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EFFECT OF THE PRESENCE OF SALTS
ON THE HYDROGEN OVERVOLTAGE OF SOLUTIONS

by

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for the Degree of

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I. INTRODUCTION

The electrochemical theory of corrosion is the commonly accepted explanation of the action of a water solution of an electrolyte on a metal immersed in it. Corrosion is caused by local galvanic couples set up between two metals, the more positive of the metals going into solution and hydrogen being liberated at the surface of the other. Solution of the metal is accompanied by the passage of an electric current, external to the solution, equivalent in amount to the metal dissolved. It is not necessary that the couple be made up of two pure metals, but it may be composed of a metal in contact with an impurity that is embedded within the surface, or between two parts of the same piece of metal if the two parts are in different physical conditions; for example, local cells may be caused by differences in crystal structure within the various parts of the metal, or by one part being in a state of strain.

On the basis of this theory, the amount of local current determines the amount of corrosion. The amount of current is dependent upon several factors, namely, the resistance of the cell, the electrolyte, the difference in potential between the two poles of the cell, and the potential necessary to liberate hydrogen at the cathode.

The last of these factors is dependent upon the nature of the electrolyte and upon the type of material acting as the cathode. Hydrogen is liberated at a lower voltage from an acid solution than from an alkaline solution. With any given electrolyte, some metals, such as platinum and gold allow hydrogen to be liberated at a lower voltage than other metals, such as mercury, cadmium, and zinc. This phenomenon has been called overvoltage and is defined as the electromotive force which is the difference of potential between a reversible hydrogen electrode and an electrode surface at which hydrogen is being liberated. Overvoltage acts as a back electromotive force opposing the electrolyzing current and thus tends to prevent its action. Since the overvoltage of certain metals is very high, it plays an enormous role in the prevention of corrosion. Any condition that tends to produce a higher overvoltage at the cathode retards corrosion, while a lowering of the overvoltage increases the corrosion rate.

Overvoltage is affected by many factors, the most of which have been carefully studied and are generally understood. Factors that have been thought by investigators to affect overvoltage are:

(a) Cathode material.

(b) Current density.

(c) Physical condition of the electrode.

(d) Length of time of the passage of current.

(e) Pressure and temperature changes.

(a) The magnitude of overvoltage is dependent upon the cathode material. Caspari (4) has arranged the more common metals in the following order of their increasing overvoltage: Pt (platinized), Au, Pt (polished), Ag, Cu, Pd, Sn, Pb, Zn, and Hg.

(b) The effect of increasing the current on overvoltage has been carefully studied by a number of investigators. At low current densities the overvoltage is very small, increasing rapidly at first with increased current density and then gradually approaching a constant value at higher currents. Tafel (27) has shown that when the logarithm of the current density is plotted against the overvoltage a straight line is obtained. He expressed this relationship in the equation:

$$n = a + b \log I$$

In this equation, n is the overvoltage, I is the current density, and a and b are constants depending upon the material used for the cathode. This work has been confirmed by a number of men and the values for a and b have been worked out for most of the pure metals and a number of alloys.

(c) Overvoltage may be affected by a number of physical conditions, such as hardness, previous treatment, and the condition of the electrode surface. An electrode surface that has been prepared by electroplating the metal generally has a different overvoltage value than the pure cast metal. Overvoltage is always lower when the electrode surface is rough than when it is smooth, the minimum overvoltage for any metal being produced when the metal has a spongy surface. This is thought to be due to a lowering of the current density because of the increased surface. The overvoltage of a metal containing impurities is not the same as that of the pure metal, the direction and magnitude of the difference being dependent upon the nature of the impurities.

(d) The effect of the length of time that the electrolyzing current has been flowing has been investigated. In some cases it was found that the maximum overvoltage was reached after only a few minutes of electrolysis, while at other metallic surfaces the value continued to rise slowly for as much as four or five hours. Denina and Ferrero (6) found that in all cases there was a very rapid rise in the first minute or two and that on prolonged passing of an electrolyzing current a maximum was finally reached. A slight decrease was noted if electrolysis was continued for several hours after the maximum had been reached. He attributed this decrease to a roughening of the electrode surface.

(e) The effects of changing pressure and temperature have been investigated. Bircher, Harkins, and Dietrichson (2) have reported a slight decrease in overvoltage with increasing temperature. Authors are not in agreement on the effect of changing pressure. MacInnes and Contieri (21) have reported a decrease in overvoltage with increasing pressure. This work has been confirmed by Bircher and Harkins (1) and by Goodwin and Wilson (11). Knobel (17) reports no change in overvoltage over a rather wide range of pressure changes.

Many materials have been suggested to be added to solutions that come in contact with iron to prevent its corrosion. The range of materials is very great, including many organic compounds, a large variety of colloidal materials, and some inorganic salts. According to Warner (28), the inorganic salts that have been the most widely used and have met with the greatest success are silicates, arsenates, chromates, and phosphates. Parr and Straub (26) have shown that the presence of sulfates in boiler water containing a high amount of carbonate tends to prevent the deterioration of boiler tubes and plates. Since there is a definite relationship between overvoltage and the extent of corrosion, it is possible that a correlation between the salts present in an electrolyte and overvoltage might be obtained. The purpose of this investigation is to determine the effect of the presence of salts on the hydrogen overvoltage of solutions. The effect of adding salts in various concentrations to 0.1 N sulfuric acid and 0.1 N sodium hydroxide has been determined at different current densities. In addition, the effect of concentration on overvoltage was determined by adding various amounts of pure salts, sulfuric acid, or sodium hydroxide to distilled water.

II. REVIEW OF LITERATURE

A vast majority of the numerous studies on overvoltage have dealt with the effects of electrode materials, electrode conditions, and work on testing the many theories that have been advanced to explain or account for overvoltage. Only a very few studies on the effect of electrolyte material have been reported. Iszarishew and Stepanor (15) have investigated the effect of fluorides on overvoltage in both acid and alkaline solutions using gold, silver, and graphite electrodes. They have reported an increase in anodic overvoltage as the concentration was increased until a maximum value was reached above which a further increase in concentration of the salt caused a lowering of the reading. This increase was ascribed by them to the formation on the anode of fluorine compounds which were soluble in fluorides of higher concentration.

Iofa, Kabanou, Kechinski, and Chistyakov (13) have measured the effect of adding potassium chloride, potassium bromide, and potassium iodide to hydrochloric acid solutions using both a large mercury surface as the cathode and a dropping mercury electrode. Their measurements have all been made at the same concentration of the salt and acid solution, that is, they have noted the shift in overvoltage when a solution of 0.1 N hydrochloric acid contained 1 mole per liter of the salt as compared with the overvoltage in 0.1 N hydrochloric acid alone. They have reported a lowering of the overvoltage at these surfaces over a wide range of current densities.

The effect on anodic overvoltage of adding certain salts to acid solutions has been investigated by Mazzucchelli and Romani (24). Perchlorates when added to sulfuric acid solution cause a rise in anodic overvoltage. They have also studied the effect of adding sodium chloride, sodium fluoride, and hydrofluoric acid to a solution of sulfuric acid. In each case they found an increase in the overvoltage when the concentration of the salt was increased followed by a subsequent decrease when higher concentrations were reached.

Kobozev and Nekrasow (18) have reported that the addition of mercuric chloride or hydrogen sulfide produces an increase in the decomposition potential at a platinized platinum electrode.

Lukoutsev, Levina, and Frumkin (20) have found that sodium chloride and lanthanum chloride when added to acid solutions cause an increase in hydrogen overvoltage. The same materials cause a decrease in overvoltage when added to an alkaline solution.

There has been some specific work done by Chappell, Roetheli, and McCarthy (5) and by Jimeno, Griffoll, and Moral (16) on the effect that addition of certain organic corrosion inhibitors to sulfuric acid solutions has on overvoltage. These organic inhibitors are materials that are commonly added to the solutions used in the pickling of iron. Their function is to retard the solution of the metal while in the pickling bath. Organic corrosion inhibitors are also added to boiler water and to other solutions that come in contact with metals that are easily corroded. In both of these studies it was found that there was an increase in overvoltage proportional to the amount of material added to the acid solutions. This work has been reviewed and extended by Warner (28). His work shows that small quantities of quinoline, aniline, bases from petroleum fractions, and bases from coal tar oil, all cause the overvoltage on iron in acid solution to be increased. Warner's work is summarized by the statement, "Any substance which will form a large, positively charged, oily ion, or a positively charged, oily, colloidally dispersed particle, in acid solution should inhibit the acid corrosion of iron if the substance cannot be electrolytically reduced." These positively charged particles, it is thought, migrate to the cathode and are there adsorbed on the surface of the cathode material thus causing the overvoltage to increase.

The effect of adding colloidal material to an acid bath was studied by Marie (22) and by Marie and Auduberr (23). They found an increase in overvoltage with the addition of a colloid. Similar experiments have been carried out by Isgorishes and Berkmann (14) who have reported that when adding colloidal material to sulfuric acid solutions the overvoltage is increased in proportion to the amount of colloid added. They have attributed the rise to adsorption compounds formed between the colloid and the electrolyte ions.

The effect of hydrogen ion concentration on overvoltage has been investigated by a number of men who are not in complete agreement as to the results. Perhaps the most reliable results were obtained by Bowden (3) who has determined the overvoltage of buffered and unbuffered solutions over a wide range of current densities. The buffered solutions were prepared from solutions of sodium phosphate, citric acid, and potassium chloride. He has found that for low current densities the overvoltage remains constant regardless of the hydrogen ion concentration of the solution. At higher current densities, there is a decrease in overvoltage with increasing hydrogen ion concentration of the solution. The fact that the effect is different depending upon the current density used may account for the disagreement among different authors.

III. EXPERIMENTAL

A. Methods for Measuring Overvoltage

Two distinctly different methods have been used for the quantitative measurement of overvoltage. The first of these, the direct method, was originally developed by Fuchs (10) and has since been the method used in the greater part of the work on overvoltage. The second, the indirect or commutator method,was first used by LeBlanc (19) and has since been further developed by Newbery (25), Glasstone (12),and Ferguson (8). The two methods differ from one another essentially in that as the first measures the extent of polarization of an electrode as the polarizing current is flowing, while the commutator method measures the back electromotive force of an electrode the instant the current is interrupted. When using the direct method, the electrode being investigated is made to serve as the cathode at which hydrogen is liberated by electrolysis. This electrode is at the same time connected to any standard electrode. The potential set up by the cell thus created is measured by means of a potentiometer. The overvoltage is given by subtracting from the potentiometer reading the voltage measured between the standard electrode and a reversible hydrogen electrode in the same solution. The indirect method makes use of a commutator which alternately connects a pair of electrodes with a source of polarizing current and then connects the cathode and a standard cell to a potentiometer. During the first part of the cycle electrolysis takes place and the electrodes become polarized. During the latter part of the cycle the current is interrupted and the back electromotive force of the cathode is measured by means of the potentiometer. Any standard electrode can be used to measure this voltage, the overvoltage being obtained by subtracting the potential of the standard cell measured against a reversible hydrogen electrode in the same solution. The two methods do not give the same numerical results, the direct method invariably giving higher results than the commutator method.

The question of which of the two methods gives the true results has been a source of controversy for many years during which time hundreds of researches have been carried out in an effort to discover the discrepancy. Newbery (25) and Glasstone (12) have been most active in supporting the commutator method. According to them an extra resistance other than that caused by overvoltage exists at the surface of an electrode and is measured by the direct method and not by the commutator. According to those favoring the direct method the interrupter does not permit the measurement of the total discharge potential because of the rapid drop in potential during the interval between the interruption of the current and the measurement of the potential. Ferguson and others (9) have carried out a series of researches in which they have developed a method for measuring the overvoltage at an electrode by both methods at the same time. In their work they have shown that the commutator method gives results that are average and that the maximum values thus obtained are the same as those obtained by the direct method. Ferguson also states that the direct method not only gives the true values for overvoltage but the results are more reproducible and are more reliable.

B. Apparatus

Because it has been demonstrated that the direct method gives better results, it has been used in this investigation. All measurements have been made using a nickel cathode. Nickel was chosen because its overvoltage is high and any effect produced by the addition of salts to the electrolyte should be more noticeable than at a metal having a low overvoltage. The electrode was made by sealing a nickel wire, one millimeter in diameter, into a glass tube by means of wax. A portion of wire, one and one-half centimeters in length, was exposed as the active electrode. The glass tube served as a mercury reservoir for making the necessary electrical connections. The surface of the electrode was polished by lightly buffing it with fine sandpaper. Since in this work it was the effect of the addition of salts that was important rather than the actual overvoltage, further polishing of the electrode was unnecessary. The apparatus was arranged as illustrated by Dole (7) and is the conventional arrangement when using the direct method for the measurement of overvoltage.

The source of polarizing current was a 100 volt direct current line. Two variable resistances were placed in the line. One contained eight resistors by means of which resistance from 10,000 to 100,000 ohms could be obtained. The other was a Leeds Northrup decade box, 1 to 9,999 ohms. With this arrangement, the resistance could be regulated very accurately to give any desired current over a wide range of amperages. Currents of 10 milliamperes or less were measured by means of a milliammeter that was accurate to 0.01 milliamperes. The higher currents were read on an ammeter with an accuracy of 0.1 milliamperes. The polarization potentials were measured by means of a standard Leeds Northrup Student Type potentiometer using a Leeds Northrup galvanometer as the null point instrument. The positive pole of the potentiometer was connected to the nickel electrode and the negative to a saturated calomel half cell against which the potential of the nickel electrode was measured. Connection between the electrolyte and the calomel half cell was made by means of a potassium chloride salt bridge. The bridge also contained agar-agar to prevent one solution from siphoning into the other and to minimize diffusion.

