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ANODIC POLARIZATION OF TITANIUM IN FORMIC ACID

by

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SUMMARY

The anodic behaviour of titanium in various concentrations of formic acid has been studied by means of voltage-time curves at constant current using a sensitive recorder to obtain the detailed shape of the curve. It has been shown that, depending on electrolytic conditions, the titanium will either remain passive, micropit or corrode uniformly.

The shape of the V-t curves in the micropitting region depends on concentration and temperature and many of the curves are characterized by a plateau in the region 7 - 12V.

Optical studies of micropitting have shown that different interference colours form on different grains and that pits are initiated on the thinner oxide films. Electron microscopy has revealed the formation of 'mounds' (solid or hollow) which appear to rupture at the breakdown potential at which micropitting commences.

The uniform and dense distribution of micropits has been explained on the basis of the formation of blisters on the thinner oxide films resulting from stresses within the oxide.

ANODIC POLARIZATION OF TITANIUM IN FORMIC ACID

The anodic behaviour of a given metal is usually dependant on the nature and concentration of the electrolyte solution and the conditions of electrolysis, such as temperature, current density, etc. A comparison of the behaviour of aluminium and titanium shows that there are many similarities and, for example, both metals will pit when anodically polarized in chloride solutions, although much higher potentials ($>$ 12 - 14V) are required for titanium.[1] Both metals form dielectric oxide films during anodic oxidation but whereas this occurs with titanium in a variety of acid and alkaline solutions, with aluminium it occurs only in a limited number of near-neutral buffer solutions. The formation of porous oxide films when aluminium is anodically polarized in a variety of solutions of inorganic and organic acids appears to be a unique feature of the anodic behaviour of this metal.

The present study originated from the use of anodic films on titanium as a means of preventing galling during wiredrawing. Thus, Richaud[2] formed anodic films on titanium in 20% sulphuric acid at 20°C and 18V and considered that these films were porous or fissured as they had the ability to absorb lanoline. Miller, Jeffery and Pray[3] found that the oxide film with the best anti-galling properties was obtained using 5% sodium hydroxide at 205°F; the use of a phosphoric/sulphuric acid solution at room temperature for anodizing titanium is a subject of a patent which claims that the oxide film prevents galling.[4]

It should be observed that no direct evidence of porous films appears to have been submitted and claims for porosity have been based largely on the ability of the film to absorb oil.

The anodic behaviour of titanium in various solutions has been the subject of numerous studies which have been concerned with the dielectric properties of the film, passivity of the metal, breakdown of the oxide in chloride, etc. Bohm[5] determined the i - t relationship at constant voltage (60V) in potassium hydroxide, borax, sulphuric acid and in chromic acid solutions and showed that the oxide behaved as a typical valve electrode. Tajima and Mori[6] have claimed that films can be formed to 1300V in borate solutions.

There have been several studies of the nature of the anodic oxide film although in many cases the results appear to be contradictory. Rivolta,[7] who used optical microscopy and electron diffraction, showed that the interference colour varied with the orientation of the grain. He considered that this was due to different thicknesses of oxide on different grains. Electron diffraction studies revealed the presence of titanium hydride or rutile and/or anatase or hydrated oxide according to the nature of the solution and polarizing conditions. Stripped films have been studied by Yamaguchi[8] who found brookite to be present.

The corrosion behaviour of titanium in aqueous solution is characterized by the marked tendency of the metal to exhibit passivity. Stern and Wissenberg[9] have shown that although the exchange current for the hydrogen reaction, and other electrochemical reactions, is low (a condition which is not conducive for the establishment of passivity) this is offset by the unusually electronegative critical potential (approximately -0.23V with reference to the saturated calomel electrode) required for passivity. The metal thus exhibits passivity in solutions of redox potentials no higher than that of the $2H^+ + 2e = H_2$ equilibrium so that passivity can be achieved by alloying or coupling the metal with platinum or palladium.

Hall and Hackerman[10] have studied the cathodic and anodic behaviour of titanium in neutral chloride solutions under galvanostatic conditions and have shown that at low current densities the potential increases linearly with time until oxygen evolution occurs; the potential then remains constant. They consider that their data does not permit an unequivocal choice between chemisorption or oxide film formation as a first step prior to oxygen evolution.

The ahodic protection of titanium in non-oxidizing acids has been the subject of numerous studies and Inglis and Cotton[11] have shown that in 40% sulphuric acid at 60°C, a slight increase of potential results in a marked reduction in the corrosion rate.

