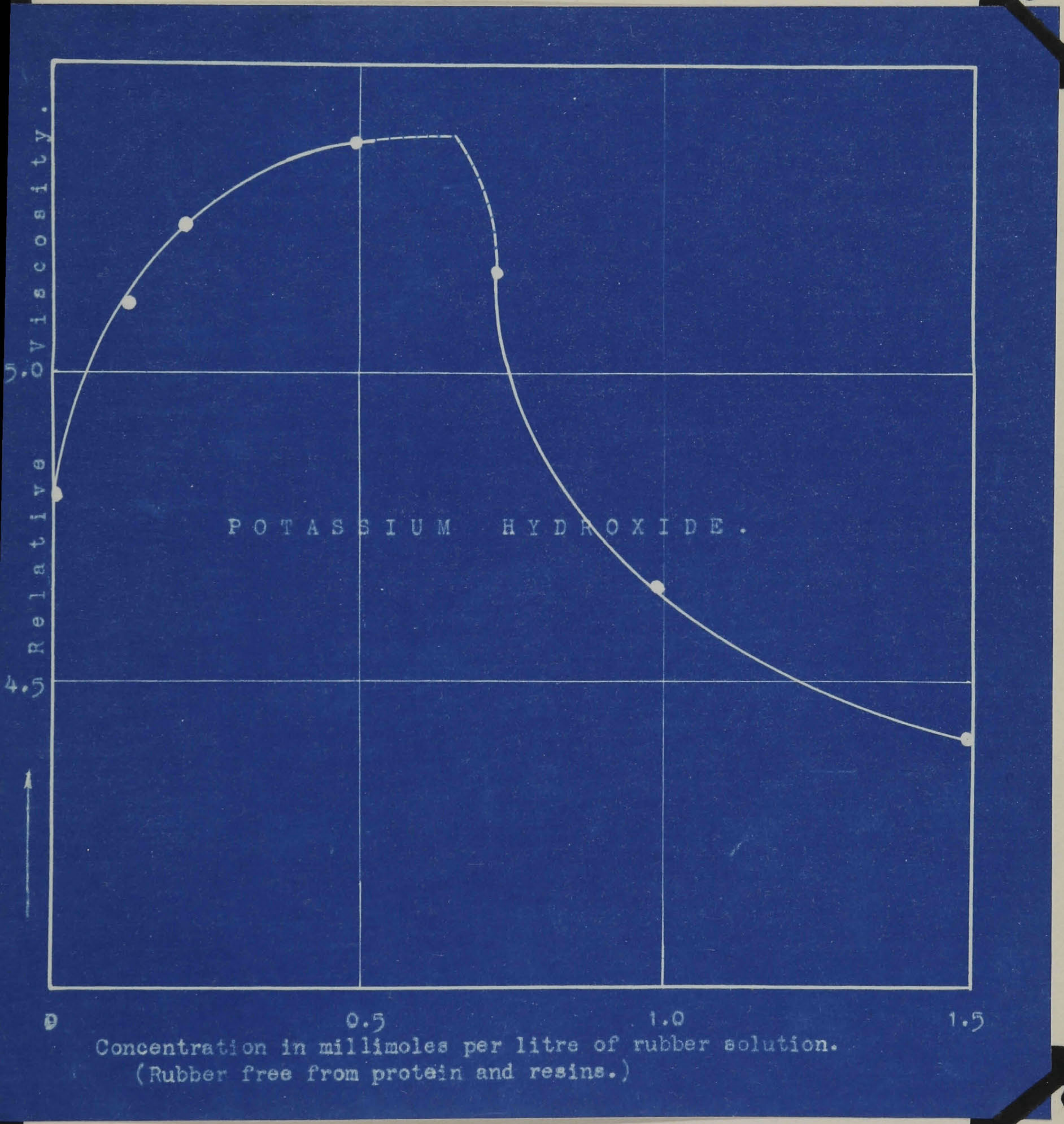

Relative Viscosity
70
THORIUM OLEATE
ALUMINIUM OLEATE
0.1
0.2
0.3
Concentration in millimoles per litre of rubber solution.
(Rubber free from protein and resins)

FIGURE XIV


Relative Viscosity.
5.0
4.5
POTASSIUM HYDROXIDE.
0
0.5
1.0
1.5
Concentration in millimoles per litre of rubber solution.
(Rubber free from protein and resins.)

THEORETICAL DISCUSSION

For the purpose of clarity in presenting the theory of the phenomena observed above, the author assumes that the samples of rubber used consisted entirely of the pure caoutchouc hydrocarbon. This certainly would not be permissible were it not for the fact that in Section II of this paper the question of the effect of impurities has been studied in detail. The results recorded in Section II show conclusively that the non-caoutchouc constituents are not responsible for the behaviour of rubber sols towards chemical agencies.

