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EFFECT OF STRESS ON ELECTROLYTIC SOLUTION POTENTIAL.

A thesis submitted in partial
fulfilment of the requirements
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in
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EFFECT OF STRESS ON ELECTROLYTIC
SOLUTION POTENTIAL.

by

Basil McDonnell

ABSTRACT

Uni-directional stresses have been applied to copper wires, and the potential difference between such wires and unstressed wires determined in various electrolytes. The potential differences have been determined both by a galvanometer method and potentiometrically. The latter method gave more consistent results and is thought to eliminate some of the possibilities of polarization. Some correlation has been found between the amount of applied stress and the potential difference observed, and thermodynamic arguments have been advanced to explain such results, at least qualitatively. A correlation of these same results with time has led to the conclusion that the potential difference is essentially due to a surface effect.

Approved

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Effect of Stress on Electrolytic Solution Potential.

I INTRODUCTION.

The presence of stress affects the electrochemical corrosion of most metals (1). Stress may influence corrosion by creating potential differences between stressed and unstressed parts of a metal. These potential differences can cause localized attack by galvanic currents.

To further the understanding of corrosion this investigation that is reported here was to measure the effect of stress on the electrolytic solution potential of copper. Because of bearing on the results reported here, the work of other experimenters will be outlined. But first the theoretical basis for assuming that stress changes the potential of a metal will be discussed.

II THEORY

Walker and Dill (2) suggested that work done on a metal would be available as potential energy, and that work done on a metal electrode increases the chemical potential, making the metal more electronegative. The European and N.B.S. Convention

is used so that more electronegative means

1. a greater tendency for the metal to form ions
2. the metal is less noble
3. the metal is more anodic.

When a tensile force that is less than the elastic strength of the metal is applied to a metal electrode the work done will be

$$W = \frac{10^{-7}\ T^2}{2Y} \text{ Joules}$$

where W = work done
Y = modulus of elasticity
T = tension in dynes.

Since joules are equal to volt-coulombs, it was suggested by Walker and Dill (2) and by Miniato (3) that the potential change would be

$$E = \frac{10^{-7}\ T^2\ M}{2Y\rho n F} \text{ volts}$$

where E = Potential change, volts
ρ (rho) = density of the metal, gram/cm^3
M = molecular weight of the metal
n = equivalents formed per gram-mole when the metal enters solution
F = coulombs/equivalent.

Then a tension of 1 kg on 24 British Standard Gauge (S.W.G.) copper wire would produce a potential change of 2.46×10^{-7} volts. However, it is not theoretically possible to associate internal energy directly with chemical potential.

The reversible electrode potential of a metal can be related to the free energy. Consider a metal

M in a solution of a salt of the metal as a part of a reversible electrochemical cell. If E is the single electrode potential and ΔG is the change of free energy in the reaction

$$M \rightleftharpoons M^{+n} + n\varepsilon$$

then $-\Delta G = nEF$

where $\Delta G = G_{M^{+n}} - G_M$

G_M = free energy/gm-mole of metal
$G_{M^{+n}}$ = free energy/gm-mole of ion
= quantity of electricity that passes through cell per gm-mole of ion formed.

So to calculate the change of the single electrode potential caused by a mechanical force it is necessary to calculate the change of free energy of the metal (ΔG_M).

When a mechanical force is applied to the electrode the termodynamic properties of the metal will be altered (4). Assume that the metal is homogeneous. Let the electrode have a uniform cross-section of A cm^2 and let the length be L cms. per gram-mole. Apply a longitudinal strain of f dynes. Then for the isolated system of the electrode, considering the process as reversible,

$$đQ = dU - fdL$$

where đQ is the heat entering the system
and dU is the change of internal energy of the system.

Using the thermodynamic identities

$$H = U - Lf$$
$$G = H - TS$$

we can write

$$dG_m = - Ldf - SdT$$

where H is the enthalpy, U is the internal energy, S is the entropy, T is the absolute temperature and G is the free energy of the system. If the process is isothermal,

$$dG_M = - Ldf.$$

If it is assumed that the length remains substantially constant for stresses below the elastic limit,

$$\Delta G_M = - \frac{\bar{L}}{10^7} \int_0^f df = - \frac{\bar{L}\, f}{10^7} \text{ joules.}$$

But $\bar{L} = \dfrac{\text{molecular weight}}{(\text{density})(\text{area})} = \dfrac{M}{\rho A}$

So $\Delta G_M = - \dfrac{fM}{10^7 \rho A}$ joules.

For the reaction $M \rightleftarrows M^{+n} + n\varepsilon$; $-\Delta G = nFE$ when the metal electrode is unstressed. When the electrode is stressed with a tension f, ΔG and E change so that $-\Delta G_f = nFE_f$. Let $\Delta E = E_f - E$ be the change of the single electrode potential caused by the tension f. Then

$$\Delta E = \frac{-(\Delta G_f - \Delta G)}{nF}$$

But $\Delta G = G_{M^{+n}} - G_M$

$$\Delta G_f = G_{M^{+n}} - (G_M + \Delta G_M)$$

$$\Delta G_f - \Delta G = -\Delta G_M = + \frac{M\ f}{10^7 \rho\ A}$$

Therefore $\Delta E = - \dfrac{M\ f}{10^7 \rho\ A}$ volts.

Theoretically the tension on the metal makes it more electropositive. According to this equation a tension of 1 kg. on a reversible electrode of 24 S.W.G. copper wire would make the electrode potential 1.99 mv more electropositive. This has not been observed. However Des Coudres (5) verified a similar equation with a mercury electrode that was under a pressure head.

The properties of metals are not suitable for a simple mathematical treatment of strain effects such as has been used. In particular, metals are usually heterogeneous, and accurate calculations become involved and uncertain (6). A single crystal could be used (7), but would have only slight strength.

III. REVIEW OF PREVIOUS OBSERVATIONS.

There have been many observations and measurements of potential changes produced by stressing metals; there has been little agreement of results.

Andrews (8) measured the change of electrode potential produced in steel by deformation and found that samples elongated 20% and placed in sodium chloride solution were 1 - 19 mv. more electronegative, the amount depending on the type of steel.

Hambuechen (9) tested steel, copper brass, zinc and wrought iron by stressing up to the yield point in ferric chloride solutions. Measurements were made by

the compensation method. In all tests the potential of the metal became more electronegative. With wrought iron samples changes varied from 0.6 to 29 mv.

Walker and Dill (2) in reviewing Andrew's work showed that the potential difference between strained and unstrained steel in sodium chloride solutions depends upon the method of handling and the length of time in the solution. In reviewing Hambuechen's work they showed that the potential changes may not have been caused by straining effects since his samples could not have reached equilibrium with the electrolyte in the time allowed before testing.

Walker and Dill tested steel samples by stressing up to the breaking point in ferrous sulfate solutions and measuring the potential changes against a calomel cell by the potentiometric compensation method. The surface of the sample was prepared by polishing with emery. Below the elastic limit the potential was changed little or not at all. Above the elastic limit the potential was changed electronegatively under load. When the load was removed the potential became slightly more electropositive than it was initially. At the breaking point the potential change was 50 mv. more electronegative at the time of breaking and with time the potential changed toward the initial value.

Measurements of the electode potential at several temperatures and measurements of the temperature of the steel during stressing showed that the potential changes could not be caused by temperature changes, because the temperature coefficient under test conditions was positive and the temperature did not fall during the tests.

Mercia (10) stressed specimens of annealed α-brass in solutions of zinc and copper salts. The surface of the samples was prepared by polishing with emery and etching with nitric acid. The potential changes were measured against a calomel cell using a potentiometric method. Air was excluded by oil on the surface of the electrolyte. He found that the potential changed 0.2 mv. more electronegative when stressed to the elastic limit, and 1.0 mv. more electronegative when stressed to the yield point. The change in potential was not permanent.

Endo and Kamazana (11) conclude from experiments with variously prepared iron samples in a IN. ferrous sulfate solution that the rougher the surface the greater the electrode potential. Electrolytic iron, electrically polished, was 12 mv. more electropositive than iron as deposited, and 6 mv. more electronegative than annealed but unpolished iron.

They also found the effect of slight strain on potential using a single crystal of iron. Strain made the crystal slightly more electropositive. They conclude from potential time curves that the surface of the electrode was partially covered by an invisible film of $Fe(OH)_2$ and $Fe(OH)_3$, whose effect could not be evaluated or eliminated.

Nikitin (12) measured the changes of electrode potentials of samples of copper, silver and iron during deformation in solutions of N/10 copper sulfate, N/10 silver nitrate and N/10 ferrous sulfate respectively. Tests were made with the metal to be stressed as one electrode of the circuit and a small piece of the same sample as the test specimen as an auxiliary electrode. It was shown to be unnecessary to cover the surface of the electrolyte with oil. The potential change increased with the speed of testing. In all tests with copper the potential became more negative. The maximum change was 7 mv. The potential of hard copper changed more than the potential of soft copper. When stressed by continuous tension till rupture the copper became abruptly more electronegative at rupture. After rupture the potential returned toward the initial value rapidly at first and then slowly but did not reach it in ten hours. If the copper deformed by load was left loaded

the electrode potential, after linear dimensions of the sample had ceased to change, began to return to the initial value, at first rapidly and then more slowly. The potential returned toward initial values at the same speed whether the samples were loaded or not loaded. Deformation changed the potential of silver a maximum of 20 mv. positively and changed the potential of iron a maximum of 40 mv. negatively. Nikitin states that potential changes may be attributed to temperature changes since copper and iron show negative potential changes when deformed and have negative temperature coefficients of electrode potential while silver shows positive potential changes when deformed and has a positive coefficient of electrode potential.