Had a platinum black electrode saturated with hydrogen in the same electrolyte that surrounded the nickel been used, the voltage readings on the potentiometer would have given the overvoltage directly. Because of the difficulty in maintaining a reproducible hydrogen electrode and because of the ease with which it becomes poisoned, the more reliable calomel cell was used. The potential difference between the same calomel cell and a hydrogen electrode was determined in each of the different electrolytes and these values subtracted from the potentiometer readings. The anode for the polarizing current was a platinum electrode made by sealing a platinum wire into a glass tube. The platinum and nickel electrodes and the salt bridge were mounted by inserting them through holes in a rubber stopper. The nickel electrode and the tip of the salt bridge were close together and always in the same position with respect to one another. In order to prevent polarization due to concentration of the electrolyte at the electrodes, the electrolyte was stirred with a small, glass, air-driven stirrer.

C. Procedure for Measuring Overvoltage

At first a series of solutions each containing the same concentration of sulfuric acid but differing in the amount of a salt added was prepared. Each solution was then in turn made the electrolyte and the overvoltage determined at a number of current densities. The electrolyte was then replaced with a solution of a different salt concentration and the procedure repeated. The data thus obtained showed very nicely the effect of changing the current density on overvoltage for each solution, but were of little value when attempting to find the effect of increasing the salt concentration at any one current density. This was due to the fact that handling the electrode while changing from one solution to another caused slight changes in the electrode surface which produced variations in the overvoltage readings. The general trend of the results could be observed but no definite conclusions could be drawn.

The method that was decided upon was to place a standardized solution of acid or base in the electrolyzing beaker and adjust the current to the desired amperage. Keeping the amperage constant, the overvoltage was determined after the addition of each of a series of measured portions of a standard salt solution. In this manner a series of readings for one amperage at various concentrations of the salt were obtained without the necessity of moving or in any way disturbing the electrodes. This proved to be a very convenient method and all the results reported were obtained in this manner. In order that concentration of the original electrolyte should not change, due to the diluting effect of the solution being added, the salt solution was also made the same normality with respect to acid or base as the original electrolyte. To obtain overvoltage readings for any series of solutions 100 milliliters of a 0.1 N acid or base solution was placed in a 400-milliliter beaker, the electrodes inserted, and the current regulated to the desired amperage. Since the value of overvoltage increases with time, it was necessary to let the current flow until constant readings were obtained. The constant value is reached at a nickel electrode in a relatively short time, fifteen to twenty minutes being required when low current densities were used, and slightly longer times when the current density was higher. The reading was recorded as soon as it remained constant for one minute or longer. A measured amount of a solution of the salt being studied was then added from a burette. Enough time was allowed for the solutions to become thoroughly mixed before the second reading was taken. It was found that when the addition of a salt caused any change in the overvoltage the change was almost instantaneous and that readings could be taken just as soon as the mixing of the two solutions was complete. The addition of small portions of the salt solution, followed by recording of the potentiometer reading, was continued until 50 milliliters of solution had been added. In obtaining the voltage of the calomel cell measured against a reversible hydrogen electrode in the same solution, a similar procedure was followed. Most of the materials added were not neutral salts but hydrolyzed to form either an acid or basic solution. Thus, in most cases the pH of the original electrolyte varied over a wide range. Since the electromotive force of a hydrogen electrode is dependent upon the pH of the electrolyte, the voltage difference between the calomel and hydrogen electrodes had to be determined over the entire range of concentrations for each solution. To do this, 100 milliliters of the desired solution, 0.1 N sulfuric acid or 0.1 N sodium hydroxide, were placed in a 400-milliliter bottle. A rubber stopper carrying a platinum black electrode, a salt bridge for connecting with the same calomel cell used in the other measurements, an inlet tube for bubbling hydrogen into the solution, and a short tube through which the salt solution could be added was inserted. The two electrodes were connected to the potentiometer and hydrogen passed through the solution until it was saturated. This was indicated by the fact that the voltage of the cell became constant. A measured amount of the salt solution was then added from a burette and after allowing time for saturation of this new solution with hydrogen the voltage was again read. The potential of the cell was determined in this manner over the same range of concentrations that had been used in the previous measurements. The value of the overvoltage at each concentration was obtained by subtracting the electromotive force of the calomel cell measured against the hydrogen electrode in any given electrolyte from the potential read when hydrogen was being liberated at the nickel electrode in the same solution.

D. Results

The effects of the addition of ten different materials to an acid electrolyte were studied. In each case the material added was in the form of a concentrated solution of known molarity. The salts used were sodium sulfate, trisodium phosphate, potassium oxalate, sodium formate, sodium acetate, sodium fluoride, sodium dichromate, sodium nitrate, and sodium chlorate. The solutions were either 1 molar or 0.5 molar. They were prepared by adding the calculated weight of the Reagent Grade of the salt to a 1-liter volumetric flask, then adding exactly 100 milliliters of 1 N sulfuric acid, and diluting to one liter. In addition to the salts mentioned, the effect of adding 1 molar sodium hydroxide to the sulfuric acid was determined. The data obtained from these studies are presented graphically by Figures 1 through 10. These graphs have been prepared by plotting the overvoltage in volts against the milliliters of solution added at each of six different amperages. The curves on any one page represent the effect of the same salt on the overvoltage, each curve representing the effect at a different amperage.

Figure 1 shows the effect of adding a 1 molar solution of sodium sulfate to 100 milliliters of 0.1 N sulfuric acid. The effect was a gradual lowering of the overvoltage at every current density. The data obtained from the addition of each of the following, 0.5 molar trisodium phosphate, 1 molar potassium oxalate, 1 molar sodium formate, 1 molar sodium acetate, and 1 molar sodium fluoride to 100 milliliters of 0.1 N sulfuric acid are represented in Figures 2, 3, 4, 5, and 6, respectively. These graphs each show a marked similarity, that is, a sharp increase in the overvoltage with increasing concentration of the salt until a maximum is reached followed by a subsequent decrease with the addition of more of the salt. The maximum in each case comes very close to the point at which the equivalent amounts of sulfuric acid and salt are present in the solution. The salts that produced this effect have been decidedly basic in all but two cases. Potassium oxalate and sodium fluoride produce nearly neutral solutions but when added to 0.1 N sulfuric acid cause a decided rise in the pH. Since these salts have the ability to neutralize an acid, the effect of the addition of a 1 molar sodium hydroxide solution to 0.1 N sulfuric acid was determined and the data presented in Figure 7. The same general type of curve is produced, showing a sudden rise to a maximum followed by a decrease in the overvoltage as the concentration was further increased.

Figures 8, 9, and 10 show the effect of adding oxidizing agents to sulfuric acid solution. One molar solutions of sodium nitrate, sodium chlorate, and sodium dichromate were added to 0.1 N sulfuric acid. The result in each case was a lowering of the overvoltage. With sodium nitrate and sodium chlorate, the addition of a very small amount of the salt caused a rapid drop in overvoltage followed by a very gradual lowering as the concentration was increased. In the case of sodium dichromate the lowering was very great with very small concentrations when the current density was small. With increasing currents there was still a lowering of the overvoltage but the concentration of the salt had to reach a higher value before the effect was noticeable. At higher current densities there was a slight rise followed by a lowering that took the value below that of the original acid solution.

The effect of adding salts to a solution of sodium hydroxide has been studied for four different salts. In each case the original electrolyte was 0.1 N sodium hydroxide and the salts were either 0.5 molar or 1 molar solutions which had been made 0.1 N with respect to sodium hydroxide. The determinations were run in exactly the same manner as when sulfuric acid was used as the electrolyte. Figures 11, 12, and 13 show the results of adding 1 molar sodium sulfate, 1 molar potassium oxalate and 0.5 molar trisodium phosphate to sodium hydroxide. In each case there was a gradual decrease in the overvoltage as the concentration was increased. At low amperages the effect was less pronounced than when the current was higher. The effect of adding sodium dichromate to sodium hydroxide solution was a small rise in overvoltage followed by a decrease as the concentration was further increased. These results are presented in Figure 14. This is the same type of curve that was produced when basic substances were added to sulfuric acid. Sodium dichromate hydrates to produce primary sodium chromate which is an acid salt and thus acts to neutralize the sodium hydroxide.

The effect of increasing the concentration of a pure electrolyte has been studied for sulfuric acid, sodium hydroxide and six different salts. In these determinations, 100 milliliters of distilled water were put into the electrolyzing beaker, a measured volume of the salt solution was added and the amperage adjusted. When the readings were constant, more of the same solution was added and the voltage read again. The results of these determinations are shown in Figures 15, 16, 17, 18, 19, 20, 21, and 22. In every case there is a very high overvoltage when the concentration of the solution is very low. With increasing concentration the overvoltage drops very rapidly at first and then more slowly.

In addition to the graphical presentation of the data three tables have been included. These are typical data sheets, selected from each of the three conditions under which overvoltages were measured, namely, the addition of a salt to sulfuric acid, the addition of a salt to sodium hydroxide, and the addition of a salt to water. Table I was obtained by adding sodium acetate to sulfuric acid, Table II by adding sodium phosphate to sodium hydroxide, and Table III by adding sodium sulfate to water. These same results are shown graphically in Figures 5, 13, and 17, respectively. The first column of each table indicates the milliliters of salt solution added to 100 milliliters of the original electrolyte or water.

Each of the other columns gives the overvoltage values at a different amperage. Each vertical column shows the effect of increasing the concentration of the salt at that current. Horizontally the effect of increasing the current at any given concentration is given.

TABLE I

Addition of 1 Molar Sodium Acetate to 100 Milliliters of 0.1 N Sulfuric Acid

Milli-liters added	Overvoltage at 5 milli-amperes	at 10 milli-amperes	at 15 milli-amperes	at 20 milli-amperes	at 30 milli-amperes	at 50 milli-amperes
0	0.555	0.688	0.822	0.946	1.206	1.318
1	0.566	0.701	0.845	0.980	1.259	1.402
2	0.576	0.730	0.873	1.010	1.317	1.491
3	0.588	0.747	0.902	1.052	1.376	1.596
4	0.601	0.769	0.930	1.065	1.450	1.701
5	0.619	0.796	0.965	1.127	1.538	1.851
6	0.635	0.821	1.005	1.197	1.636	2.088
7	0.654	0.855	1.057	1.279	1.775	2.371
8	0.678	0.892	1.124	1.357	1.924	2.577
9	0.712	0.948	1.224	1.462	2.194	2.732
10	0.761	1.012	1.310	1.547	2.230	2.824
11	0.795	1.045	1.325	1.552	2.310	2.875
12	0.768	1.014	1.283	1.513	2.250	2.654
13	0.741	0.980	1.238	1.462	2.204	2.653
14	0.735	0.970	1.229	1.420	2.159	2.553
15	0.730	0.959	1.221	1.415	2.154	2.548
17	0.722	0.942	1.199	1.377	2.003	2.462
20	0.708	0.914	1.125	1.331	1.983	2.339
25	0.682	0.872	1.065	1.254	1.833	2.233
30	0.669	0.849	1.032	1.211	1.788	2.115
35	0.664	0.833	1.006	1.182	1.687	2.042
40	0.656	0.817	0.972	1.147	1.661	1.970
50	0.651	0.812	0.960	1.126	1.628	1.892

TABLE II

Addition of 0.5 Molar Sodium Phosphate to 100 Milliliters of 0.1 N Sodium Hydroxide

Milliliters added	Overvoltage					
	at 5 milliamperes	at 10 milliamperes	at 15 milliamperes	at 20 milliamperes	at 30 milliamperes	at 50 milliamperes
0	0.366	0.515	0.625	0.724	0.880	1.199
1	0.366	0.515	0.623	0.720	0.878	1.192
2	0.366	0.515	0.622	0.719	0.874	1.177
3	0.366	0.514	0.621	0.715	0.867	1.158
4	0.366	0.511	0.617	0.711	0.860	1.141
5	0.366	0.510	0.616	0.701	0.853	1.134
6	0.366	0.509	0.610	0.700	0.847	1.120
7	0.366	0.508	0.609	0.697	0.836	1.109
8	0.364	0.506	0.606	0.694	0.832	1.100
9	0.364	0.505	0.602	0.690	0.829	1.076
10	0.364	0.503	0.601	0.687	0.821	1.068
11	0.364	0.502	0.598	0.682	0.819	1.068
12	0.364	0.500	0.595	0.681	0.814	1.062
13	0.364	0.500	0.593	0.678	0.810	1.055
14	0.364	0.499	0.591	0.677	0.807	1.048
15	0.364	0.498	0.589	0.675	0.806	1.041
17	0.364	0.495	0.587	0.670	0.794	1.024
20	0.363	0.490	0.583	0.664	0.792	1.014
25	0.363	0.489	0.577	0.658	0.772	1.000
30	0.361	0.488	0.573	0.643	0.768	0.975
35	0.361	0.485	0.570	0.648	0.758	0.965
40	0.360	0.484	0.567	0.644	0.750	0.959
50	0.360	0.482	0.565	0.635	0.745	0.936

TABLE III

Addition of 1 Molar Sodium Sulfate to 100 Milliliters of Water

Milliliters added	Overvoltage at 5 milliamperes	at 10 milliamperes	at 15 milliamperes	at 20 milliamperes	at 30 milliamperes	at 50 milliamperes
1	1.354	1.989	-----	-----	-----	-----
2	0.993	1.433	1.931	2.206	-----	-----
3	0.890	1.221	1.597	1.827	2.316	-----
4	0.833	1.113	1.389	1.610	2.034	-----
5	0.797	1.049	1.291	1.476	1.929	-----
6	0.775	0.999	1.215	1.384	1.684	2.271
7	0.761	0.968	1.162	1.312	1.582	2.120
8	0.746	0.941	1.117	1.258	1.499	1.988
9	0.737	0.921	1.085	1.216	1.444	1.898
10	0.730	0.905	1.053	1.179	1.400	1.816
11	0.729	0.891	1.041	1.156	1.362	1.746
12	0.724	0.881	1.017	1.135	1.322	1.693
13	0.719	0.873	1.001	1.116	1.294	1.644
14	0.716	0.861	0.991	1.096	1.267	1.598
15	0.714	0.853	0.977	1.079	1.246	1.572
17	0.707	0.843	0.960	1.055	1.211	1.509
20	0.700	0.828	0.934	1.027	1.167	1.437
25	0.691	0.813	0.909	0.994	1.121	1.358
30	0.689	0.804	0.892	0.973	1.086	1.309
35	0.684	0.786	0.887	0.955	1.063	1.269
40	0.680	0.782	0.866	0.941	1.044	1.238
50	0.676	0.776	0.851	0.924	1.018	1.197