In developing the theory of the action of chemical reagents on the viscosity of rubber sols, it would appear desirable to discuss the subject under those divisions into which, by experiment, they have already been classified, namely, electrolytes, reactants, precipitants and diluents. But before studying the theory in detail, it is first necessary to give some account of the probable mechanism by which the rubber was obtained in the colloidal state; and when accomplished, to predict, at least some of the physical properties characteristic of such a system.

When placed in certain organic liquids, for instance, benzene, rubber gradually imbibes the liquid and swells. The imbibition proceeds to a certain extent and finally, if allowed to stand for several days, the swollen rubber becomes dispersed in the liquid, that is, solution has taken place. The exact nature of this preliminary swelling followed by dispersion is still the subject of a great deal of controversy, and up to the present, no adequate understanding of the phenomena is in sight.

It would seem, however, that if we adopt Freundlich's view that adsorption at a surface always lowers the surface tension, a theory of dispersion or peptization follows at once. An adsorbed film of liquid with a low surface tension on the solvent side and a high surface tension on the other side will tend to disintegrate or peptize the substance as the disperse phase. In rubber, we have, presumably, a mass of $(C_5 H_8)_x$ aggregates held together by natural cohesive or molecular forces. When in contact with some swelling agent, (which is simply a liquid possessing a very considerable molecular attraction for rubber) the aggregates no longer attract one another with the same force. The solvent molecules are adsorbed on, and partially surround each rubber particle, with the result that the surface tension forces holding the material together are considerably reduced. This adsorption on each particle of rubber must necessarily force them apart, bringing about an increase in volume, that is, the rubber swells.

Dispersion will take place only when sufficient liquid has been adsorbed around the particle to decrease the surface tension forces existing between the rubber aggregates, to a value, which is less than the value of the osmotic or solution pressure tending to draw the particle from a high concentration to a low concentration. If this be the mechanism of peptizing of rubber, the solution will consist of aggregates of rubber associated with a certain amount of adsorbed liquid, dispersed in the residual unbound solvent. Whether these swollen particles are single or groups of rubber molecules is unknown and indeterminable.

If dispersion has taken place in this way, the disperse phase must in consequence have certain definite physical properties. The swelling process indicates a large amount of adsorbed liquid giving rise to a highly solvated particle. In dilute solutions these solvated particles are free to swim in the unbound solvent without appreciable interference on the part of their nearest neighbours, that is, the solution possesses a low viscosity. If, however, the concentration is increased, a point is reached at which the particles are separated by a thin film of solvent. In this neighbourhood the viscosity-concentration curve will suddenly rise. Actual experiments, as well as viscosity-diagrams show this to be true. Kirchhof (28) employing Hatschek's emulsoid formula has shown quantitatively that as soon as the percentage of the total volume occupied by the disperse phase becomes appreciable, the rise in viscosity per unit increase in concentration is relatively great. This evidence, at least indicates that a rubber sol consists of discreet solvated aggregates and not a net-work of a very complicated structure as suggested by some.

Probably one of the most important physical factors associated with a system obtained by adsorption followed by peptization is the electric charge on the colloid. It was shown by Hemboltz (29) that any solid medium in contact with a liquid medium possesses at the surface an electric double layer. Briggs (30) suggested that this was purely an adsorption phenomena produced by on
ionization of the liquid with subsequent preferential adsorption of hydroxyl ions. Obviously this cannot include non-aqueous solvents. In 1916 and 1917 Langmuir (31) and also Harkins (32) found that many of the conditions existing at solid-liquid or liquid-liquid interfaces could be accounted for by assuming an orientation of the molecules at the surface. Recently Strickler and Mathews (33) have carried out a very interesting and complete series of experiments on the endosmotic flow of organic liquids across a membrane. Using a filter paper membrane in an endosmotic

apparatus they measured the rate and direction of flow of twenty organic liquids, (including benzene), under the influence of a constant potential. The fact that there is an endosmotic flow proves the existence of a charge on the wall. They explain the origin of the charge on the basis of the orientation of the solvent molecules at the surface and within the pores of the membrane, which as shown by Langmuir (34) gives rise to a difference of potential between the liquid and the solid wall. The orientation and consequently the nature of the charge depends solely on the liquid and on the membrane.

In the rubber benzene system a similar state of affairs is seen to exist, if we imagine the membrane to be ground up and dispersed in the liquid as is done in comparing electro-endosmosis and catophoresis. Each rubber particle is surrounded by adsorbed solvent molescules which are orientated. In view of the fact that benzene is essentially a symmetrical molecule (at least when written on paper) the orientation may be rather obscure. Harkins (35) has recently pointed out that the dissymmetry of forces may cause orientation of a molecule which possesses spatial symmetry. No doubt the atoms in benzene are symmetrically arranged in space, but the forces to which the atoms give rise may be concentrated over a certain area as in the case of a dissymmetrical polar molecule.

(A cataphoresis tube experiment would prove beyond a doubt the existence or the absence of a charge. Unfortunately benzene is practically an insulator, therefore, even in the presence of relatively large charges, a movement of the particle could only be detected under the influence of exceedingly high potentials. Moreover, the relatively high viscosity of even the most dilute rubber sols would materially decrease the mobility of the particles. Experiments are now in progress by which it is hoped to be able to observe the movement of the particles under the ultra-microscope using copper electrodes separated by a fraction of a cm.)