Gautam and Jha (13) hung annealed copper wires in a solution of copper sulfate and obaerved the change in the potential difference between the wires when weights were added to one of them. The wires were annealed by heating till red hot and then dipping in methyl alcohol. Measurements were made with a potentiometer. In solutions of N/250 and N/25 copper sulfate, the maximum changes were 6.7 mv. and 2.4 mv. respectively. The strained wire always became more electropositive. After a load of about 1500 kg/sq. cm.

had been added the potential difference was nearly constant to the maximum load of about 1800 kg/sq. cm. When the load was removed the strained wire did not reach its original value.

Evans (14) measured the change of potential with time of samples of mild steel in a solution of N/10 KCl under steady stress. At any time compressive stresses gave more electropositive potentials, and tensile stresses more electronegative potentials, than when the test area was not stressed. The same final potential was reached whether the test area was compressed, extended, not stressed, or subject to alternating stress.

Miniato (3) hung pairs of wires in solutions and added weights to one wire to observe the effect of stress on potential. A galvanometer was used to measure potential differences between the test wires. Stress changed the potential of copper, brass and steel wire in 4% sodium chloride negatively. Generally the potential changed linearly with stress to near the yield point where the potential difference between the wires became constant. The maximum changes of potential as indicated by galvanometer deflections were 1.45 mv. for cold drawn copper under 2700 kg/sq. cm. stress, 0.5 mv. for annealed copper under 400 kg/sq. cm. stress, 1.75 mv. for brass under

2200 kg/sq. cm. stress, and 10 mv. for steel under 2400 kg/sq. cm. stress. Stressing cold drawn copper wires in sodium sulfate and sodium carbonate gave no galvanometer deflections. Potassium chloride solutions gave similar results to sodium chloride solutions. In solutions of cupric chloride, ammonium chloride, and acidic and alkaline sodium chloride, the initial potential differences between copper wires produced off-scale deflections.

IV. APPARATUS AND EXPERIMENTAL PROCEDURES.

Samples of wire to be tested were placed in cells like that shown in Figure 1. The wires were suspended from hooks in the top bar of a four foot square 4 by 4 wooden frame. Scale pans were attached to the wires below the cells to which weights could be added to stress the wires. The wires were insulated from the hooks and pans by bakelite. Electrical connections were made to the wires by screw fastenings and by spring clips which gave good electrical contact between the test wires and the lead wires.

Measurements were made with a galvanometer, with a sensitivity of 0.295 mv./cm. scale reading, and with a Leeds and Northrup K-2 type potentiometer. These instruments were connected to the cells in the way shown in Figure 2.

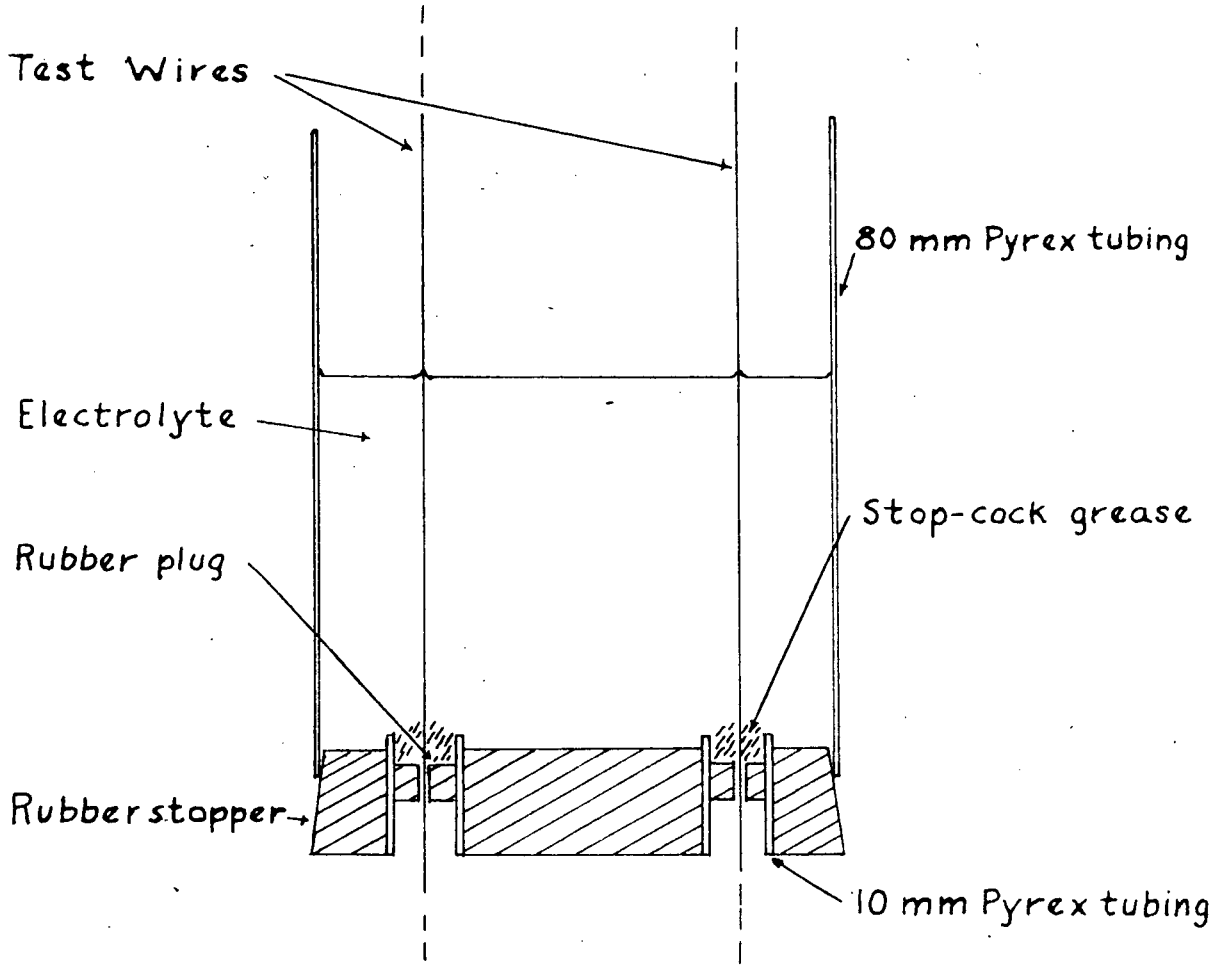

FIGURE 1.
Test Cell in Section

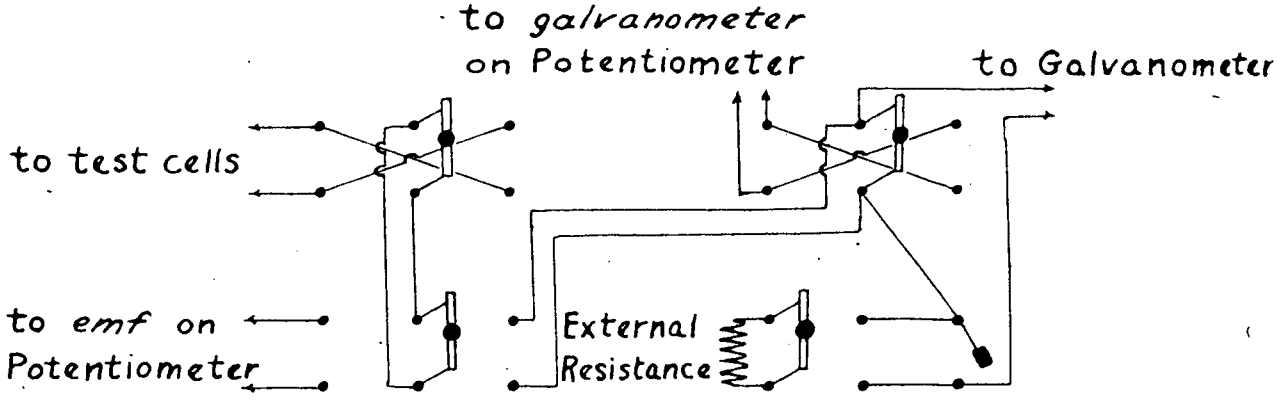

FIGURE 2.
Circuit Diagram

The wires to be tested were first cleaned with ethyl ether. They were then coated with a thin layer of paraffin wax above and below the section to be exposed to the electrolyte and placed in the cell with with sufficient weight suspended to prevent curling. The section exposed was about one centemeter long. Then the electrolyte was poured in the cell. In those tests using a deareated electrolyte , the surface of the electrolyte was covered with a layer of Stanolax, a petroleum oil, one centimeter deep.

The electrolytes were prepared using distilled water. When required the electrolytes were deareated by boiling or by placing under a vacuum of 65 cms. of mercury.