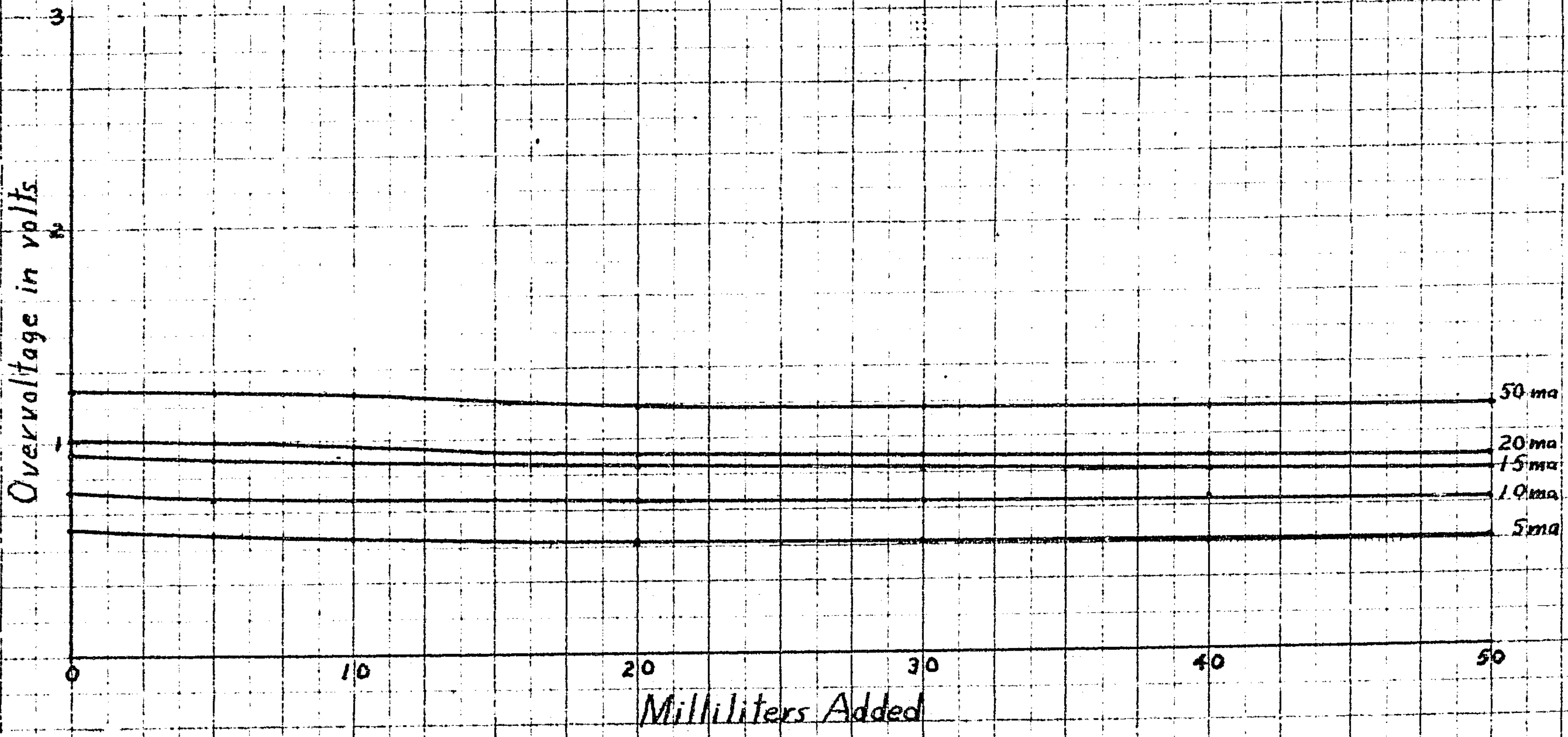

Figure I

1 Molar Sodium Sulfate Added to 100 ml. of 0.1 N. Sulfuric Acid

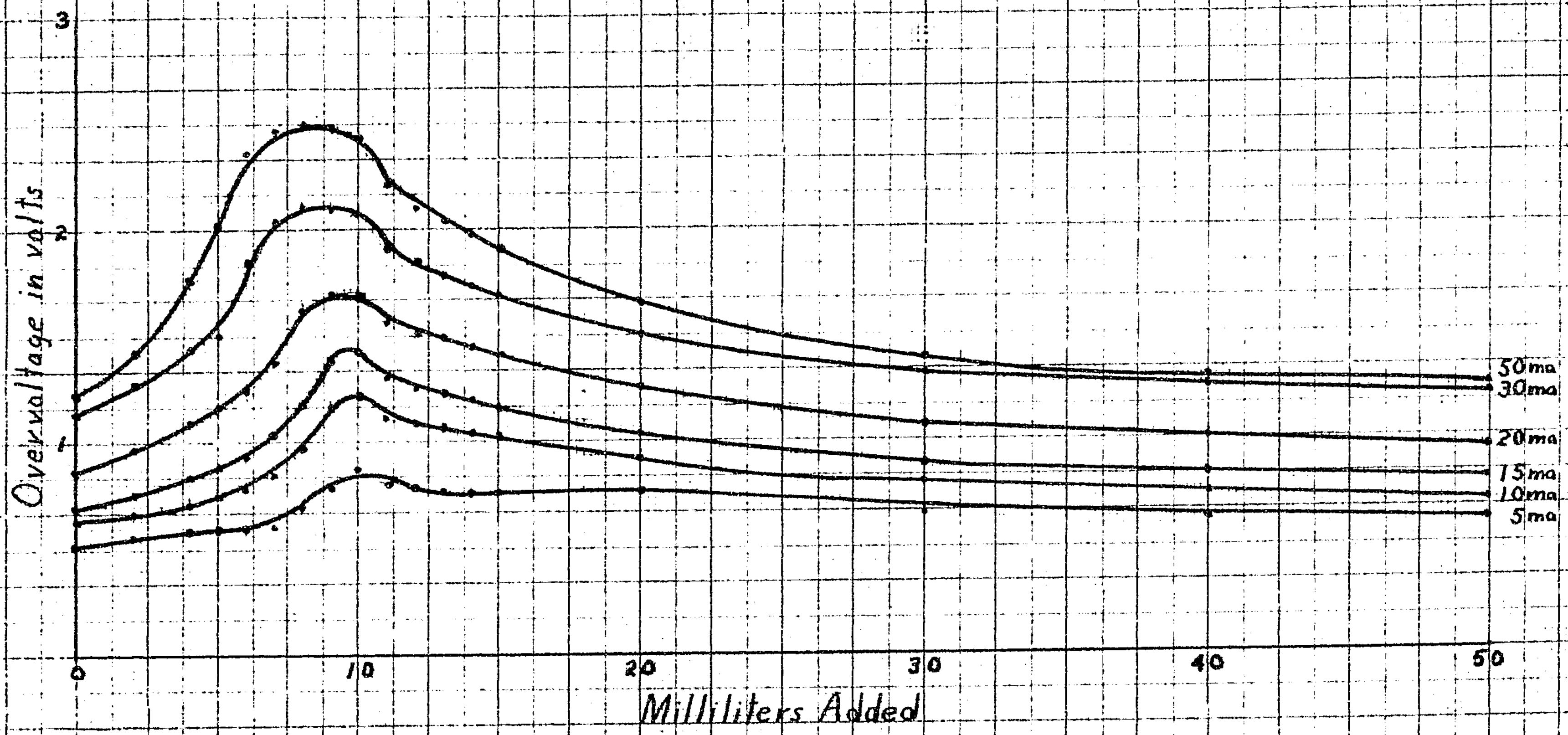

Figure 2

0.5 Molar Sodium Phosphate Added to 100 ml. of 0.1 N Sulfuric Acid

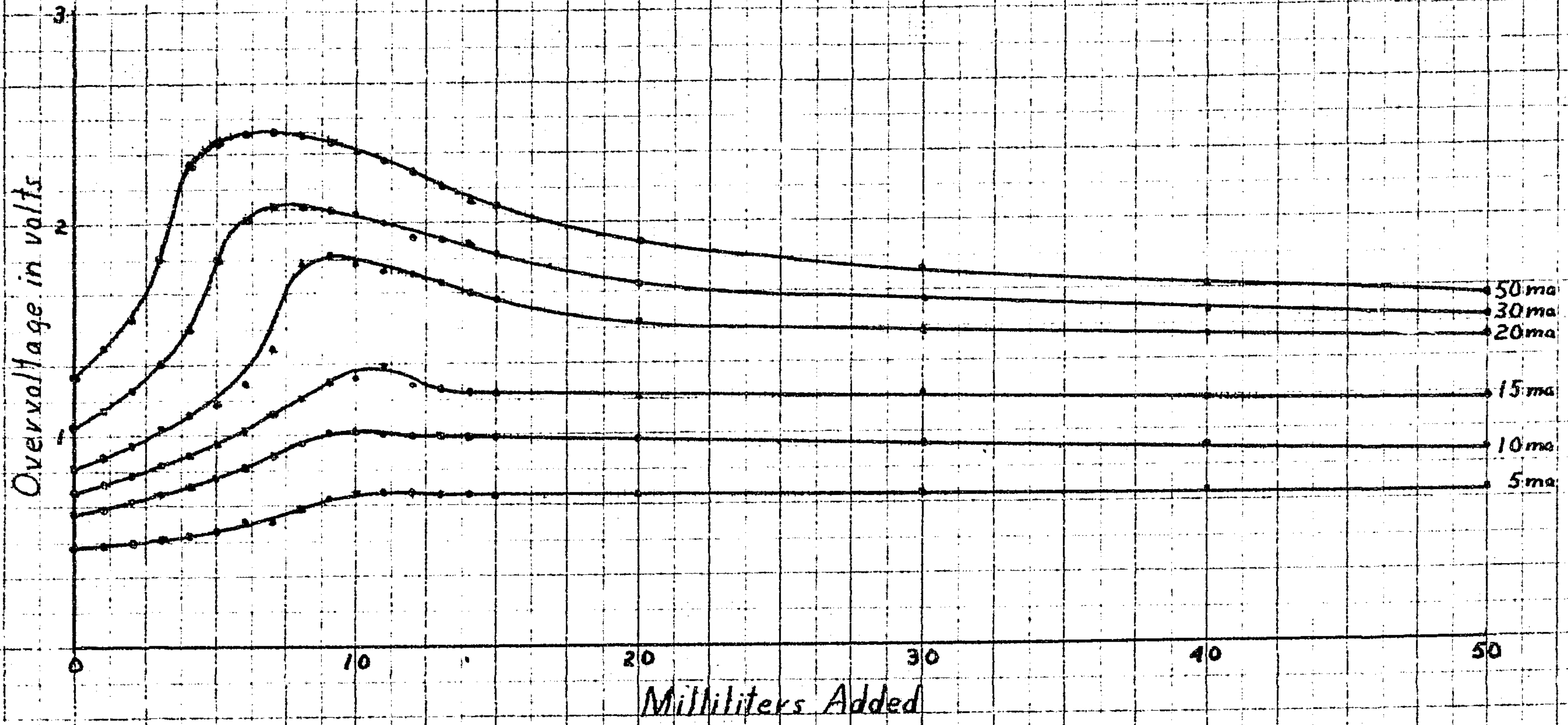

Figure 3

1 Molar Potassium Oxalate Added to 100 ml. of 0.1 N Sulfuric Acid

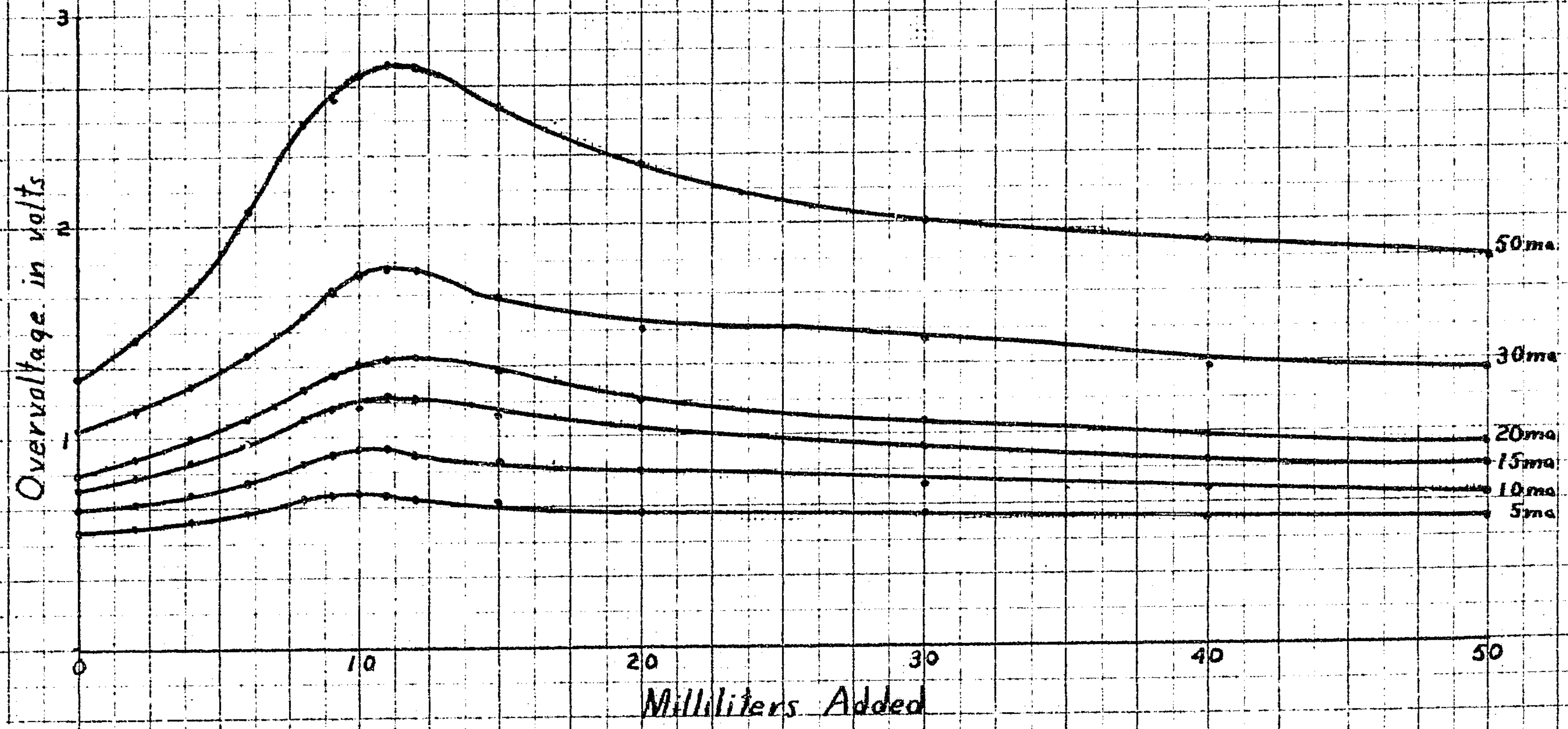

Figure 4

I Molar Sodium Formate Added to 100 ml. of 0.1 N Sulfuric Acid

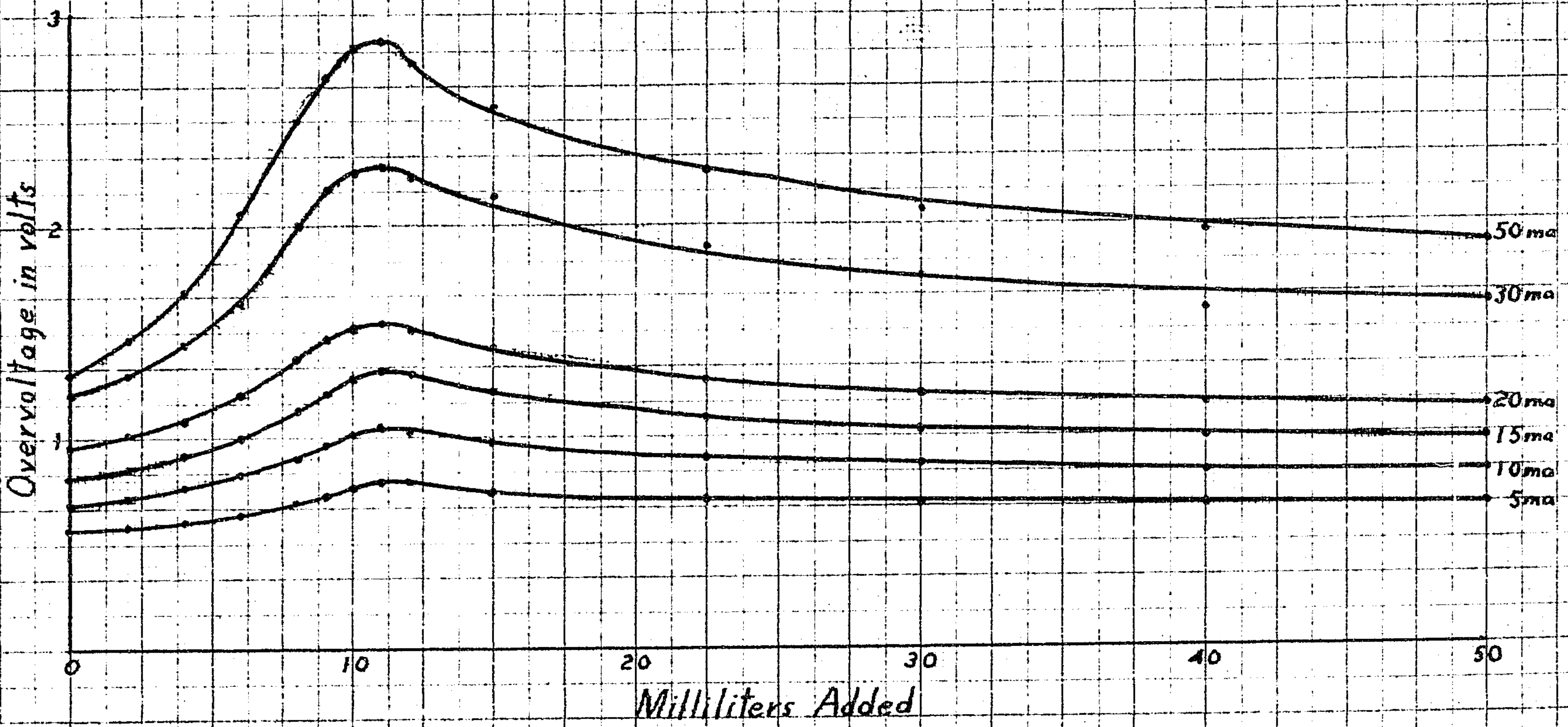

Figure 5

1 Molar Sodium Acetate Added to 100 ml of 0.1 N Sulfuric Acid

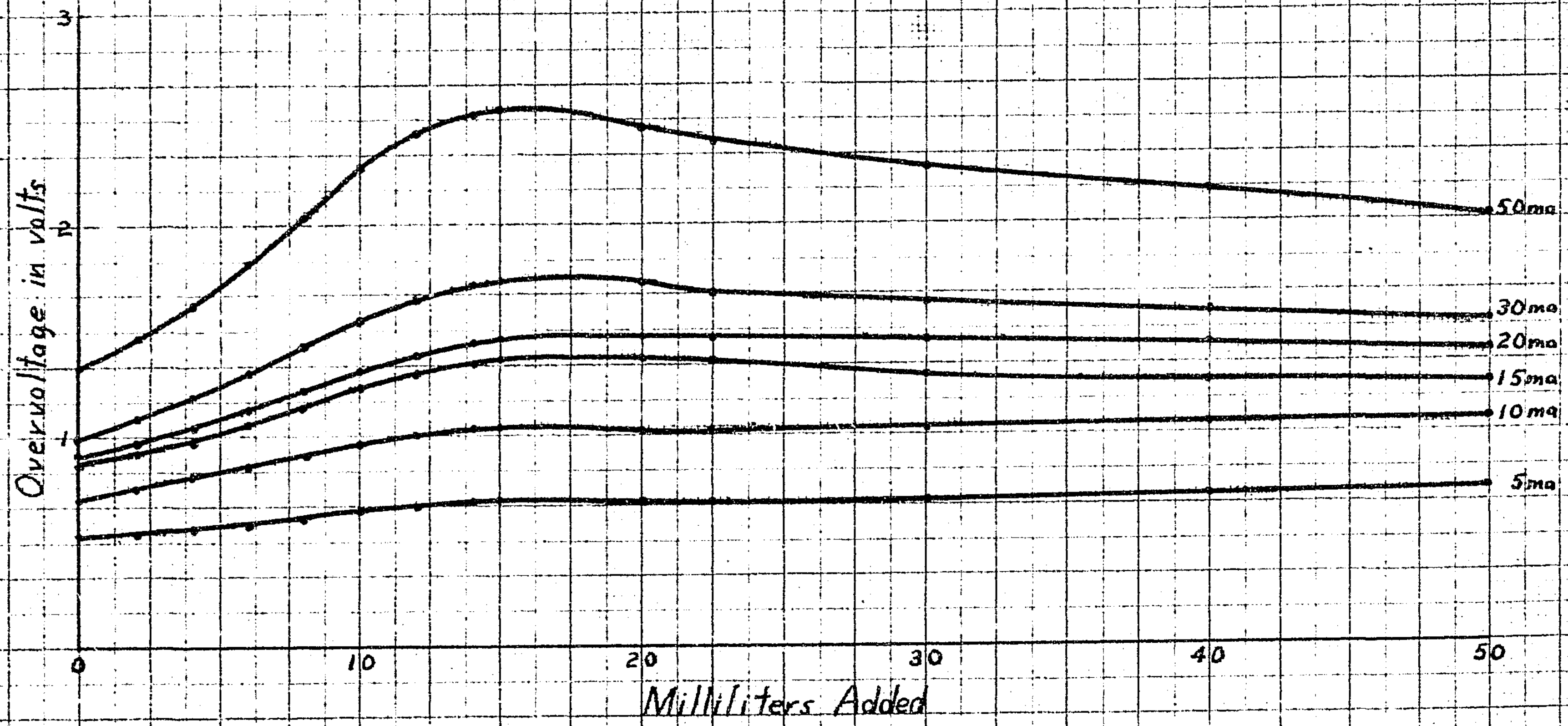

Figure 6

1 Molar Sodium Fluoride Added to 100 ml. of 0.1 N Sulfuric Acid

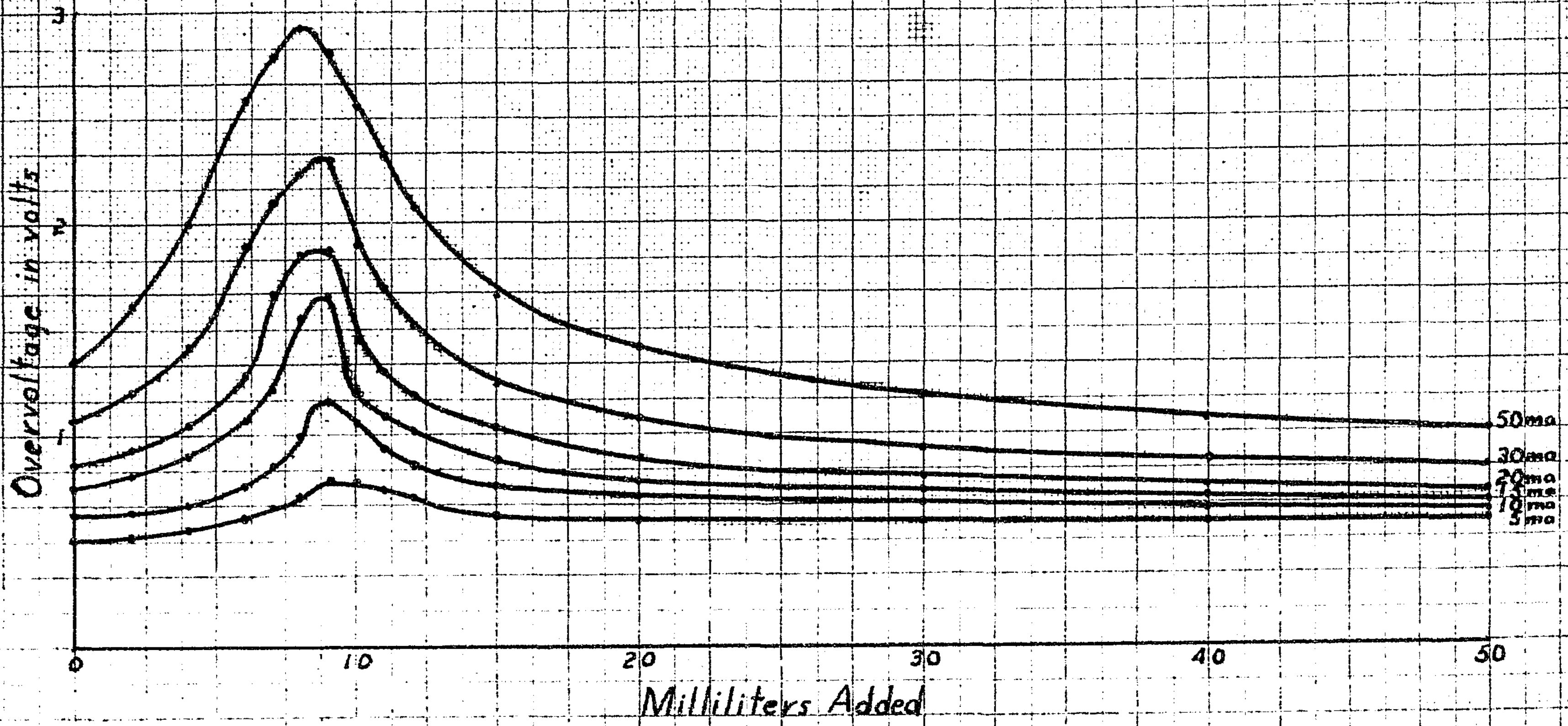

Figure 7

1 Molar Sodium Hydroxide Added to 100 ml. of 0.1 N Sulfuric Acid

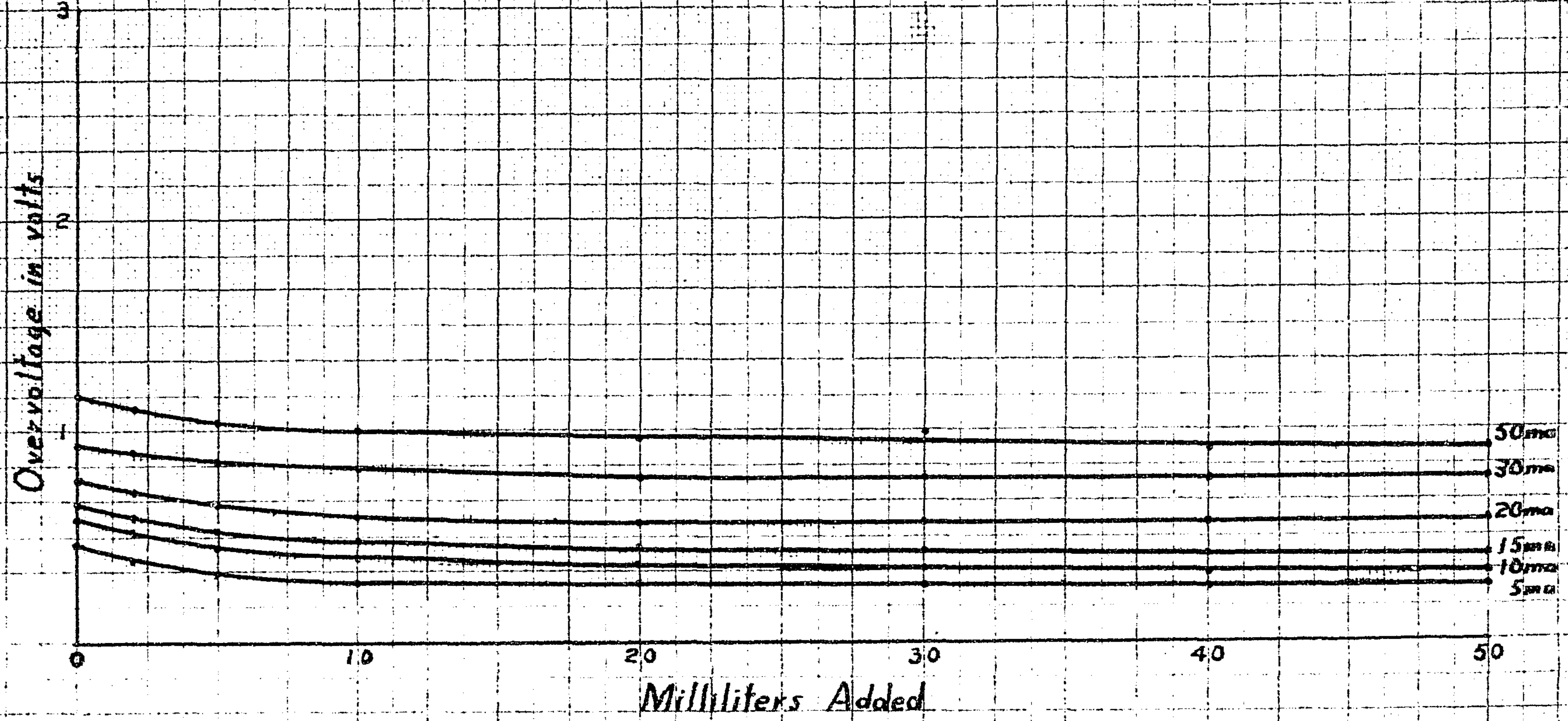

Figure 8

1 Molar Sodium Nitrate Added to 100 ml. of 0.1 N Sulfuric Acid

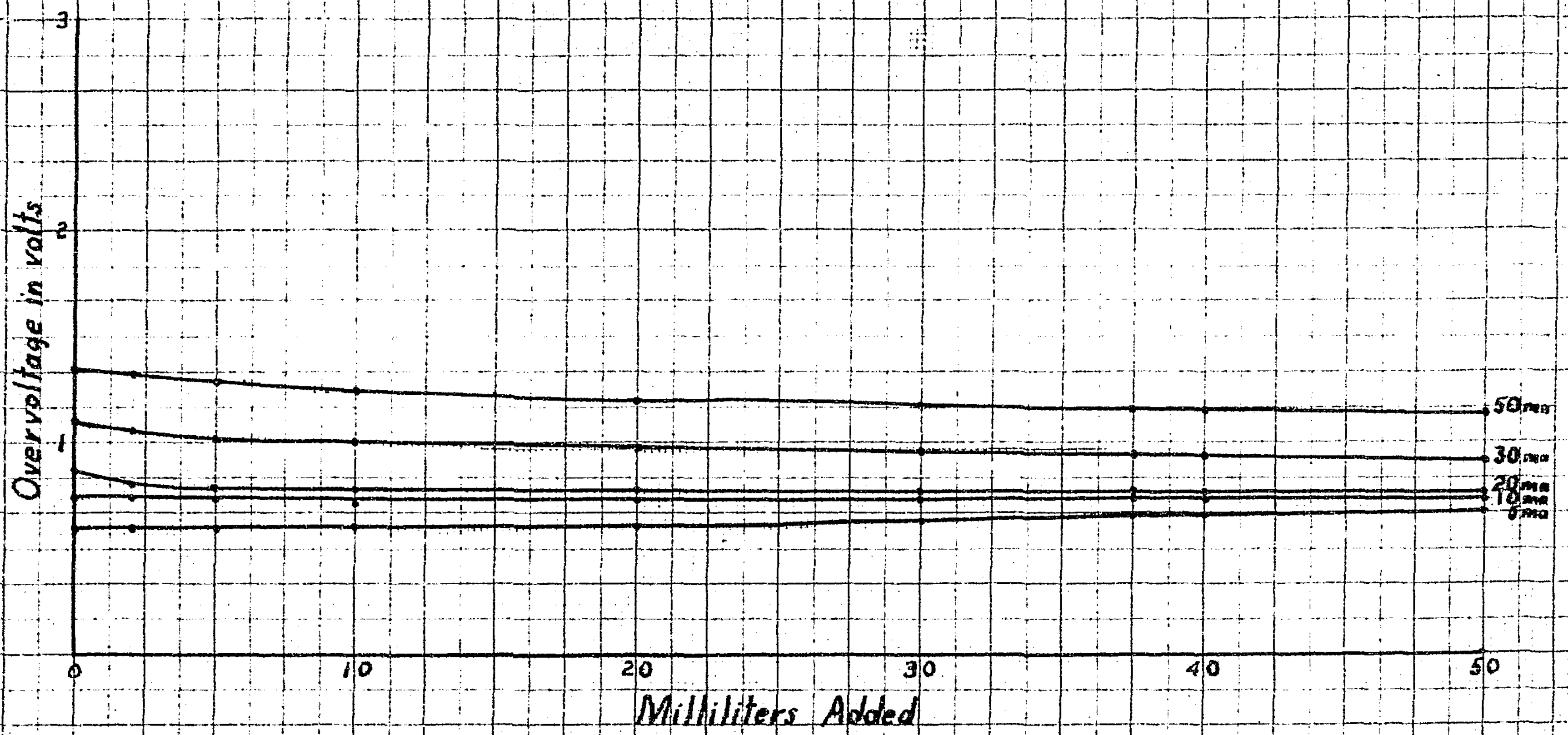

Figure 9

1 Molar Sodium Chlorate Added to 100 ml. of 0.1 N Sulfuric Acid

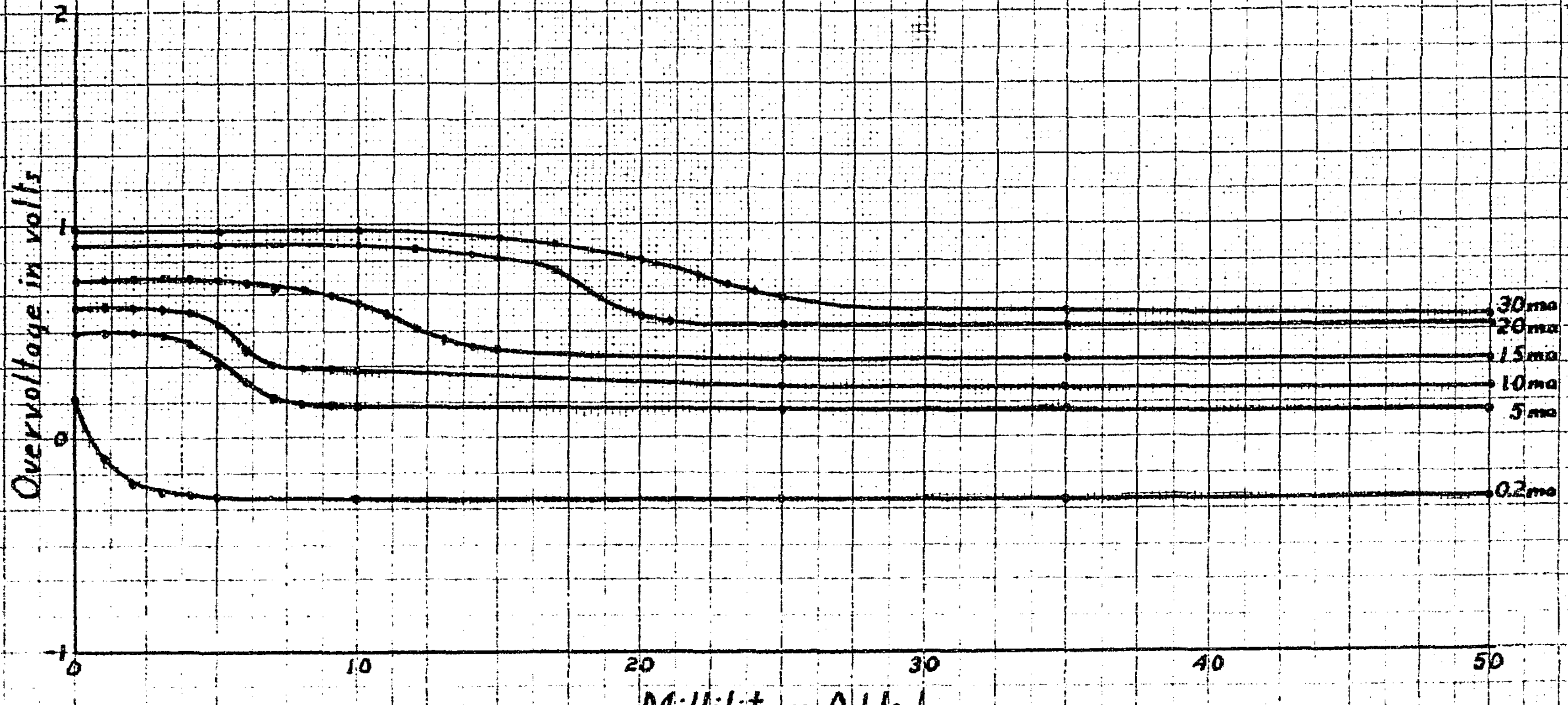

Figure 10

I Molar Sodium Dichromate Added to 100 ml. of 0.1 N Sulfuric Acid

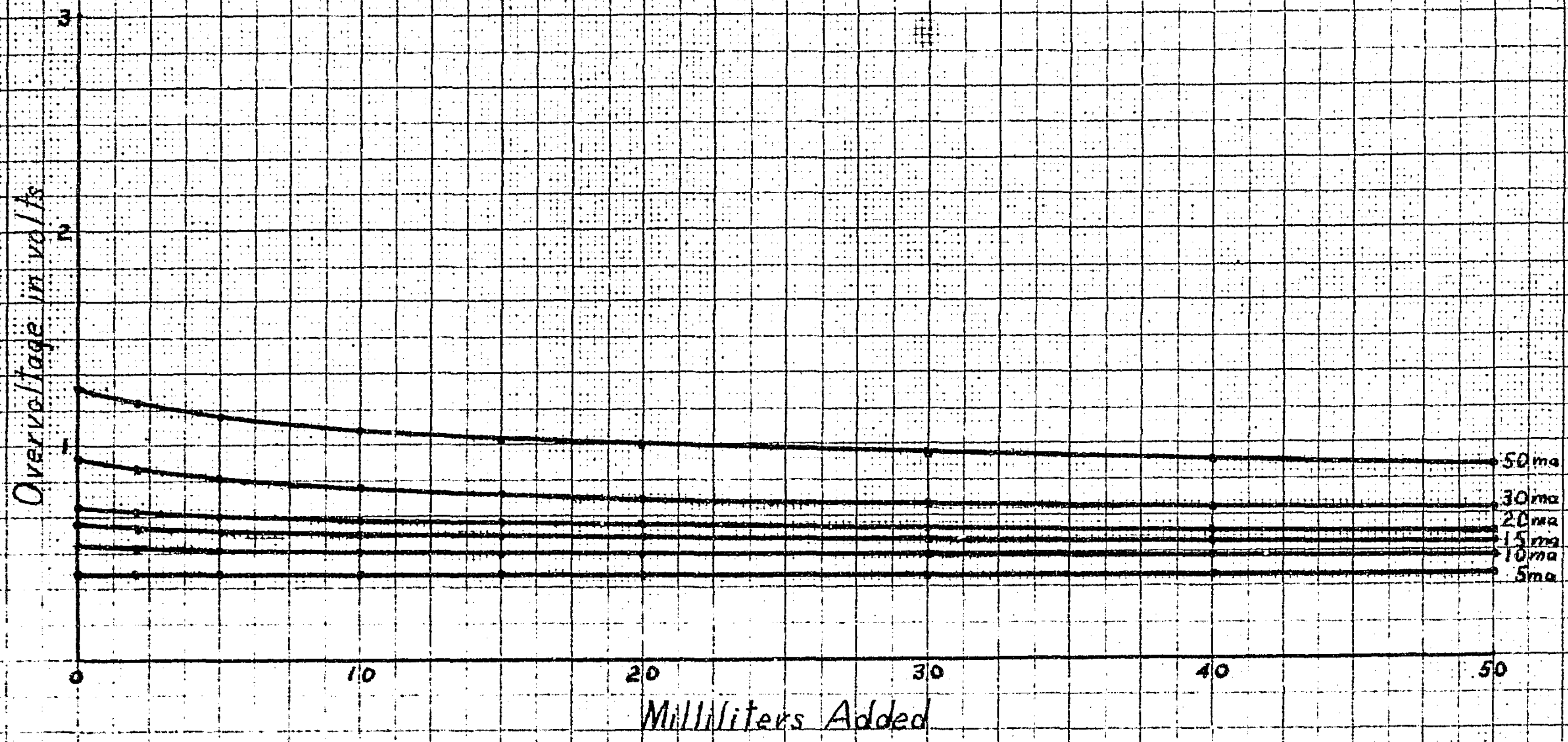

Figure 11

1 Molar Sodium Sulfate Added to 100 ml of 0.1 N Sodium Hydroxide

Figure 12

I Molar Potassium Oxalate Added to 100 ml. of 0.1 N Sodium Hydroxide

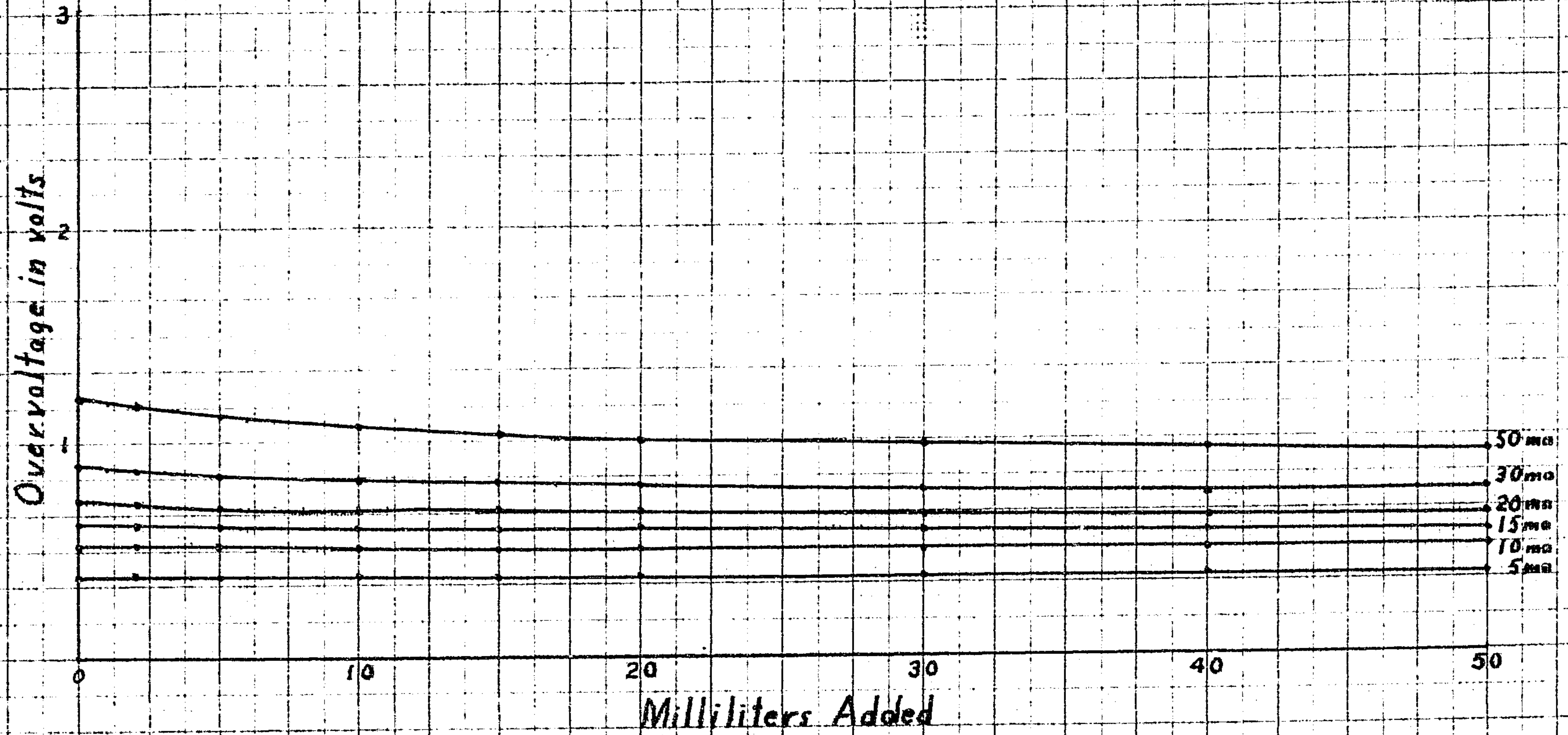

Figure 13