In 1916 Smoluchowski (36), from theoretical considerations derived an equation for the viscosity of colloids based on Einstein's and Hatschek's formulations, in which he shows that the electric charge on the particles contributes to the viscosity of the system. According to Hatschek's equation, $N_s = N_m \times (I + K\ \theta)$ the viscosity is directly proportional to the aggregate volume θ of the suspended particles; Smoluchowski, however, has introduced a term containing a function of the charge on the colloids.

$$\frac{\eta_s - \eta_m}{\eta_m} = \frac{5}{2}\theta\left[1 + \frac{\sigma}{a^2\eta_m}\left(\frac{\psi}{2\pi}\right)^2\right] = \frac{5}{2}\theta\left[1 + f(\psi)\right]$$

where η_s – relative viscosity of sol.
η_m – " " " dispersion medium.
θ – volume of the internal phase as a fraction of the total volume.
σ — specific resistance
a — radius of particle
ψ — potential difference at interface colloid particle - dispersion medium.

It is quite clear from this equation that any alteration in the charge will be accompanied by a variation in viscosity.

In the light of this formulation the nature of the effect of electrolytes on the viscosity of a rubber sol becomes understandable. From Tables XVII, page 33, and Fig. V, page 43, it appears that the magnitude of the lowering of the viscosity depends directly on the relative strengths of the acids and bases, as judged by their dissociation constants determined in water. This fact at once suggests that the effect is intimately connected with dissociation and therefore an ionic phenomena. It is proposed then, that the electrolyte dissociates in the benzene. One ion, presumably the cation, is selectively adsorbed at the interface, micelle-intermicellular liquid, causing a neutralization of the charge at the double layer and finally resulting in a reduction in viscosity according to the Smoluchowski equation.

The type of curves obtained by plotting viscosity against concentrations of electrolyte also indicates a dissociation phenomena. It has already been pointed out in connection with these curves that very small proportions of the strong electrolytes are necessary to bring about the maximal reduction of viscosity, any further increase of reagent has little additional effect. This means that the number of ions increases rapidly at first but at higher concentrations the number of ions formed per unit amount of electrolyte added is very much less; in other words, the progressive path of the curves is in accord with Ostwald's dilution law. It should be mentioned at this point that the effect of the ions in reducing the charge on the micelle is not wholly proportional to the number of ions present, but depends also on the selective adsorbability of the ion in question.

Concerning this conception, a question may be raised. What evidence is there for assuming that electrolytes dissociate in a solvent like benzene, having such a low dielectric constant? The evidence is forthcoming from Walden's(37) investigations on the dissociation of electrolytes in non-aqueous solutions. Walden formulated an equation according to which ionization of a typical electrolyte is the same in different solvents when the products of the dielectric constant and the cube root of the dilution have the same value. More recently a number of writers have proposed theories of electrolytic solutions which lead to Walden's relation as a consequence. Expressing the relation in the form of a mathematical equation.

$$D_2\sqrt[3]{V_2} = D_1\sqrt[3]{V_1}$$

where $D =$ dielectric constant; $V =$ volume. Comparing water and benzene with each other we can write:

$$\frac{D_w}{\sqrt[3]{c_w}} = \frac{D_b}{\sqrt[3]{c_b}}$$

where c_w concentration of electrolyte in water
c_b " " " " benzene

$$\therefore \frac{D_w^3}{D_b^3} = \frac{c_w}{c_b}$$

Now for water $D_w = 81.7^3$ and for benzene $D_b = 2.26$

Therefore $$\frac{c}{c1} = \frac{81.7^3}{2.26^3} = 47240$$

In other words the dissociation of an acid in benzene at a concentration of say .1 millimoles per litre is equal to that of the same acid in water at a concentration of 4.7 moles per litre.

A mathematical analysis of the ionization of a typical electrolyte in benzene is given below. Hydrochloric acid is selected for this purpose as all the data necessary for the calculation is on record. (Analysis according to the method of Eggink.)

A .1 N solution of hydrochloric acid in water is 91% dissociated. In benzene the concentration necessary for the same degree of ionization is

$$c = \frac{100}{47240} = 0.0021 \text{ millimoles per litre}$$

If the degree of dissociation a is known for a concentration c, the degree of dissociation a_1 for a concentration c_1 may be calculated from the following expressions:

$$K = \frac{a^2}{(1-a)v} \qquad \text{or} \qquad K = \frac{Ca^2}{1-a}$$

For this case we have

$$c = 0.0021 \qquad a = 0.91$$

$$K_1 = \frac{C_1 a_1^2}{1 - a} \quad \text{in which } C_1 = 1$$

and hence: $K = \frac{a_1^2}{1 - a}$

According to Walden (38) we have

$$\frac{K_1}{K} = \frac{1 - a_1}{1 - a} = \frac{1 - a_1}{0.09}$$

Now $K = \frac{0.0021 \times (0.91)^2}{0.09}$

Hence $\frac{0.09K_1}{0.0021 \times (0.91)^2} = \frac{1 - a_1}{0.09}$

or since $K_1 = \frac{a_1^2}{1 - a_1}$ we find

$$(0.09)^2 \times a_1^2 = (1 - a_1)^2 \times 0.0021 \times (0.91)^2$$

or $0.09\, a_1 = (1 - a_1) \times 0.046 \times 0.91$

whence we find

$$a_1 = 0.32$$

Therefore, for a solution of 1 millimole of hydrochloric acid in one litre of benzene the extent of dissociation is 0.32 percent.