In tests by Miniato's method the lead wires from the cell were connected to the galvanometer. The galvanic current in the cell was shown by the deflection of the galvanometer-mirror's image on the galvanometer scale. The circuit was arranged so that a resistance of 10,000 or 20,000 ohms could be inserted to reduce initial currents that might produce off-scale deflections. Weights were added to the scale pan on one of the wires and the effect of straining this wire on the current in the cell was found by reading the deflection of the image on the

scale. Since the current is caused by potential differences between two wires, changes in the current may indicate changes in the potential difference and so the change in the electrode potentials of the strained wire.

In potentiometric tests the lead wires from the cell were connected to the potentiometer. The potential difference between the two wires in the test cell was thus measured against a standard Weston cell. Weights were added to the scale pan on one of the wires and the effect of straining this wire on the potential difference between the two wires was observed by adjusting the potentiometer to obtain a balance of the potentials in the circuit, and then reading the potentiometer scale.

To measure the extension of a wire marks on the wire, above and below the cell, were observed through the two telescopes of a cathetometer capable of measuring 0.001 cm.

V. RESULTS OF EXPERIMENTS.

Galvanometer Measurements.

The use of a galvanometer to indicate the changes in electrode ptoential produced by strain was not altogether successful. The principle difficulty was that the mirror image shifted continuously, showing

that the current was not steady. Since Miniato (3) had been successful in obtaining steady conditions many tests were made, but these and correspondence with Miniato, failed to show the reason for lack of agreement.

Tests were made on the wires that are listed as follows.

5	pairs	of	soft drawn	14 S.W.G.	copper	wire
5	"	"	cold drawn	14 S.W.G.	"	"
7	"	"	soft drawn	18 S.W.G.	"	"
12	"	"	cold drawn	21 S.W.G.	"	"
7	"	"	cold drawn	24 S.W.G.	"	"

The results may be summarized as follows.

1. The initial potential difference between two apparently similar wires was sometimes as large as 20 mv.

2. By varying the resistance of the circuit it was found that the apparent potential difference depended upon the current. Large deflections could be reduced shorting the test wires. This indicated polarization.

3. Reporting only those tests of loading and unloading the wires which indicated some consistency, there were 48 tests showing no strain effects, 9 tests indicating electronegative potential changes due to strain, 8 tests indicating electropositive potential changes due to strain, and 2 tests indicating electropositive potential changes for small strains and electronegative potential changes for large strains.

The results and conditions of three tests which showed a strain effect are tabulated in Table 1. (See appendix) and plotted in Figures 3, 4 and 5.* These tests are included to show the method used to determine the effect of stressing the wires. They are not

EFFECT OF STRAIN ON GALVANIC CURRENTS

Current indicated by galvanometer deflection

$.315 \times 10^{-7}$ amps/cm.

Weight added

Deflection

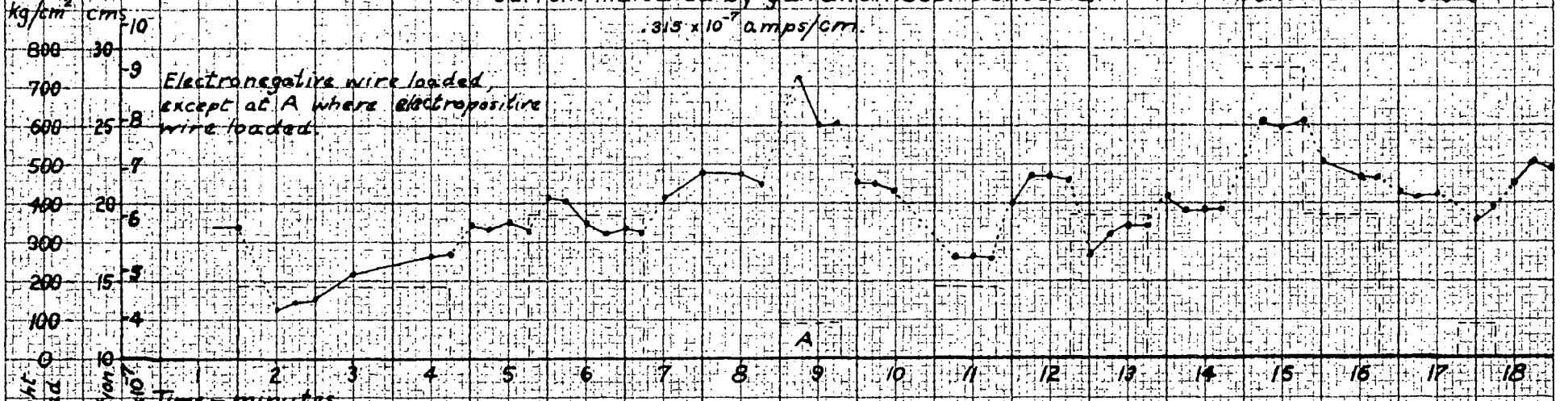

FIGURE 3. 21 Cu cd 6 Solution – $\frac{N}{250}$ $CuSO_4$

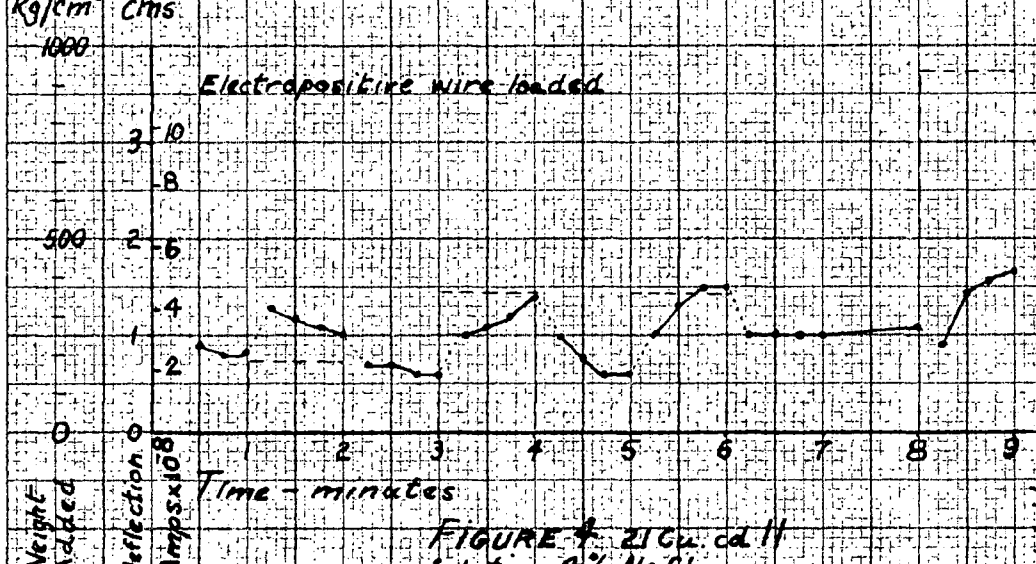

FIGURE 4. 21 Cu. cd 11
Solution 4% NaCl

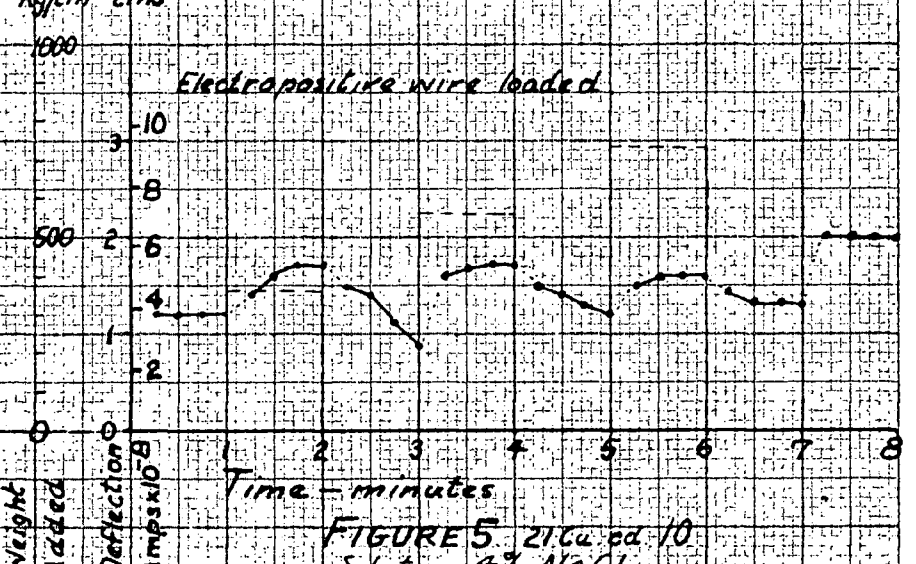

FIGURE 5. 21 Cu cd 10
Solution 4% NaCl

typical of the general results because in these the currents are fairly steady and because the strain effect could be repeated several times.

In Figure 3 during the time interval 1.5 to 4.25 minutes a stress of 190 kg/sq. cm. on the negative wire reduced the current, seemingly indicating that the strained wire had become more electropositive. In the time interval 5.25 to 6.75 minutes a stress of 390 kg/sq. cm. increased the current, indicating that the strained wire had become more negative. In Figure 3 small stresses seemed to change the electrode potential of the strained wire positively, and large stresses negatively. In Figure 4 and 5 the electrode potentials of the wires seemed to become more electropositive with strain. For example, in Figure 5 in the time interval 3 to 4 minutes, a stress of 550 kg/sq. cm. on the positive wire increased the current, indicating that the wire had become more electropositive.