0.5 Molar Sodium Phosphate Added to 100 ml. of 0.1 N Sodium Hydroxide

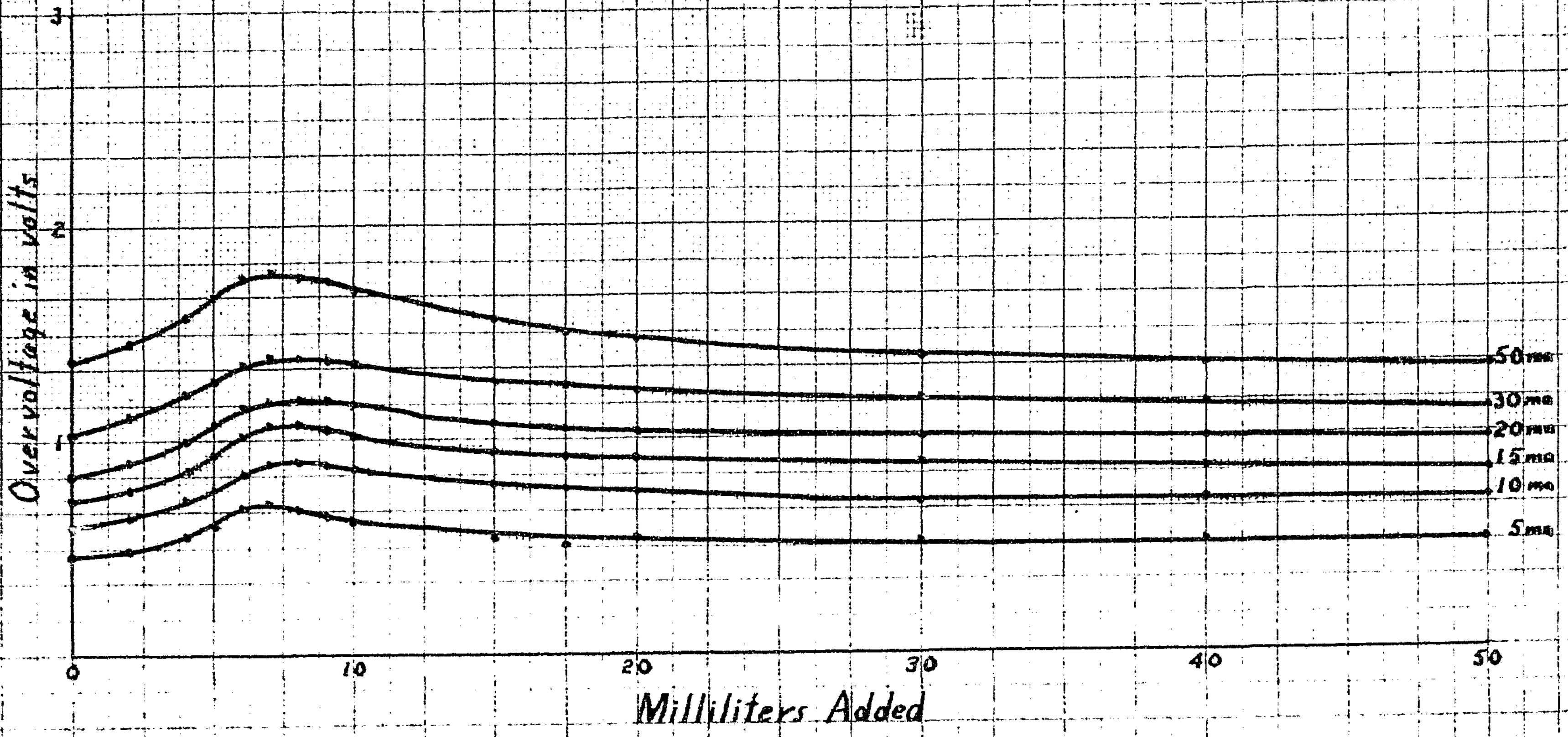

Figure 14

I Molar Sodium Dichromate Added to 100 ml. of 0.1 N Sodium Hydroxide

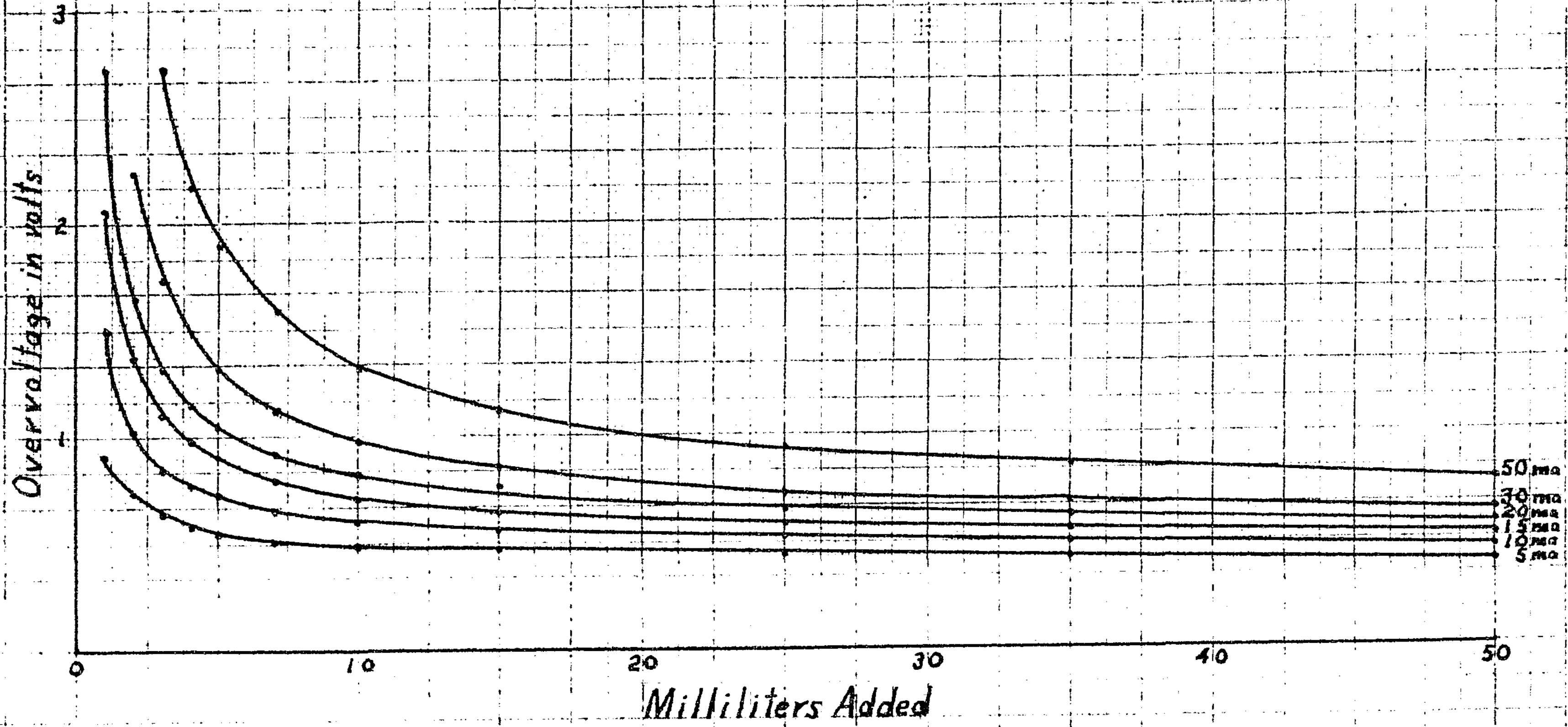

Figure 15

1 N Sulfuric Acid Added to 100 ml. of Water

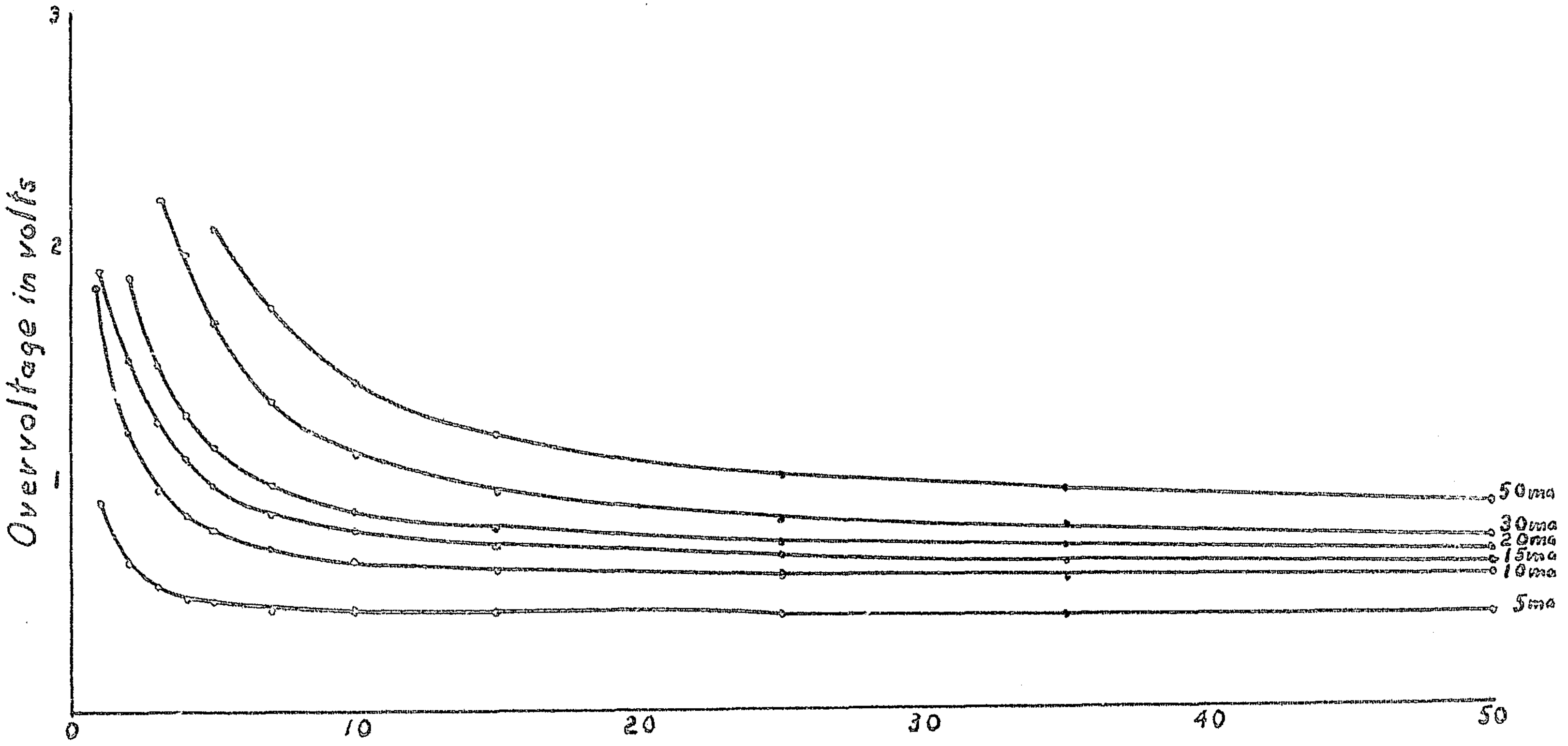

Figure 16

1 Molar Sodium Hydroxide Added to 100 ml. of Water

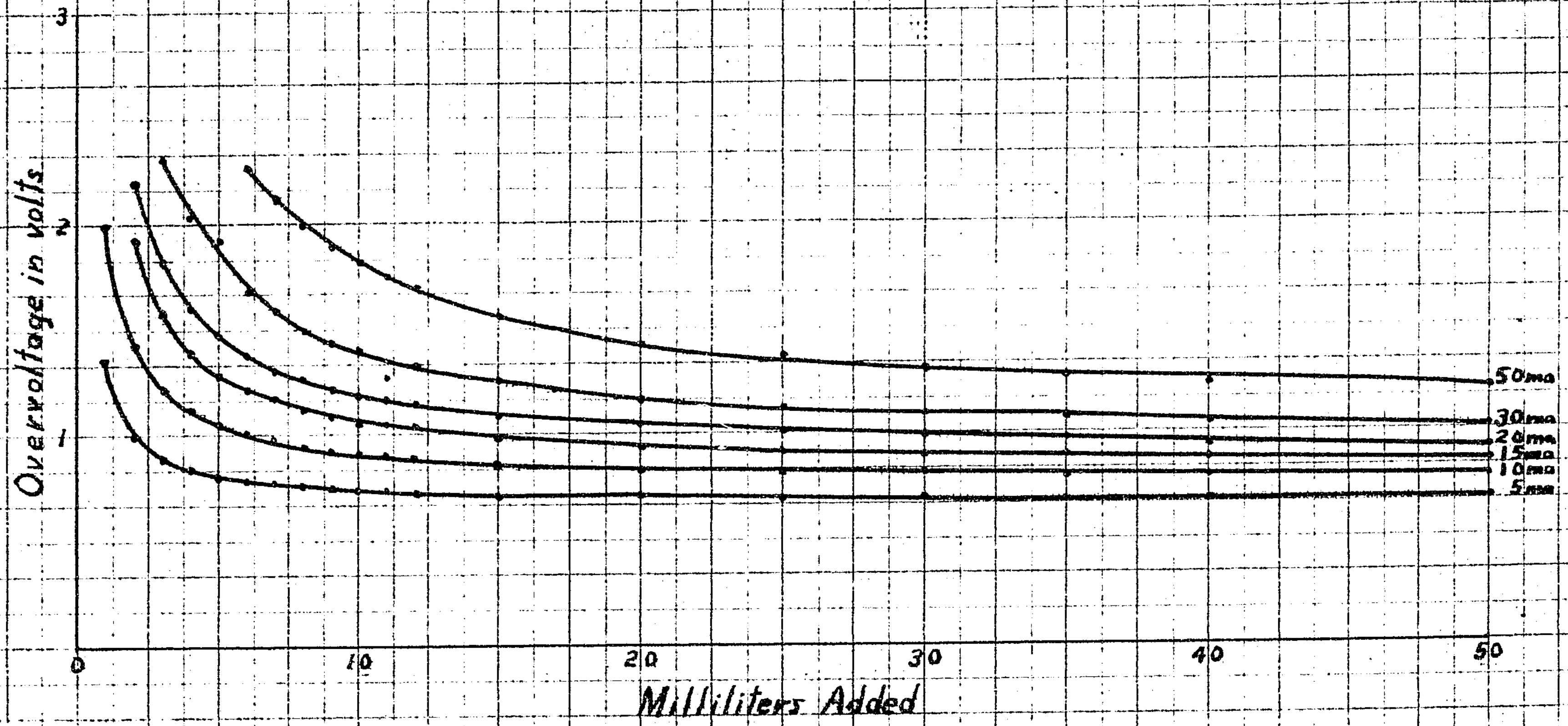

Figure 17

1 Molar Sodium Sulfate Added to 100 ml. of Water

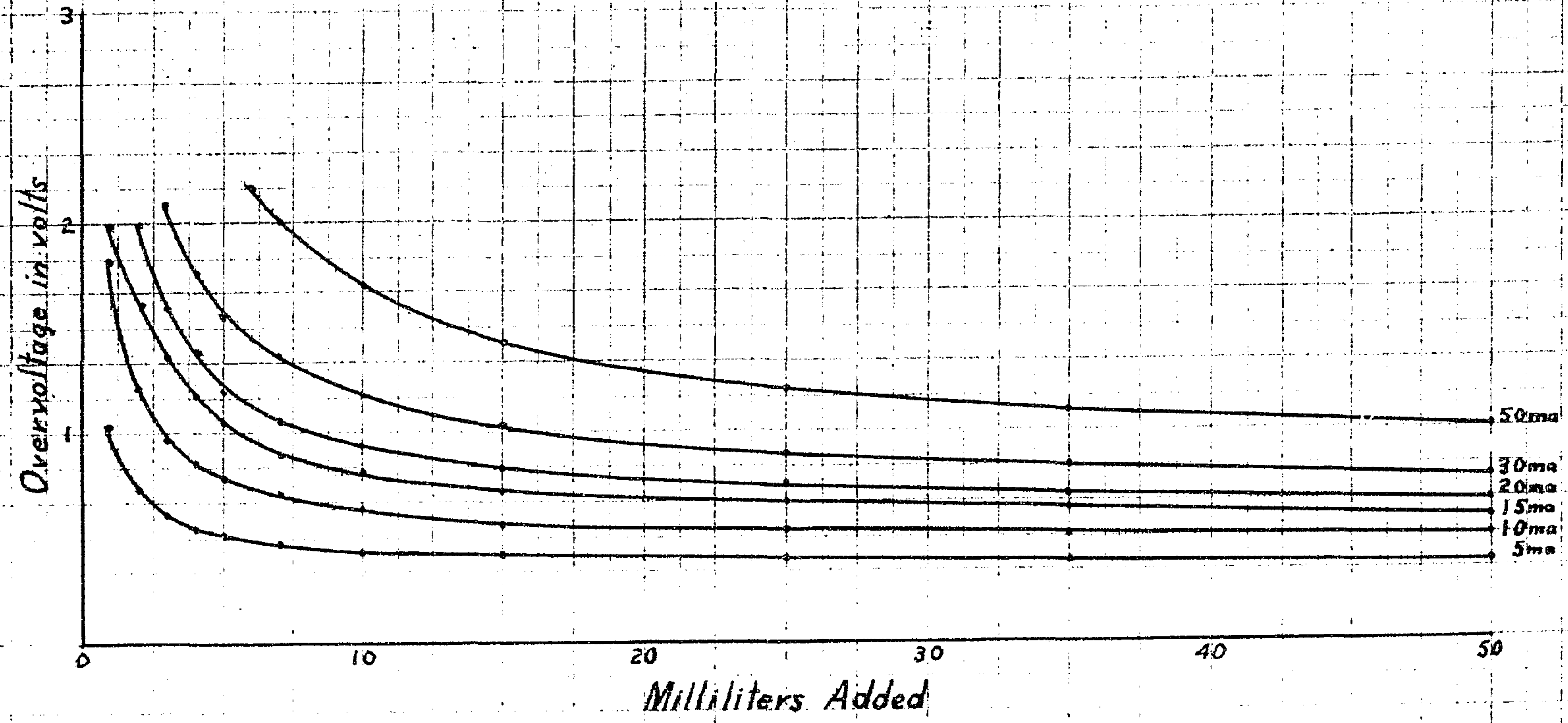

Figure 18

0.5 Molar Sodium Phosphate Added to 100 ml of Water

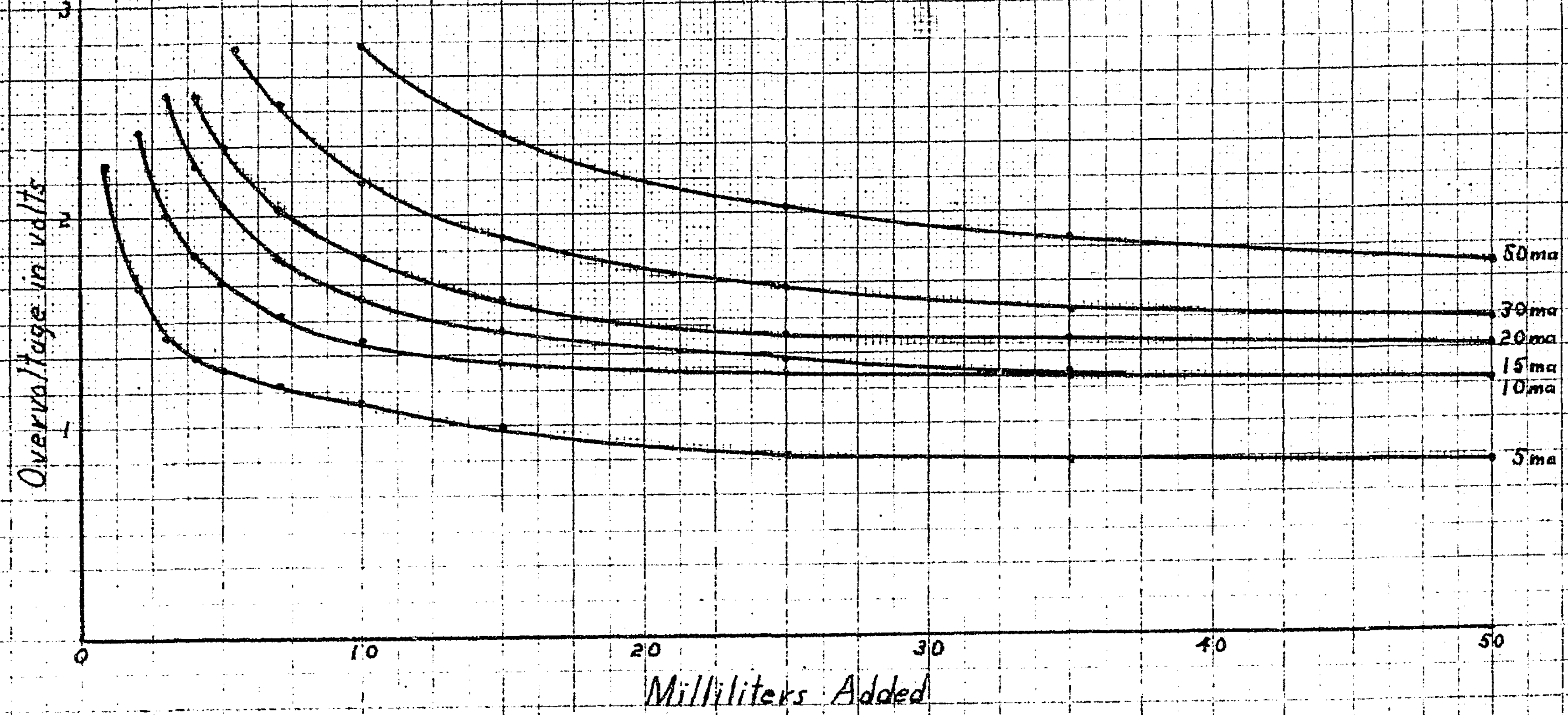

Figure 19

1 Molar Sodium Nitrate Added to 100 ml. of Water

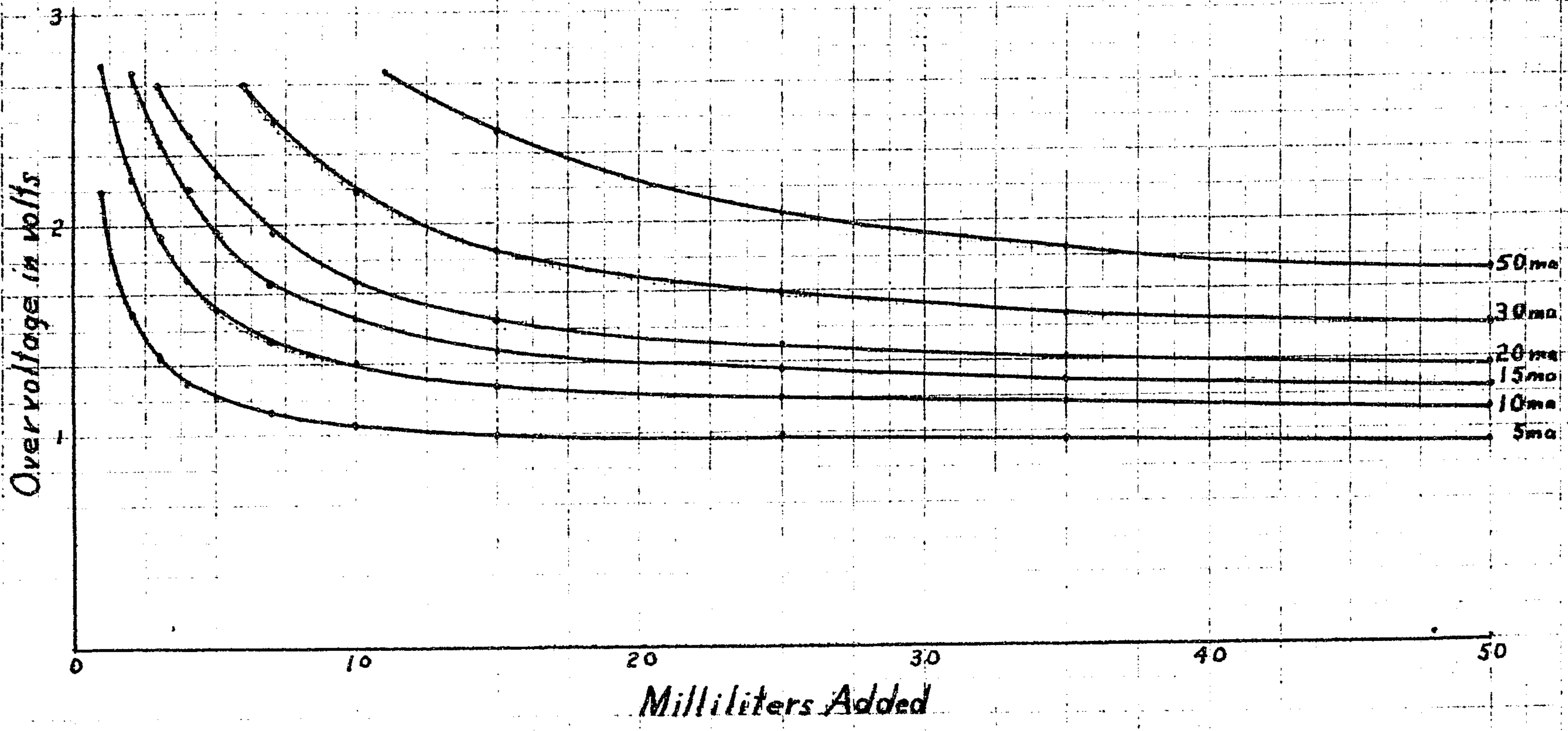

Figure 20

1 Molar Sodium Chlorate Added to 100 ml. of Water

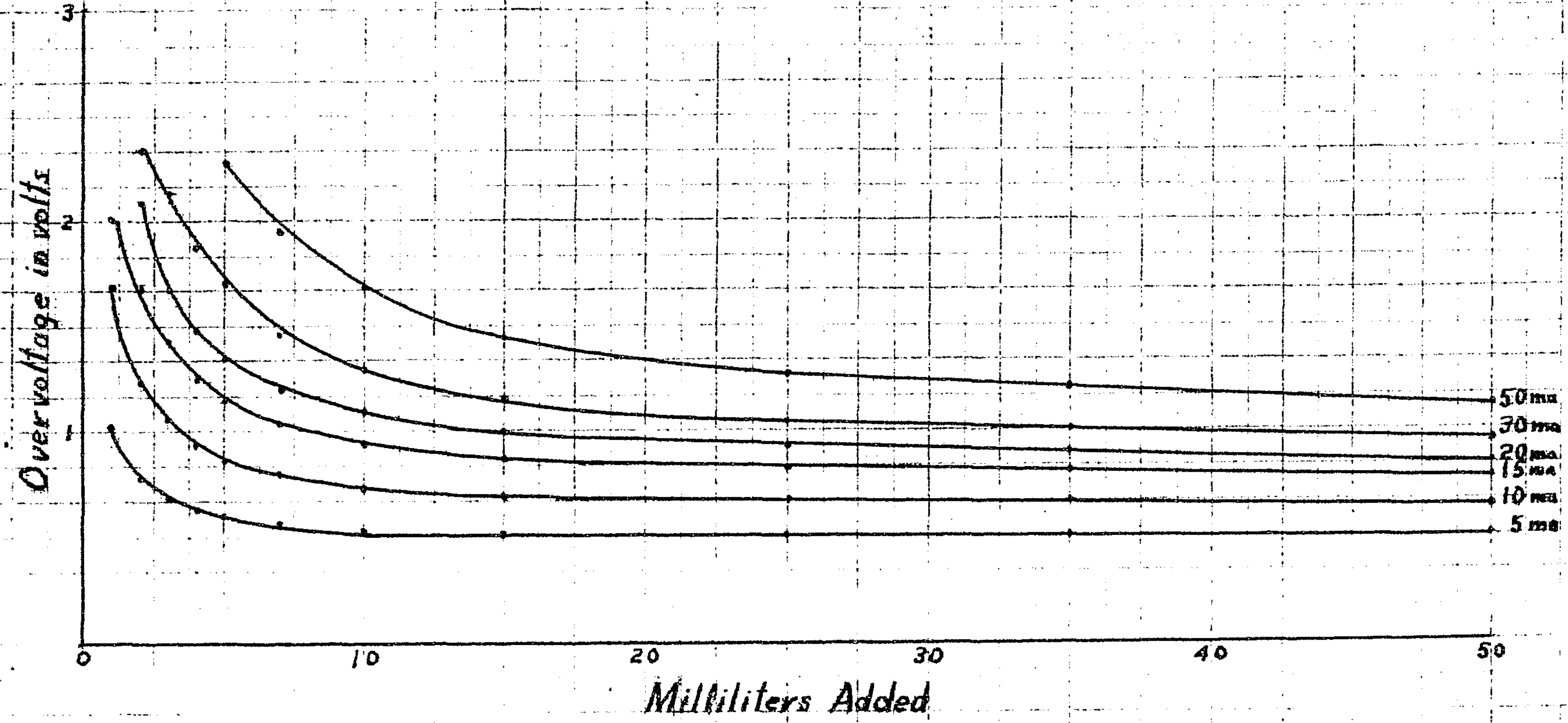

Figure 21

1 Molar Potassium Oxalate Added to 100 ml. of Water

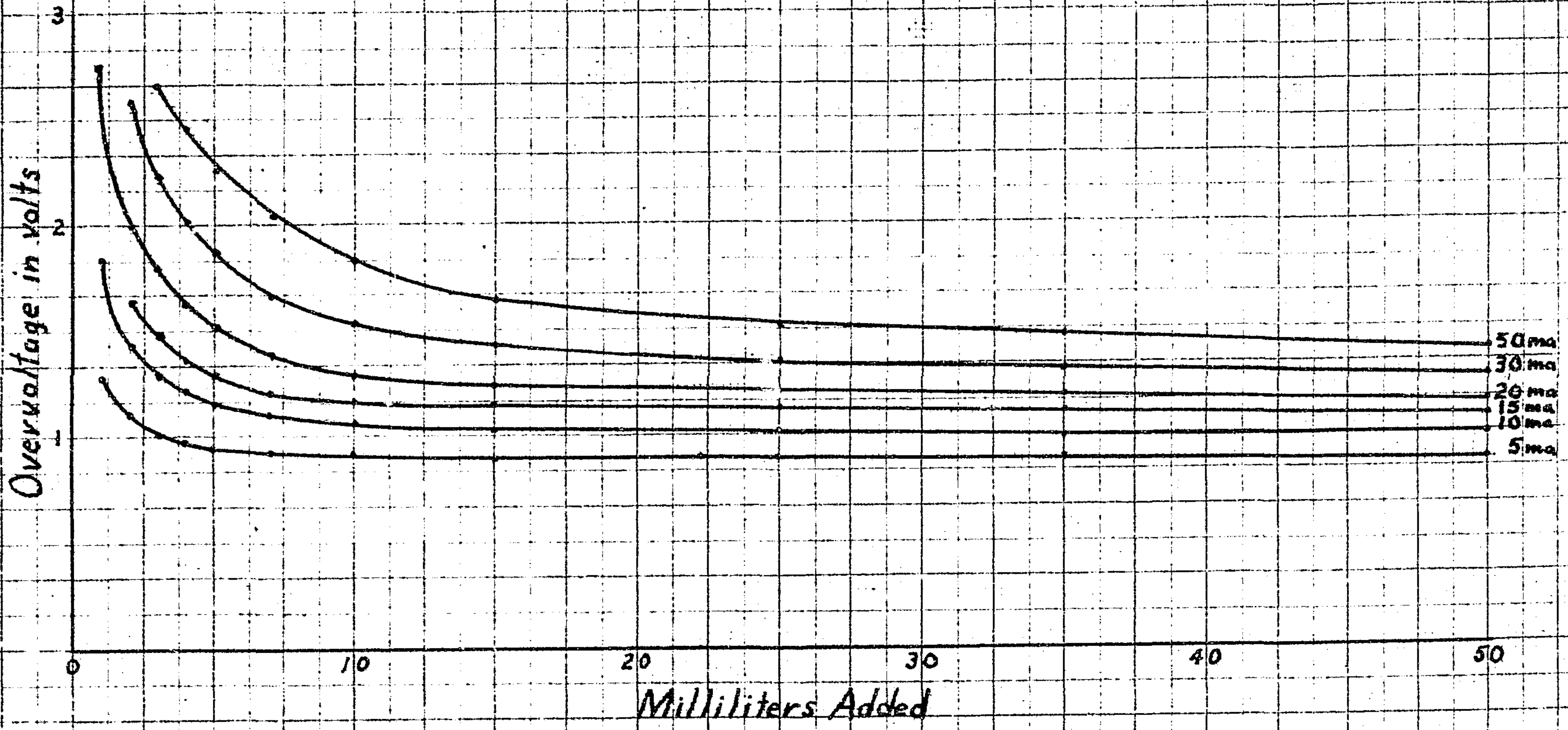

Figure 22

1 Molar Sodium Chromate Added to 100 ml. of Water

IV. DISCUSSION OF RESULTS

It can readily be seen from the results obtained by increasing the concentration of a pure electrolyte, that for the materials studied, there is a direct relationship between the concentration of the solution and the overvoltage. This is true for salt solutions, sulfuric acid, and sodium hydroxide. At low concentrations the overvoltage is high, dropping rapidly at first and then more gradually as the concentration is increased.