The calculation shows that even in benzene with an extremely low dielectric constant there still occurs ionization of some significance. This, therefore, justifies the assumption that the effect of electrolytes on the viscosity of rubber sols is due to the formation of ions which are selectively adsorbed on the colloid particle causing an alteration in the magnitude of the charge thereupon.

ORGANIC ACIDS & BASES.

In considering this phenomenon as an electro-viscous one (so-called by Smoluchowski) several noteworthy features present themselves. Both organic acids and bases reduce the viscosity of the rubber sol. If it is assumed that acids exercise their effect by virtue of hydrogen ions to which they give rise, then it would appear to be necessary to suppose that bases also act by virtue of the cations, to which they give rise and which are adsorbed in preference to their anions. In any case there arises the problem - what are the ions to which amines give rise in benzene?

Eggink (39) in explaining the rise in viscosity on addition of ammonia to the rubber sol, assumes the presence of sufficient quantities of water in the benzene to give rise to ammonium hydroxide which dissociates into ammonium and hydroxyl ions. It is unlikely that in the benzene used in the present work there would be sufficient water to enable the bases to ionize to substituted ammonium cations and hydroxyl ions and, even if such ions did arise, it would still seem to be necessary to assume that the organic cation is adsorbed in preference to the hydroxyl ion. It is, too, unlikely that the effects are explicable by the presence of ions, of the types $R_2 NH_2$ - and A - derived from salts produced by reaction of the amine (say $R_2 NH$) with acid (say H A) naturally present in the rubber. Furthermore, it was shown (page 58) that the addition of small quantities of acids found in natural rubber to a sol containing rubber free from acid, did not increase the effect of piperidine when introduced into the sol at the same time. It seems then that the question of the nature of the ions to which amines give rise in benzene rubber sols, is still doubtful. Since there is insufficient data on record to enable one to state definitely one way or another the subject, for the present at least, must be left open.

INORGANIC BASES

The effect of potassium hydroxide, shown in Fig. IX and XIV is markedly different from the effect of organic bases. In very small amounts it produces a rise in viscosity; as the amount is increased, the viscosity suddenly falls below its initial value. On the basis of the electro viscosity equation of Smoluchowski, the initial rise may be explained as being due to an increase in the negative charge on the disperse phase as a consequence of the adsorption of hydroxyl ions to which the alkali gives rise. The sudden depression of the viscosity at a certain concentration of the base is not entirely clear. It is presumably due to a desolvation process occuring at the surface of the highly charged micelle. Alkalis present a similar behaviour in several hydrophilic systems. This analogy is discussed in detail in a later portion of the discussion.

SALTS

The explanation of the behaviour of rubber sols towards salts of organic and inorganic acids presents no great difficulty. The curves Fig. VII, VIII, XII, XIII, pages 45, 46, 74, 75 show, diagrammatically the effect on the viscosity of small quantities of salts over a range of concentration. It is at once seen that there is no relation existing between the valence of the ions and their effectiveness in bringing about a reduction of viscosity. This is in strict accordance with the results obtained by Strickler and Mathews (40) on the influence of electrolytes on the rate and direction of the endosmotic flow of organic liquids. They found that the addition of a salt changed the rate, and in a few cases the direction of flow, but in a very complete series of determinations, using a variety of salts there was no indication that the relative change in flow was proportional to the valence of the ion. The dissolved salt added to, or deducted from the charge on the membrane through selective adsorption. The order of the effect was specific for the ion and the solvent employed and was not determined by the valence of the ion. The effect of dissolved salts on the rubber micelle presents an analogous phenomena. It appears that the magnitude of the effect of an ion on the charged micelle depends primarily on the amount of the ion that is adsorbed, the valence being of secondary importance. On the other hand, if two ions of difference valence are adsorbed in exactly the same amounts, the magnitude of the charge on the ion becomes the determining factor. Zinc, mercuric mercury, and cupric copper, Fig. VII, page 45, each have a valence of two, but their capacity for reducing the charge on the micelle varies considerably, while aluminium and thorium, Fig. VIII, page 46, with valences of three and four have about the same effect; the slight difference being in favor of the ion of lesser valence.