* System of numbering tests. Example, 21 Cu cd 6. This means the sixth test with a pair of cold drawn 21 S.W.G. copper wire. "sd" stands for soft drawn wire and "a" stands for annealed wire.

The differences between the results in Figure 3 and those in Figure 4 and 5 cannot be attributed to differences of solution. This was found from the results of other tests.

Quantitative estimates of the change of potential could not be made because the current did not depend solely on the potential difference between the wires. The resistence in the circuit could be determined easily but the degree of polarization depended upon the current and was difficult to evaluate because the current was always changing. The effect of polarization was large. For example, in a test with 21 S.W.G. cold drawn copper wire in 4% sodium chloride the potential difference one hour after filling the cell was 5.5 mv. as found by the potentiometer with no current flowing and 0.02 mv. as indicated by the IR drop with a current of 1.4×10^{-7} amps.

Other causes than the change of electrode potential may change the current flowing in the cell when one of the wires is strained. If there is a film of corrosion products on the surface of the metal changes in current could be caused by changes of the resistence of the film by distortion.

Potentiometric Measurements.

For potentiometric measurements of the potential

change produced by stress most of the wires tested were annealed.

Two methods of annealing were followed. In the first, that used by Gautam and Jha (13), the section of the cold drawn wire to be tested was heated to redness in a bunsen flame and quenched in methyl alcohol. In the second method, the wires were heated to about 400° C. in an atmosphere of nitrogen by an electric furnace, kept at this approximate temperature for 20 to 30 minutes and cooled, still in nitrogen. Both methods of annealing gave the same apparent result when tested. No difference in behavior was observed between using areated and deareated electrolytes.

Tests were made on the wires that are listed as follows.

31	pairs	of	annealed 24 S.W.G. copper wire
4	"	"	cold drawn 24 S.W.G. copper wire
20	"	"	annealed 21 S.W.G. " "
3	"	"	cold drawn 21 S.W.G. " "
2	"	"	annealed 14 S.W.G. " "

In Table II (see appendix) and in Figure 6 are some typical results showing the potential changes produced by adding weights quickly to one wire. One potential reading was taken after each increase of stress. Weights were added as rapidly as readings could be taken. The length of these tests was about

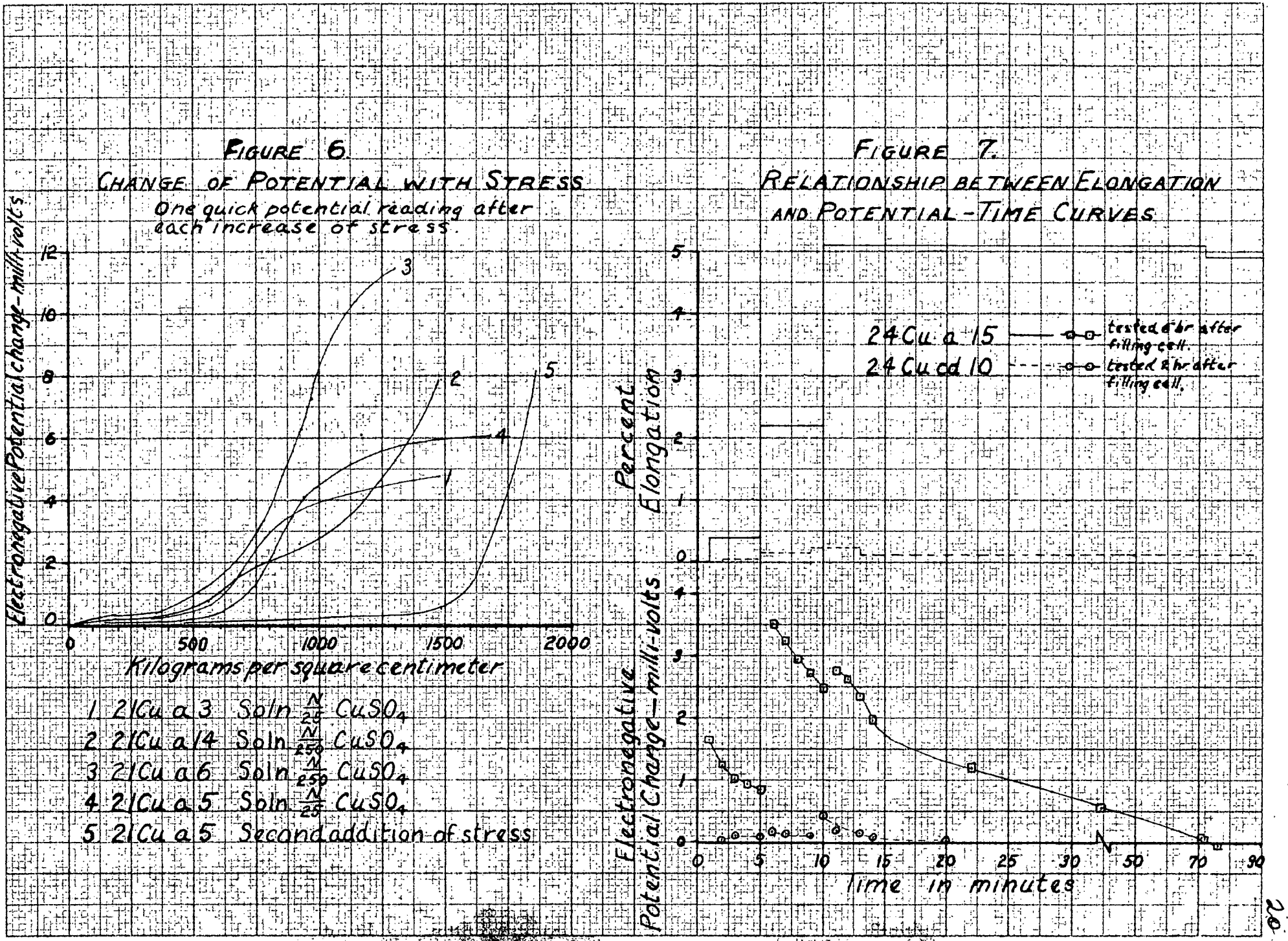
FIGURE 6.
CHANGE OF POTENTIAL WITH STRESS
One quick potential reading after each increase of stress.
Electronegative Potential change - milli-volts
Kilograms per square centimeter
1 2/Cu a 3 Soln N/25 CuSO4
2 2/Cu a 14 Soln N/250 CuSO4
3 2/Cu a 6 Soln N/250 CuSO4
4 2/Cu a 5 Soln N/25 CuSO4
5 2/Cu a 5 Second addition of stress
FIGURE 7.
RELATIONSHIP BETWEEN ELONGATION AND POTENTIAL-TIME CURVES
24 Cu a 15 tested 6 hr after filling cell.
24 Cu cd 10 tested 2 hr after filling cell.
Percent Elongation
Electronegative Potential Change - milli-volts
Time in minutes

five minutes (see Table II). These results compare with those of Guatam and Sha in magnitude, but are electronegative potential changes, whereas their potential changes were electropositive. No reason for this contradiction has yet been found. There was a slightly greater potential change in dilute solutions. Compare curves 1 and 4 with curves 3 and 2. Gautam and Jha also observed this. Comparison of curve 5 to curve 4, Figure 6, shows that a greater load is required to produce a particular change of potential at the second loading (curve 5) than is required at the first loading (curve 4). A greater stress is required to elongate the wire after it has been strained than when it is freshly annealed. It will be shown that the potential effects are related to elongation.

If the weights were added intermittently so that several potential readings could be taken between additions, results were obtained like those given in Tables IV and V (see appendix) and plotted in Figures 8 and 9. These curves show the tendency of the potential change produced by straining to drop toward zero as time passes. Note in these curves that the removal of the load causes little or no change in the potential.

Figure 7 (Table III) compares percent elongation and the potential - time relationship following stresses on cold drawn and on annealed copper. The greater elongation with annealed copper gives a greater strain potential effect.

Sections A and B of the curves in Figure 8, and sections C, D and E of the curves in Figure 9, are plotted in Figure 10 showing that the relationship between the potential change following deformation and the time elapsed is approximately logarithmic in some tests.

An explanation of these effects is that copper, when placed in contact with an electrolyte, does not reach a steady state with the electrolyte immediately. The potential may change during the formation of some surface film. The potential will be steady when the film is completely formed. Then if copper is elongated fresh surface may be exposed and the potential will change quickly toward the original value, and will return with time to the steady state potential as the breaks in the film repair.

Thus in Figure 7 the greater elongation of annealed copper may have broken the surface film more completely and so given the greater strain-potential effect.