An entirely different effect is produced by the addition of basic materials to sulfuric acid solution. In every case of this type there has been a decided increase in overvoltage to a maximum followed by a decrease as the concentration was increased. There are, in all probability, two factors at work producing this effect, namely, (a) reduction of the hydrogen-ion concentration due to neutralization, and (b) increasing the total concentration of the ions in the solution. The first of these two factors should cause an increase in overvoltage and the second should cause it to decrease. At first the effect of neutralization of the acid is more predominant and the overvoltage value increases. This continues until the effect of increasing the concentration of the material being added has the greater effect and causes the readings to drop. The maximum value is in most cases very close to the equivalent point, that is, the point at which the normal concentrations of the material added and the sulfuric acid are the same. This need not be true in all cases. This may occur at any point before the acid had been completely neutralized. After the equivalent point has been passed the effect is the same as increasing the concentration of the solute. In the cases that an acid salt, sodium dichromate, is added to sodium hydroxide, the same two factors are at work. There is an increase at first due to the neutralizing of sodium hydroxide followed by a decrease as the concentration increased.

The addition of neutral sodium sulfate to sulfuric acid produced a gradual lowering of the overvoltage. Since there was no neutralizing effect, the only factor that was producing any change was the increase in the total concentration. Similar results were obtained when neutral salts or salts of weak acids were added to sodium hydroxide solution. The addition of the salt of a weak acid has little effect on the pH of a 0.1 N sodium hydroxide solution; thus the concentration of the solution was the most important factor in these cases.

A striking similarity is seen between the curve produced when a neutral salt of a weak acid was added to sodium hydroxide and to the curve obtained when a salt was added to pure water. The curve obtained in the latter case shows a rapid drop, at concentrations less than 0.1 N, followed by a more gradual lowering of overvoltage. This original rapid drop is not seen when a salt is added to sodium hydroxide, but in this case the concentration of the solution was 0.1 N at the beginning. At corresponding total concentration, however, the curves are very similar.

The addition of oxidizing agents to an acid electrolyte produces a decided drop in the overvoltage. This would indicate that oxidation of hydrogen was taking place at the cathode surface thus decreasing its polarization. The fact that negative values for overvoltage were obtained at low current densities is not