It has already been pointed out that some of the salts examined, for instance aluminium and thorium oleates, Fig. VIII, page 46, showed a charging effect on the micelle when introduced into the sol in extremely minute quantities of the order of .05 millimoles per litre of sol. In the case of zinc chloride the effect is very small, the initial rise in viscosity being only .05 units, but in the case of the oleates, the effect is somewhat greater, being .79 units. In seeking an explanation for these irregularities the possibility of impurities in the form of hydroxides is always worthy of consideration. This is particularly true in the case of the oleates, as it is well-known that to obtain a pure sample is almost an impossibility. It has been recently shown by Kirchhof (41) that the addition of traces of water appreciably raise the viscosity of a rubber sol. In spite of the fact that all care was observed in preparing the zinc chloride in the anhydrous condition, it is not improbable that an appreciable quantity of water was taken up by the salt during the preparation of the solutions.

THE DE-SOLVATION PHENOMENUM

It is exceedingly difficult to conceive how the neutralization of the relatively small charge on a solvated particle could possibly account for the enormous reduction of viscosity observed in rubber sols. That the charge in all probability is quite small makes the conception all the more difficult. It is quite probable, however, that relatively great diminutions in viscosity may be produced if some secondary change in state were to take place as a consequence of the disappearance of the electric charge. After a diligent search such a secondary change, in the form of a DE-SOLVATION PROCESS, was discovered.

In the description of the results obtained from the ultra-microscopic examination of a few rubber sols, it was pointed out that mastication, thermal treatment and exposure to actinic light, not only greatly reduced the viscosity of the sols but also enhanced the resolvability of the particles under the ultra-microscope. Much more important, however, was the discovery that the addition of electrolytes to the sol had precisely the same effect.

The mechanism of the action of mastication and light on the viscosity of rubber sols has been the subject of several published papers (42) and almost invariably the authors have sought to explain the phenomenum on the basis of depolymerization. Without ultra-microscopical evidence such an explanation appears to be quite adequate, but in the light of the present work an explanation must be sought elsewhere than in the direction of depolymerization. It is quite inconceivable that depolymerization could have taken place with the formation of a sol that is typically colloidal, with its particles in a mobile condition, rapidly moving about as in an ordinary suspensoid system. Depolymerization would, by necessity, bring about the reverse effect; the sol would approach a molecular solution where optical resolvability becomes impossible.

The writer suggests that the phenomenum is essentially a de-solvation process. By de-solvation is meant a process by which the solvated particle gives up a portion of its bound solvent. If a de-solvation process takes place, the aggregate volume of the disperse phase is decreased and the quantity of unbound solvent is increased, both of which are factors tending to bring about a reduction in viscosity.

That lyophilic sols are unresolvable under the ultra-microscope on account of the large quantity of solvent associated with each particle, has already been mentioned. If de-solvation occurs the liquid solvent is removed from the particle, reducing the system to the form of a normal suspensoid where no difficulty is encountered in obtaining optical resolvability.

The fact that the addition of chemical reagents reduces the viscosity and increases the resolvability of rubber sols at once indicates that they too, exercise a de-solvating action on the micelle. In the case of electrolytes the de-solvation is a direct consequence of the neutralization of the charge. Wo. Pauli (43) and Bogue (44) have observed that certain proteins have their minimum viscosity and lowest degree of hydration at the isoelectric point. Furthermore, it is well-known that globulins after being denied their charge through the removal of adsorbed electrolyte by dialysis, become de-solvated to such an extent that the system becomes exceedingly unstable and the disperse phase precipitates from solution. Such observations leave little doubt that the de-solvation phenomena are intimately associated with, if not altogether dependent on the electric charge on the particle.

Neither Pauli nor Bogue offer an explanation for the simultaneous disappearance of the charge, reduction in viscosity and de-solvation. The writer suggests that an explanation may be looked for in the direction of surface tension. That the interfacial tension is reduced by the presence of an electric charge at the interface is well-known. The neutralization of the charge on a solvated particle would lead to an increase in the interfacial tension, followed by a contraction of its surface. A decrease in surface area can only take place through the liberation of a portion of the bound solvent, which is obviously de-solvation. Unfortunately, a theor y of this kind cannot be verified experimentally owing to the difficulties encountered in determining the interfacial tension of the micelle-intermicellular liquid interface.

THE ELECTRO-KINETIC EFFECT IN RUBBER SOLS AND OTHER SYSTEMS.

Analogies that have been found in the behaviour of electrolytes towards lyophilic sols dispersed in aqueous and non-aqueous media are rather remarkable. In a study of agar and starch sols, Kruyt and Bungenberg de Jong (45) have shown that the effect of electrolytes on the viscosity of these sols can be explained on the basis of the Smoluchowski equation. They have examined the influence of a number of typical electrolytes and have obtained curves, strikingly similar in type to those described above for rubber sols. The amounts which lower the viscosity to the flat portions of the curves are extremely small, the addition of more electrolyte having no appreciable effect. The analogy extends to the effect of alkalis, for it was found by Bungenberg de Jong that the addition of a trace of hydroxyl ion to a starch sol caused a considerable rise in viscosity. On the other hand, however, the differences between the two types of lyophilic sols are quite pronounced. In the aqueous sols the magnitude of the diminution of the electro-viscous effect is controlled entirely by the valence of the oppositely charged ion, the cation, while rubber sols show that the strength or the degree of dissociation of the electrolyte, followed by the preferential adsorption of ions plays an important role. A strong acid-like trichloracetic exercises a much more vigorous discharging effect that a weak acid-like acetic, while Th^{++++} , with a valence of four is essentially less effective than Fe^{+++} with a valence of three.