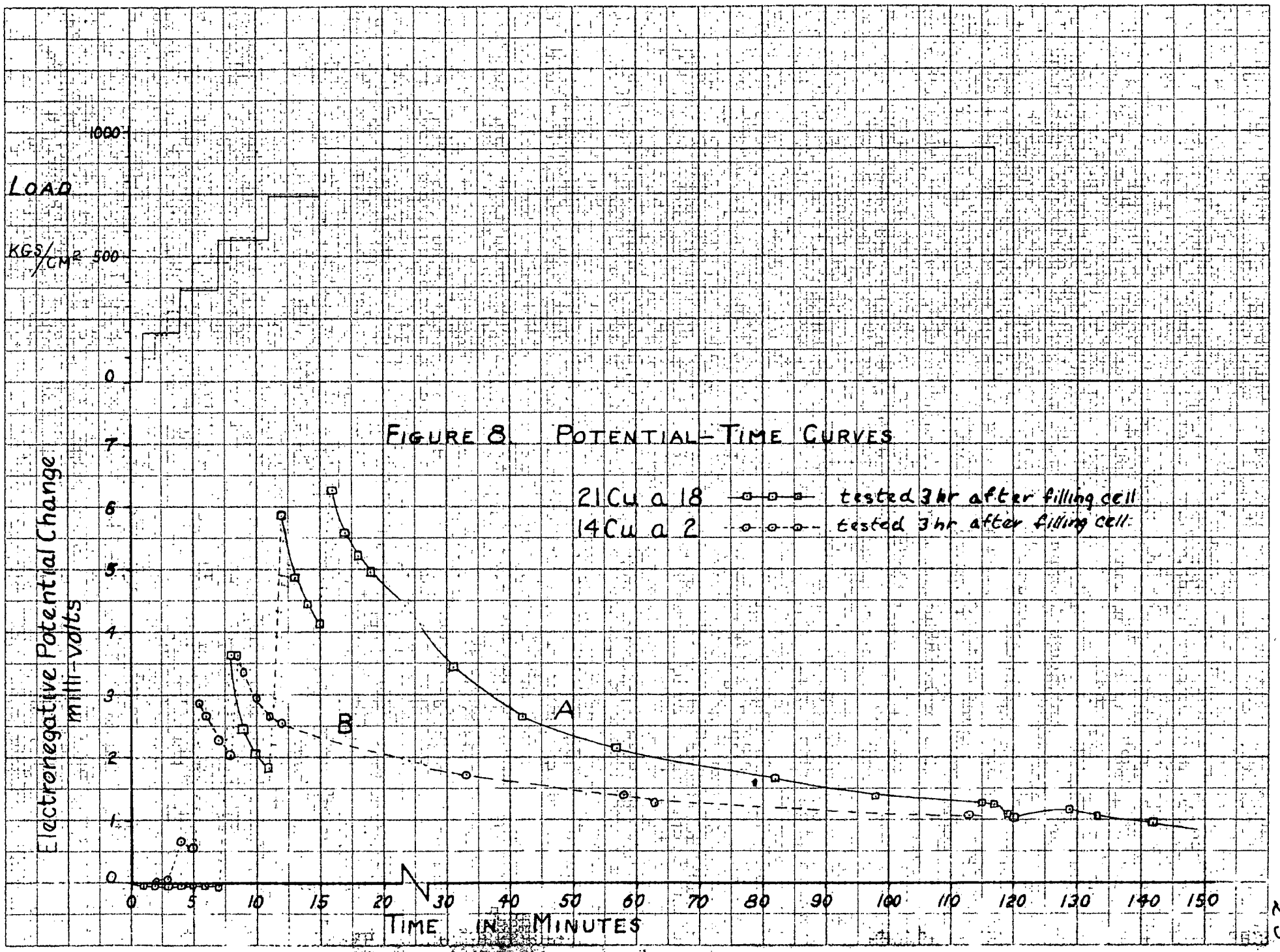

FIGURE 8. POTENTIAL-TIME CURVES

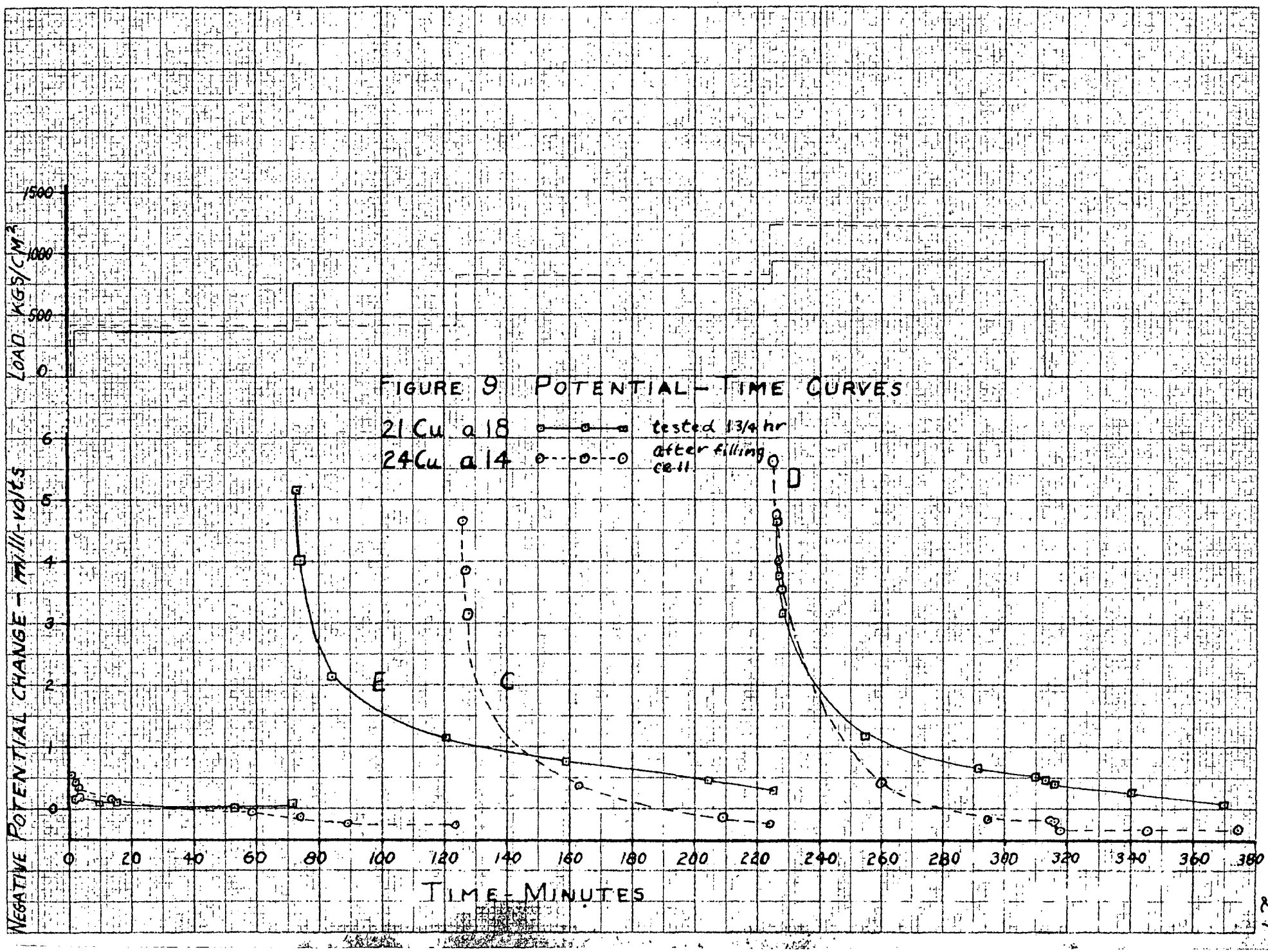
FIGURE 9 POTENTIAL - TIME CURVES
21 Cu a 18 tested 1 3/4 hr
24 Cu a 14 after filling cell
LOAD KGS/CM²
1500
1000
500
0
NEGATIVE POTENTIAL CHANGE - MILLI-VOLTS
6
5
4
3
2
1
0
E
C
D
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
TIME - MINUTES