at all unreasonable. With no oxidizing agent present hydrogen would be liberated from the electrode in the gaseous form. The extent of polarization of the electrode would be dependent upon the potential necessary to liberate hydrogen in this form. With a strong oxidizing agent, such as the dichromate ion, hydrogen could be oxidized while still in the atomic state. It could in this way be liberated at a lower potential. Very little hydrogen is liberated when the current density is low and a low concentration of the oxidizing agent is sufficient to produce quite a large depolarizing effect. At higher currents hydrogen is liberated more rapidly and a greater concentration of oxidizing agent is required to produce any noticeable depolarization.

V. CONCLUSIONS

1. Hydrogen overvoltage at a nickel electrode is affected by the concentration of the electrolyte. With sulfuric acid, sodium hydroxide, and salt solutions the overvoltage is high in dilute solutions and decreases as the concentration is increased.

2. The addition of salts of weak acids to sulfuric acid causes an increase in overvoltage followed by a decrease as the concentration is further increased.

3. The addition of sodium dichromate, a salt which hydrates to produce an acid, to sodium hydroxide causes an increase in overvoltage followed by a decrease at higher concentrations.

4. Increasing the concentration of a neutral salt, sodium sulfate in sulfuric acid, causes a gradual lowering of the overvoltage.

5. As the concentration of a neutral salt or the salt of a weak acid in sodium hydroxide is increased the overvoltage is lowered.

6. Oxidizing agents in sulfuric acid solution produce a decided lowering of overvoltage.

VI. SUMMARY

1. In this investigation the direct method for determining overvoltage in a number of solutions at a nickel electrode has been used.
2. By adding concentrated solutions of various salts to sulfuric acid, sodium hydroxide, or water, the effect of the presence of salts on the overvoltage of solutions was determined.
3. In acid solution:
    - a. The addition of a neutral salt produced a slight lowering of the overvoltage.
    - b. The addition of a basic material caused an increase in the overvoltage followed by a decrease as the concentration was increased.
    - c. Oxidizing agents caused the overvoltage to be lowered.
4. In sodium hydroxide solution:
    - a. The addition of a neutral salt or salt of a weak acid caused a slight lowering of the overvoltage.
    - b. The addition of sodium dichromate caused the overvoltage to rise followed by a lowering as the concentration was further increased.

5. At low concentrations of sulfuric acid, sodium hydroxide, or a salt in pure water, the overvoltage is very high. The value drops very rapidly at first and then more slowly as the concentration of the solute is increased.

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