Another exceedingly important feature is that the effect of electrolytes on rubber sols finds a general parallel in the effect of electrolytes on electro-endosmosis in water. Elissafoff (46) has found that in the latter phenomenon both acids and bases act in the same direction, viz, to cause a reduction of the charge at the interface liquid-solid. The analogy again extends to caustic alkalis. As recorded above, increasing amounts of potassium hydroxide added to a rubber sol produces, at first a rise, and then a sudden fall in viscosity. In a parallel way alkalis added in increasing amounts at first enhance electro-endosmosis and then reduce it. Elissafoff has not been able to submit an adequate explanation for the effect of hydroxyl ions in bringing about a maximum charge in the wall of the endosmotic cell.

Ellis (47) while investigating the potential of the double layer at an oil water interface in a dilute oil emulsion, found that extremely small amounts of electrolytes were effective in reducing the potential at the interface. When the concentration of electrolyte had reached a certain value the curves connecting potential and concentration flattened out. The influence of alkalis on the electric charge on an oil particle was also examined by Ellis, and again the effect is strikingly similar to the effect of this substance on the viscosity of rubber sols. In slightly alkaline solution a distinct maximum potential of the double layer was observed. By increasing the concentrations of alkali beyond the maximum in the curve, the potential was reduced to its original value.

Powis (49) also working with dilute oil emulsions observed that certain salts, for example, potassium chloride and potassium ferrocyanide had the property of first increasing the charge on the oil particle followed by a reduction of the double layer potential below its original value. A number of other salts, for example, barium and aluminium chlorides did not show this maximum in their curves. It will be remembered that a similar observation was described above for the action of salts on the viscosity of rubber sols. Aluminium and thorium oleates showed a distinct maximum in their viscosity concentration curves.¶ As far as the present investigation is concerned, the significance of these analogies lies in the fact that the effect of electrolytes (a) on the viscosity of agar and starch sols, (b) on the electro-endosmotic flow of water (c) on the potential of the double layer existing at an oil water interface, has been proven definitely to be due to an electro-kinetic phenomenon, which is a phenomenon directly associated with the electrical charge at an interface. In view of the fact that in rubber sols one finds such an exceedingly close parallel to the electrokinetic phenomena in other systems, it is not only logical but also scientific to assume that the effect of electrolytes on the viscosity of rubber sols is intimately associated with the electric charge on the rubber micelle.

The evidence presented in the above theoretical discussion is strong in favor of the theory that the influence of electrolytes on the viscosity of rubber sols is of electrical origin. The electrolytes dissociate in the benzene giving rise to ions. The rubber micelle adsorbs one of the ions, in amounts depending on the nature of the ion and the sign of its charge. In the case of acids and salts, it is presumably the cation, but in the presence of potassium hydroxide the hydroxyl is adsorbed in preference to the potassium ion.

The effect of the adsorption of ions is to alter the magnitude of the charge on the rubber micelle, giving rise to a corresponding change in viscosity according to the equation of Smoluchowski. The alteration of the electrical environment at the surface of the colloidal particle is accompanied by a de-solvation of the micelle.

REACTANTS

That the proportion of iodine which is capable of reducing the viscosity is surprisingly small indicates that only a fraction of the rubber is transformed into the addition compound $(C_5 Hg I_2)_n$. In all probability the rubber micelle is an aggregate of a large number of molecules C_5 Hg. Whether or not these molecules are united in the form of polymers $(C_5 Hg)_n$ does not matter for the moment. In any case the number of molecules on the immediate surface of the micelle is small compared to the number in the micelle taken as a whole. Now, if iodine, for instance, is added in exceedingly small amounts there is a sufficient number of iodine atoms present to react with the greater portion of the molecules on the surface of the micelle. The addition compound $(C_5 Hg I_2)n$ is known to have very little affinity for benzene, consequently a rubber micelle on the addition of iodine, becomes partially surrounded with a superficial layer of addition compound which is incapable of adsorbing large quantities of solvent. The process then is one of de-solvation of the micelle causing a lowering of the viscosity of the sol. On increasing the concentration of iodine the layer of compound gradually penetrates the micelle until the disperse phase consists entirely of caoutchouc iodide. A system in which the particles have become de-solvated by chemical reaction is by nature bound to be unstable. There is a certain amount of solvent adhering or weakly adsorbed to that portion of micelle acted upon by the iodine. Agitation or mechanical treatment, such as drawing the sol through a capillary tube, would readily cause further de-solvation or even might disintegrate the micelle into smaller particles, both of which would cause further reduction in viscosity. Also de-solvation will extend over a period of time since the chemical reaction between iodine and caoutchouc is not by any means instantaneous. This is brought about very clearly by the time curves, Fig. IV, page 42, showing that the viscosity decreases rapidly with time. The time factor curves for electrolytes, Fig. II and III, page 41, on the other hand, represent a process which is practically instantaneous, the maximum effect having taken place during the first few minutes. This behaviour would be anticipated from what has already been said regarding the mechanism of the effect of electrolytes on the colloidal state of the rubber sol. The neutralization of a charge followed by an alteration in surface tension are essentially instantaneous processes.