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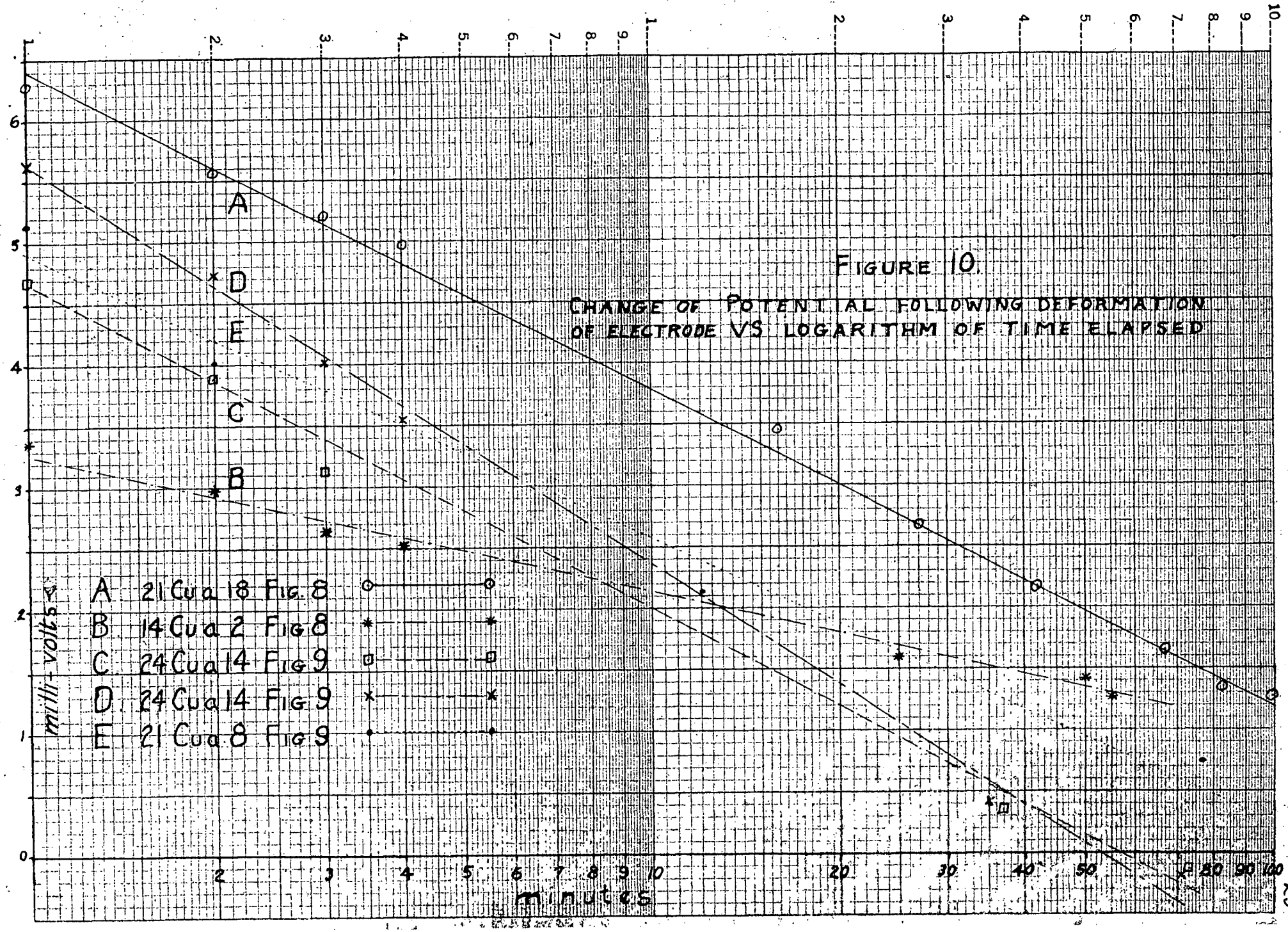


FIGURE 10.
CHANGE OF POTENTIAL FOLLOWING DEFORMATION OF ELECTRODE VS LOGARITHM OF TIME ELAPSED

The results plotted in Figure 11 and Figure 12 (Table VI) show that different solutions give markedly potential-time curves. It has been shown (15) that the magnitude of the steady state potential depends upon the acidity and salilinity of the electrolyte.

It was also found that if a wire was stressed immediately after the addition of the electrolyte no strain potential change was produced. Possibly the film was not then formed.

In these experiments no increase was observed in the initial potential difference between a pair of annealed wires, usually less than 2 mv., when one of the wires was strained before the addition of the electrolyte. Newberry (16)treated copper in several drastically different ways but no difference in the initial potential was observed that could be attributed to mechanical conditions. "On the other hand the nature of the surface certainly affects the speed of the reaction which occurs between the electrode and the electrolyte."

VI. CONCLUSIONS.

The measurements made with a galvanometer show how galvanic currents are reduced by polarization. It is not possible from the experiments reported here

FIGURE II.

POTENTIAL-TIME CURVES

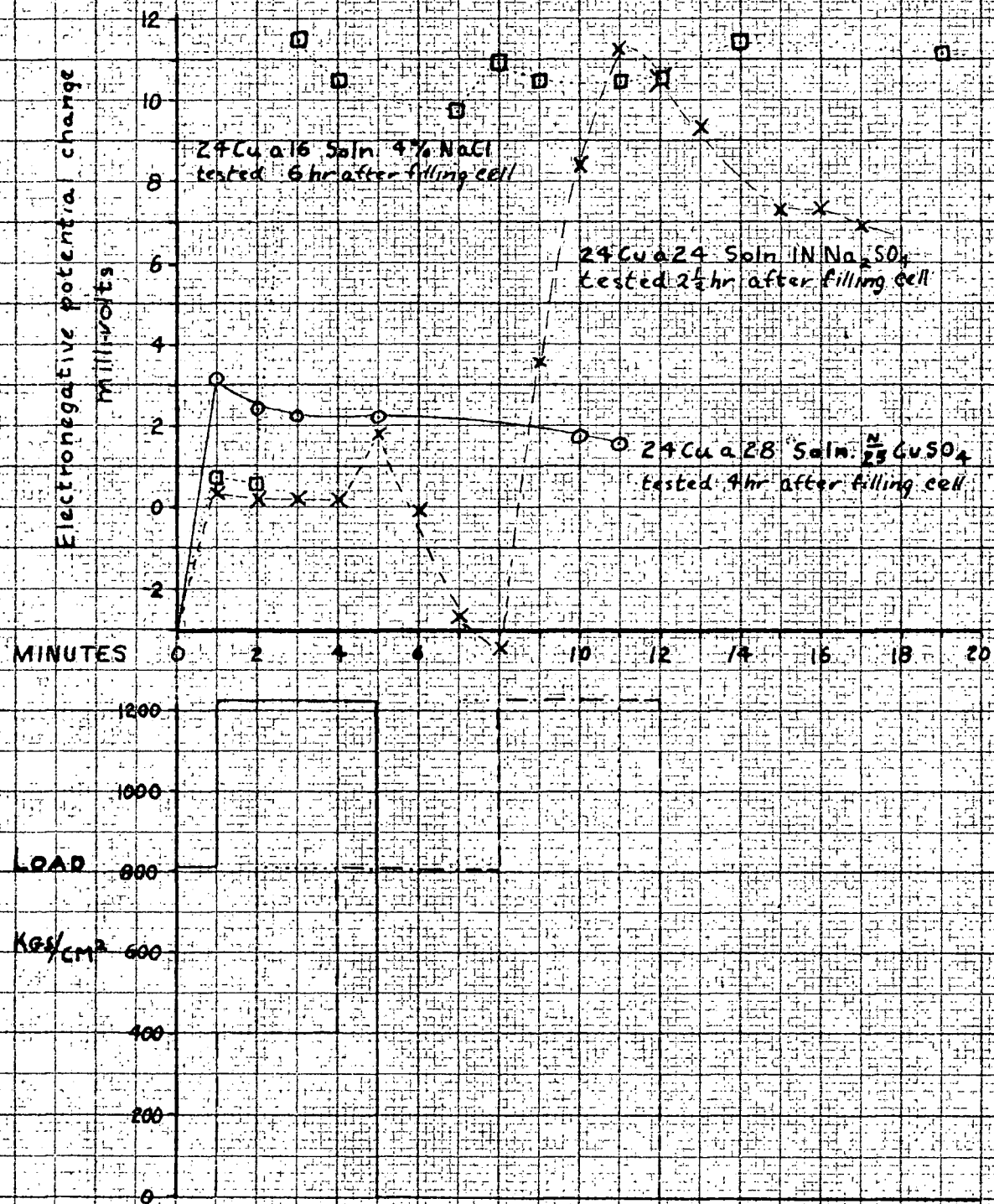
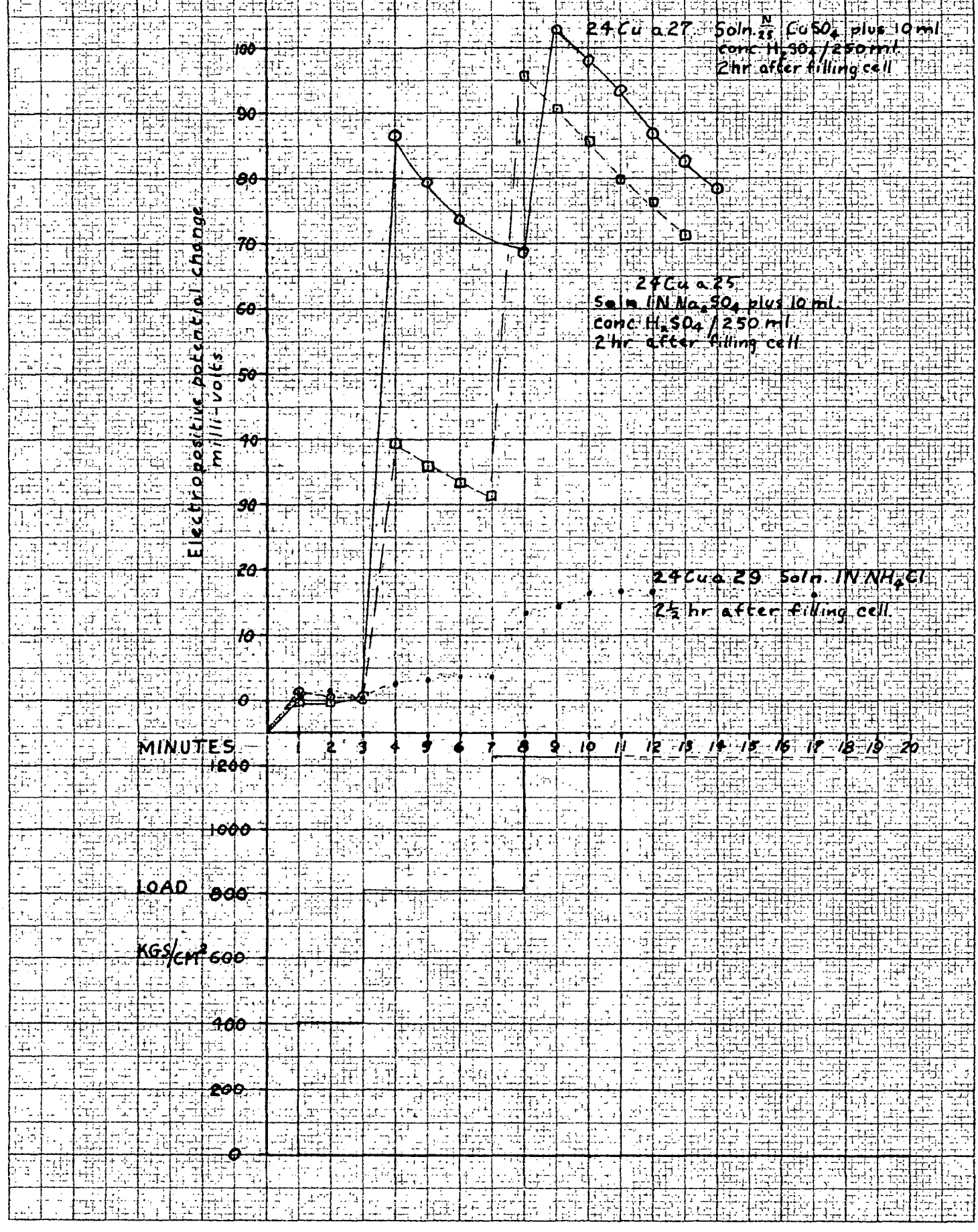


FIGURE 12

POTENTIAL - TIME CURVES



to make any conclusion as to the effect of strain upon the electrolytic solution potential of copper.

The measurements made with a potentiometer are summarized as follows.

1. The direction and magnitude of the potential change produced by straining copper depends upon the electrolyte. According to the theory if strain only affects the electrolytic solution potential of the metal, the nature of the solution should have no influence.

2. Strain did not appreciably influence the electrolytic solution potential of copper unless accompanied by elongation. This indicates that the potential changes produced by stressing were surface effects.

3. The magnitude of the potential change produced by stressing copper wire in copper sulfate solutions was a logarithmic relationship to time. This also indicates that the potential changes were surface effects. The potential may depend upon the regrowth of a film on the fresh surfaces exposed by elongation of the metal. It might be supposed the growth of a film would be according to a parabolic equation but many metals oxidize according to a logarithmic equation (17).

4. Potential changes that could be attributed to stressing did not occur unless the copper had been exposed to the electrolyte for a sufficient time for a film to form.

5. Removal of the load caused little change in the potential. Annealed copper is inelastic (18) and so the wire that had been stressed did not return to its original length. So the removal of the load did not much alter the conditions at the surface of the wire that controlled the potential change.

The original intention of measuring the effect of stress on the electrolytic solution potential of copper and applying the results to a theoretical equation has not been fulfilled. The strain potential

changes reported here and by others are primarily surface phenomena. The condition of strain on the metal electrode has little influence on the electrode potential. To make measurements that can be interpreted the complicating effects of the surface film must be avoided.

On the subject of strain potentials Copson writes (19): "It is frequently stated that energy stored in a distorted metal makes such metal ..... more electronegative than ..... stress-free material, and that as a result galvanic effects may cause rapid corrosion of the distorted metal. Attempts have been made to arrive at the potential difference. Results vary but in general indicate that the difference in emf. is only a few mv. This difference is too small to have much effect on corrosion and could easily be upset by such factors as concentration cells."

It is possible that while the state of strain on a metal has little influence on the electrode potential, the increased internal energy of the strained metal (20) may contribute to the energy necessary for activation of the reactions involved in corrosion, and thus strain may speed corrosion.

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APPENDIX

TABLE I (FIG. 3, 4, 5)

21 S.W.G. cold drawn copper wire. Test 6.
Soln. N/250 $CuSO_4$ Initial load. 229 gms on each wire.

Time mins + secs.	Deflection cms	Weight Added kgs
1:00	—	
30	18·4	
2:00	13·0	1. on neg. wire
15	13·5	
30	13·7	
3:00	15·5	
4:00	16·4	
15	16·5	removed
30	18·5	
45	18·5	
5:00	18·5	
15	18·3	
30	20·4	2. on neg. wire
45	20·0	
6:00	18·5	
15	17·8	
30	18·2	
45	18·1	
7:00	20·4	removed
30	21·9	
8:00	21·9	
15	21·2	
45	28·0	0·5 on pos. wire
9:00	25·0	
15	25·2	
30	21·2	removed
45	21·0	
10:00	20·9	
45	16·3	1. on neg. wire
11:00	16·4	

Time mins + secs	Deflection cms	Weight added Kgs
11:15	16·3	
30	20·0	
45	21·7	
12:00	21·6	
15	21·4	
30	16·6	2. on neg. wire
45	18·0	
13:00	18·3	
15	18·5	
30	20·5	removed
45	19·4	
14:00	19·4	
15	19·6	
30	25·0	4 on neg wire
15:00	25·0	
15	25·2	
30	22·5	2 removed
16:00	21·6	
15	21·6	
30	20·8	2 removed
45	20·4	
17:00	20·5	
30	18·7	0·5 on neg.
45	19·9	
18:00	21·1	removed
15	22·8	
30	22·2	1 on neg. wire
45	19·0	
19:00	19·7	removed
30	23·0	

21 S.W.G. cold drawn copper wire Test 11.
Soln 4% NaCl
Initial load 229 gm Add to pos. wire

Time mins + secs	Deflection cms	Weight added kgs
—	—	0
:30	0·9	
45	0·8	
1:00	0·8	1
15	1·3	
30	1·2	
45	1·1	
2:00	1·0	
15	0·7	0
30	0·7	
45	0·6	
3:00	0·6	
15	1·0	2
30	1·1	
45	1·2	
4:00	1·4	
15	1·0	0
30	0·8	
45	0·6	
5:00	0·6	
15	1·0	2
30	1·3	
45	1·5	
6:00	1·5	
15	1·0	0
30	1·0	
45	1·0	
7:00	1·0	
8:00	1·1	5
15	0·8	
30	1·5	
45	1·6	
9:00	1·7	

21 S.W.G cold drawn copper wire Test 10
Soln 4% NaCl deareated. covered Stanolax
Initial load 229 gm Add to pos. wire

Time mins + secs	Deflection cms	Weight added kgs
—	—	0
:15	1·2	
30	1·2	
45	1·2	
1:00	1·2	
15	1·4	2
30	1·6	
45	1·7	
2:00	1·7	
15	1·5	0
30	1·4	
45	1·1	
3:00	1·0	
15	1·6	3
30	1·7	
45	1·7	
4:15	1·5	0
30	1·4	
45	1·3	
5:00	1·2	
15	1·5	4
30	1·6	
45	1·6	
6:00	1·6	
15	1·4	0
30	1·3	
45	1·3	
7:00	1·3	
15	2·0	5
30	2·0	
45	2·0	
8:00	2·0	
15	1·8	0
30	1·7	
45	1·7	

TABLE II (FIG 6)

21 S.W.G. annealed copper wire Test 3.
Soln N/25 $CuSO_4$. filled 8:55. Initial load 100 gms

Time	Weight added kg	Potential difference mv	ΣΔE mv
10:50	0	1·13	0
	1	1·27	0·14
	2	1·38	0·25
	3	2·39	1·26
	4	3·95	2·82
	6	5·33	4·20
10:55	8	5·88	4·75

21 SWG annealed copper wire Test 5.
Soln N/25 $CuSO_4$. filled 2:30. Initial load 129 gms

Time	Weight added Kg	Potential difference mv	ΣΔE mv
4:33 p.m.	0	2·88	0
	1	2·84	0·04
	2	2·78	0·10
	3	1·60	0·20
	4	1·58	1·30
	5	-1·20	4·08
	6	-2·17	5·05
	8	-3·04	5·92
4:39 p.m.	9	-3·16	6·04
9:00 am	0	0·07	0
	2	0·0	0·07
	4	-0·11	0·18
	6	-0·23	0·70
	8	-0·45	0·52
9:05 a.m.	10	-8·08	8·15

21 SWG annealed copper wire Test 14.
Soln N/250 $CuSO_4$. filled 2:20. Initial load 129 gms

Time	Weight added kg	Potential difference mv	ΣΔE mv
3:01	0	-0·62	0
	1	-0·38	0·24
	2	-0·26	0·36
	3	-0·07	0·69
	4	1·25	1·87
	6	2·96	3·58
	7	4·67	5·29
3:08	8	7·18	7·80

21 S.W.G annealed copper wire Test 6.
Soln N/250 $CuSO_4$. filled 7:20. Initial load 129 gms

Time	Weight added Kg	Potential difference mv	ΣΔE mv
7:45	0	0·58	0
	1	0·38	0·2
	2	0·43	0·15
	3	-0·15	0·73
	4	-0·19	2·48
	5	-5·67	6·25
	6	-9·69	10·27
8:00	7	-10·86	11·44