PRECIPITANTS

A satisfactory explanation of the action of precipitants on the viscosity of rubber sols presents no great difficulty. The rubber micelle is in a dynamic equilibrium with the solvent, that is to say, the number of solvent molecules being adsorbed on the micelle per second is equal to the number per second passing from the micelle into the unbound solvent. Obviously then, the number of solvent molecules that are present on the micelle at any one moment depends on the number of solvent molecules per cc in the dispersion medium. Now, if some substance is added, alcohol for instance, which has no molecular attraction for rubber, the equilibrium becomes upset. The number of solvent molecules leaving the micelle is greater than the number returning per second, so that when equilibrium has been again established, the quantity of solvent in the micelle has been decreased. It is evident thatthe addition of a trace of alcohol, see Fig. I, page 40, would have no detectable influence on the solvation of the micelle, but if additions are made in large quantities the particles become almost completely de-solvated and precipitate from the colloidal solution.

DILUENTS

The name of this class of substances suggests the mechanism by which they effect the viscosity of rubber sols. Like benzene itself, these substances have an affinity for rubber, the magnitude of this attraction varying from diluent to diluent. The addition of a diluent to a rubber sol effects the viscosity only in so far as it increases the volume of the unbound solvent.

SECTION III

SWELLING OF RUBBER IN THE PRESENCE OF ELECTROLYTES.

While investigating the influence of acids and organic bases on the swelling of rubber, several results were obtained which appear to be contradictory to the theories set forth in the theoretical discussion.

The data in Table XLII below show that acids have little or no effect on swelling when present in proportions at least as great as the proportions used in the viscosity measurements. The results in Tables XLIII and XLIV reveal that small quantities of piperidine have only a slight effect on the swelling. They show, however, that in somewhat larger amounts, organic bases have a very striking influence on swelling.

The swelling measurements were made on samples of vulcanized rubber (prepared from a 90:10 rubber sulphur mixture.) Raw rubber in benzene could not be used on account of its tendency to break up and disperse before appreciable swelling occurs. However, in general, the swelling of raw rubber is parallel to that of vulcanized rubber. The samples of vulcanized rubber used weighed .087 - .089; and after being immersed in the benzene-electrolyte solution for 24 hours, were removed, dried, and weighed in a glass stoppered weighing bottle.

TABLE XLII

EFFECT OF ACIDS ON THE SWELLING OF VULCANIZED RUBBER IN BENZENE.

Acid	Amount added in Millimoles per Litre	Swelling (grams of Liquid imbibed per gram of rubber)
None		3.31
Acetic Acid	16.7	3.30
Dichloracetic	10.8	3.49
Benzoic Acid	8.2	3.48
Stearic Acid	3.5	3.57

TABLE XLIII

EFFECT OF BASES ON THE SWELLING OF VULCANIZED RUBBER.

Base	Amount added in Millimoles per Litre	Swelling (grams of Liquid imbibed per gram of rubber)
Piperidine	0	3.98
	0.15	3.98
	0.32	4.02
	0.77	3.98
	1.58	4.11
	3.18	4.19
	8.22	4.19
	16.5	4.52
	25.9	4.86
	110	6.60
	220	7.82
None		3.50
Piperidine	15.0	5.00
Diethylamine	16.0	5.61
Diproplamine	13.0	4.01

The same phenomena were observed in some experiments <u>on raw rubber</u> carried out in solutions of piperidine in petroleum ether (B.Pt.80°- 85°C.) This solvent is especially adapted for swelling experiments on account of the considerable swelling of the rubber which takes place before dispersion occurs. Table XLIV shows a few results obtained.

TABLE XLIV

EFFECT OF PIPERIDINE ON THE SWELLING OF RAW RUBBER IN PETROLEUM ETHER.

	Amount added in Millimoles per Litre	Swelling (grams of Liquid imbibed per Gram of Rubber)
Piperidine	0	12.4
	0.18	12.7
	0.92	13.2
	3.66	13.3
	33	13.8

Since small amounts of organic acids and bases have little or no influence on the swelling, and since the slight effect that organic bases do have is in the direction of increasing rather than decreasing the swelling, it would appear that the action of electrolytes on the viscosity of rubber sols cannot be explained on the basis of de-solvation. In fact, the action of such substances seems to be to solvate rather than de-solvate the rubber colloid.