TABLE III (FIG 7)

24 SWG annealed copper wire Test 15.
Soln N/25 $CuSO_4$ - deaerated - covered
Tested 2hr after filling. Initial load 100 gms

Time minutes	Weight added kg	Potential difference mv	ΣΔE mv	Length of section measured cms	Elongation %
0	0	0·76	0	14·454	
1	1	2·41	1·65	14·511	0·4
2		2·02	1·26		
3		1·82	1·06		
4		1·72	0·96		
5		1·63	0·87		
6	2	4·27	3·51	14·782	2·2
7		4·02	3·26		
8		3·73	2·97		
9		3·44	2·68		
10		3·25	2·49		
11	3	3·54	2·78	15·191	5·1
12		3·45	2·69		
13		3·13	2·37		
14		2·74	1·98		
22		2·03	1·27		
39		1·39	0·58		
71		0·80	0·04		
72	0	0·78	-0·02	15·166	4·9
75		0·72	-0·04		

24 S.W.G cold drawn copper wire Test 10
Soln N/25 $CuSO_4$. Tested 2 hr after filling
Initial load 129 gms/wire

Time minutes	Weight added kg	Potential difference mv	ΣΔE mv	Length of section measured cms	Elongation %
0	0	0·31	0	19·318	
1	2	0·37	0·06		
2		0·40	0·09	19·319	0·005
3		0·40	0·09		
5		0·48	0·15		
6	4	0·46	0·11	19·347	0·15
7		0·42	0·12		
9		0·44	0·49		
10	6	0·80	0·19	19·358	0·21
11		0·50	0·19		
13		0·50	0·11		
14	0	0·42	0	19·324	0·12
20		0·31	0		
60		0·71			

TABLE IV (FIG 8)

21 SWG annealed copper wire Test 18
Soln N/25 $CuSO_4$. Tested 3 hr after filling.
Initial load 129 gm / wire

Time mins	Weight added Kg	Potential difference mv	ΣΔE mv
0	0		0
1	1	-0.93	-0.07
2		-1.00	-0.03
3		-0.96	-0.07
4		-1.0	-0.02
5	2	-0.98	-0.04
6		-0.97	-0.07
7		-0.96	-0.03
8	3	-0.96	3.64
9		2.71	2.48
10		1.55	2.03
11		1.10	1.81
12	4	0.88	5.84
13		4.91	4.83
14		3.90	4.44
15		3.51	4.11
16	5	3.18	6.28
17		5.35	5.56
18		4.63	5.20
19		4.27	4.96
31		4.03	3.43
42		2.50	2.68
57		1.75	2.16
82		1.23	1.63
98	5	0.70	1.33
115		0.40	1.23
117	0	0.30	1.21
119		0.28	1.09
120		0.16	1.06
129		0.13	1.18
133		0.25	1.06
142		0.13	0.93
		0.0	

Fig 8 A in D

14 SWG annealed copper wire Test 2
Soln N/25 $CuSO_4$. Tested 3 hr after filling
Initial load 1000 gm on each wire

Time mins	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	-0.01	0
1	2	-0.02	-0.01
2	4	-0.01	0
3	6	0.04	0.05
4	8	0.62	0.63
5		0.54	0.55
	10	2.86	2.87
6		2.64	2.65
7		2.27	2.28
8		2.20	2.01
	12	2.60	3.61
9		3.38	3.39
10		2.98	2.99
11	0	2.65	2.66
12		2.50	2.51
33		1.69	1.70
58		1.39	1.40
63		1.27	1.28
113		1.03	1.04

Fig 8 B in D

TABLE V (FIG 9)

24 S.W.G. annealed copper wire Test 14.
Soln N/25 $CuSO_4$. Tested 1¾ hr after filling
Initial load 100 g / wire

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	1.55	0
1	1	2.10	0.55
2		2.00	0.45
3		1.90	0.35
14		1.70	0.15
57		1.53	-0.02
74		1.43	-0.12
89		1.29	-0.26
124		1.30	-0.25
126	2	6.24	4.69
127		5.43	3.88
128		4.69	3.14
183		1.88	0.33
209		1.43	-0.12
224		1.31	-0.24
225	3	7.17	5.62
226		6.26	4.71
227		5.56	4.01
228		5.01	3.54
260		1.95	0.40
295		1.37	-0.18
315		1.35	-0.20
316	0	1.34	-0.21
318		1.19	-0.36
345		1.22	-0.33
374		1.17	-0.38
442		1.07	-0.48

Fig 9

21 SWG annealed copper wire Test 18
Soln. N/25 $CuSO_4$. Tested 1¾ hr after filling
Initial load 129 gm on each wire

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	0.15	0
3	2	0.31	0.16
4		0.31	0.16
10		0.25	0.10
53		0.15	0.00
72		0.17	0.02
73	4	5.27	5.12
74		4.15	4.00
84		2.26	2.11
121		1.30	1.15
159		0.89	0.74
204		0.58	0.43
225		0.42	0.27
226	5	4.80	4.65
227		3.91	3.76
228		3.31	3.16
255		1.30	1.15
292		0.81	0.66
310		0.65	0.50
313	0	0.57	0.42
316		0.53	0.38
340		0.40	0.25
370		0.22	0.07
408		0.05	-0.10

Fig 9

TABLE VI (FIG 11)

24 SWG annealed copper wire Test 16
Soln 4% NaCl. Tested 6 hrs after filling
Initial load 100 gm on each wire

Time min	Weight added Kg	Potential difference mv	ΣΔE mv	Length of section measured cm	Elongation %
0	0	-3.17	0	13.649	
1	1	-2.97	0.70		
2		-2.62	0.55		
3	2	8.32	11.49	14.320	4.9
4		7.62	11.79		
7		6.49	9.66		
8	3	7.73	10.90	14.687	7.3
9		7.33	10.50		
11		7.27	10.44		
12	0	7.36	10.53	14.632	7.2
14		8.23	11.40		
19		7.86	11.03		
24		5.46	8.63		

24 SWG annealed copper wire Test 28
Soln N/25 $CuSO_4$. Tested after 4 hr.
Initial load 2100 gm on test wire, 100 gm on other

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	2	-1.43	0
1	3	1.65	3.08
2		0.98	2.41
3		0.75	2.18
5	0	0.74	2.17
10		0.26	1.69
11		0.08	1.51
30		-1.14	0.29

24 SWG annealed copper wire Test 24
Soln 1N Na_2SO_4. Tested 2½ hr after filling
Initial load 100 gm on each wire

Time min	Weight added Kg	Potential difference mv	ΣΔE mv	Length of section measured cms	Elongation %
0	0	1.31	0	16.017	
1	1	1.69	0.38	16.115	0.6
2		1.53	0.22		
3		1.48	0.17		
4		1.48	0.17		
5	2	3.10	1.79	16.375	2.2
6		0.12	-1.19		
7		-1.48	-2.79		
8		-2.17	-3.48		
9	3	4.80	3.59	16.808	5.0
10		9.73	8.42		
11		12.58	11.27		
12		11.79	10.48		
13	0	10.64	9.33	16.789	4.2
15		8.59	7.28		
16		8.59	7.28		
17		8.27	6.96		
82		2.32	1.01		

(FIG 12)

24 SWG an. cu wire Test 25
Soln 1N Na_2SO_4 + 10 cc. conc H_2SO_4 / 250 cc
Initial load 100 gm
Tested 2 hr after filling

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	-3.21	0
1	1	-3.36	-0.15
2		-3.23	-0.02
3		-3.17	-0.04
4	2	36.08	39.29
5		32.68	35.89
6		30.00	33.21
7		27.99	31.20
8	3	93.26	96.47
9		87.68	90.29
10		82.14	85.35
11		76.63	79.84
12		73.06	76.27
13		68.07	71.28
30		29.07	32.28

24 SWG an. cu wire Test 27
Soln N/25 $CuSO_4$ + 10 cc conc H_2SO_4 / 250 cc
Tested 2 hr after filling
Initial load 100 gm

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	-0.23	0
1	1	-0.97	1.20
2		-0.28	0.51
3		-0.27	0.50
4	2	86.34	86.57
5		79.48	79.71
6		72.88	73.11
8		68.68	68.91
9	3	102.57	102.80
10		97.76	97.99
11	0	92.83	93.06
12		86.70	86.93
13		82.58	82.71
14		78.25	78.48
46		31.00	31.23

Pot. diff approx 30 mv for 27 hr. Then 2nd wire stressed similarly - neg changes - pot. diff few mv after 1 hr more.

24 SWG an. cu wire Test 29
Soln 1N NH_4Cl
Tested 2½ hr after filling
Initial load 100 gm

Time min	Weight added Kg	Potential difference mv	ΣΔE mv
0	0	-1.72	0
1	1	-0.79	0.93
2		-0.66	1.06
3		-0.93	0.79
4	2	1.11	2.83
5		1.35	3.05
6		1.76	3.48
7		2.12	3.84
8	3	11.99	13.71
9		13.64	14.36
10		15.12	16.84
11	0	15.11	16.83
12		15.00	16.72
17		14.47	16.19

Pot. diff. approx 16 mv for 48 hr. 2nd wire stressed - similar changes. - pot. diff. few mv after about 1 hr more.