In this argument it is assumed that a liquid possessing a high swelling power gives rise to a highly solvated particle on subsequent dispersion. That such an assumption is not justified is shown by the observation referred to on page #65. It was found that amylacetate formed a sol with rubber, which on standing for a few days became quite resolvable under the ultra-microscope. This indicates a small degree of solvation on the part of the disperse phase. But amylacetate is an exceedingly efficient swelling agent, much more so than many liquids which do not give optical resolvable sols. Here then we have definite proof that a liquid with a high swelling power may give rise to particles which are only slightly solvated. The fact that the swelling of rubber in a liquid is enhanced by the presence of organic bases does not indicate that the particles, on subsequent dispersion, are likewise increased in their degree of solvation.

SUMMARY AND CONCLUSION

(1) A method for extracting the resin acids from rubber at room temperature has been described.

(2) A sample of caoutchouc free from resin acids and protein has been prepared.

(3) The influence of chemical reagents on the viscosity of rubber sols is independent of the non-caoutchouc constituents.

(4) Viscosity is not a reliable method for the evaluation of raw rubber samples.

(5) The effect of ultra-violet light, sunlight and heat on the disperse phase of a rubber sol was investigated. The decrease in viscosity and the increase in optical resolvability was attributed to a de-solvation of the micelle.

(6) It was shown that chemical reagents which influence the viscosity of benzene rubber sols could be divided into four classes (a) diluents, (b) precipitants, (c) reactants, (d) electrolytes.

(7) The theoretical portion of this paper includes a theory which satisfactorily accounts for the phenomenom of peptization and also presents a possible mechanism by which the particles of the disperse phase become associated with an electric charge.

(8) To explain the action of electrolytes on the viscosity of rubber sols, it is proposed that one of the

ions to which the electrolytes give rise, is adsorbed at the interface, micelle, intermicellular liquid. The charge on the micelle is decreased or increased depending on the nature of the ion, and the viscosity of the sol is altered in a direction in agreement with the electroviscosity equation of Smoluchowski.

(9) The discharge of the potential at the double layer brings about a de-solvation of the particle.

(10) The electro viscous effect in sols of cellulose nitrate was examined. The influence of electrolytes on the viscosity of cellulose nitrate sols was found to be parallel to that described for rubber sols.

(11) The electro-kinetic phenomena in a variety of systems have been compared with electrical properties of a rubber sol.

BIBLIOGRAPHY

1. Phil. Trans. 1861, 151, p. 183.
2. "Kapillarchemie", 1922.
3. "Applied Colloid Chemistry", 1922, p.2.
4. Eggink, Rec. Trav. Chim. 1923, 42, 317.
5. (See 4)
6. Kruyt and Eggink, Proc. Roy. Acad.Amst. 1923,26,43.
7. J.Soc.Chem.Ind. 1909, 3.
8. Koll. Zeit. 1913, 12, 131.
9. Meded. Delft. 1916, 397, (Plantation Rubber" by Whitby, p.
10. "Bijdrage tot de Kennis van het Vulc."Amsterdam, 1916.
11. Meded. overrubber, No. IV (1915)
12. Gummi Ztg. 1911, 25, 990.
13. (See 10)
14. (See 12)
15. Koll. Zeit. 1914, 15, 30.
16. Comm. Netherlands Gov.Rubber Inst. (1917) 73.
17. Koll. Zeit. (1910) 7, 301, 8, (1911) 34.
18. Zeit fur Elect. Chem. 1921, p. 349.
19. (See 4)
20. (See 4)
21. Ann. 383, 157 (1911)
22. Ann. 383, 228 (1911)
23. (See 8)

Bibliography, Cont'd.

24. Koll. Zeit 1914, 14, p. 35.

25. "Phys. and Chem. of Colloids" Far. Soc. 1920, p. 81.

26. Phil. Mag. 1871, p. 41.

27. Koll. Zeit 1924, p. 362.

28. (See 15)

29. Wied. Ann. 1879, 7, p. 337.

30. J. Phys. Chem. 1917, 21, 198; 1918, 22, 256.

31. J. Am. Chem. Soc., 1917, 39, 1848.

32. " " " " 1917, 39, 354.

33. " " " " 1922, 44, 1647.

34. (See 31)

35. "Colloid Symposium Monog."1925, p. 142.

36. Koll. Zeit, 1916, 18, p. 190.

37. Electro-chemie nicht wassiger Losungen.

38. (See 37)

39. (See 4)

40. (See 33)

41. Chemical Abstracts, Mar. 1925.

42. (See 25), also Phys. Rev. 1922,Vols.18,p.371,Vol.19,p.552.

43. Trans. Far. Soc. 1913, 9, p. 54.

44. J. Am. Chem. Soc. 1921, 43, 1764.

45. Rev. Trav. de Chim. de P.Bas. 1924, 43, p. 13.

46. Zeit. Phys. Chem. 1912, 79, 385.

47. Zeit. Phys. Chem. 1912, 80, p. 597.

49. " " " 1914,15. 89, p.91.