The anodic behaviour of titanium in chloride solutions is important for electrolytic processes, and it has been shown that film breakdown and consequent pitting at a potential of approx. 12 - 14V can be prevented by having platinum in contact with the metal surface.[12]

Although the anodic behaviour of titanium has been studied in a wide variety of electrolyte solutions there appears to be little evidence of studies using formic acid. The corrosion behaviour of the metal in formic acid has been studied by Lane, Golden and Acherman[13] who have shown that titanium is passive providing oxygen is present. In oxygen-free solutions the metal exhibits the phenomenon of 'border-line' passivity and the behaviour depends on the thickness and continuity of the air-formed film, smoothness of surface, etc. It would appear that either corrosion or passivity could result when apparently identical specimens were immersed in the same solution of formic acid. Examples of 'border-line' passivity have also been reported by Hutchinson and Permar.[14]

The corrosiveness of this acid and the manifestation of border-line passivity under certain conditions were factors which influenced the choice of this acid as a possible electrolyte solution for producing porous or fissured films. By analogy with aluminium it was considered that the electrolyte solution should be such that film growth and localized film dissolution could proceed simultaneously during anodising. The present study has been confined to the effect of acid concentration and temperature on the anodic behaviour of titanium under galvanostatic conditions and a brief account of this work has been reported previously.[15]

EXPERIMENTAL

(a) Materials. Titanium specimens 1 x 1 x 0.035 cm. were prepared from commercially pure titanium sheet (I.C.I. 130 A; a typical analysis is 0.03% C, 0.05% Fe, 0.015% N_2, 0.005% H_2, 0.1% O_2) and electrical contact was made by means of spot-welded titanium wires. Cathodes were sheet platinum of similar size with spot-welded platinum wires.

Reagents used were AnalaR grade and all solutions were prepared from doubly-distilled water. Concentrations of solutions of formic acid are expressed as vol.%.

(b) Cell. Anodic polarization was carried out in a glass cell (Fig.1) which incorporated an immersion heater H and thermoregulator T so that the solution could be maintained at any pre-determined temperature. Control of temperature was within ± 0.2°C. Agitation of the solution was achieved by passing argon through the sintered glass disc I.

The platinum cathodes C and anode A were supported by means of the connecting wire which fitted tightly in p.t.f.e. stoppers inserted in the end of the parallel ground-glass joints - the ground-glass joint supporting the titanium anode is perpendicular to the paper as shown in the plan. By this arrangement the anodes could be placed at reproducible distances on either side of the cathode.

(c) Electric Circuit. The circuit consisted of an electronic constant current/constant voltage power unit (fully stabilized d.c. up to 100 mA and 350-400V), a valve voltmeter (Mullard, Type E 7555/2) and a pen recorder (Leeds Northrup, Speedomax H) which had a 5 mV full-scale deflection - by means of an attenuator the full-scale deflection could be adjusted to give 30, 60, 100 or 200V.

Voltage-time relationships at constant current were obtained as direct plots on the recorder chart and all curves in the present paper are tracings of the recorded curve. In certain curves the potential was observed to oscillate at potentials above a certain critical value. This is shown on the curves by an 0 to indicate the commencement of oscillations; the arrows show the approximate amplitude of the oscillations of potential.

Measurements were made of the potential between the anode and cathode rather than the potential of the anode/ solution interface as the IR drop and potential of the cathode were considered to be negligible for the present study.

(d) Surface Preparation. Specimens were wet polished to 3/0 emery paper and then to 1μ diamond. They were finally chemically polished in a solution consisting of 1 part 97% H_2SO_4, 1 part 75% HNO_3, 1 part 44% HF and 1 part water. After washing they were introduced into the solution contained in the cell, the temperature set to the pre-determined value, and when the temperature was constant the V-t curve was determined at constant current.

EFFECT OF CONCENTRATION OF FORMIC ACID AND TEMPERATURE

The effect of acid concentration and temperature is summarized in Fig.2 and on the basis of the different effect produced during anodic polarization it is possible to distinguish the following zones:

(a) Micropitting zone. 0.1 - 60% formic acid and 40 - 50°C.

In this zone uniform barrier films are produced initially but at a critical potential the surface of the initially-formed oxide becomes pitted; initiation of pitting was accompanied by precipitation of titanium hydroxide from solution.

It should be noted that the term 'micropitting' is used in the present context to denote the formation of microscopic pits which are uniformly and densely distributed over the metal surface. This type of pitting should be clearly distinguished from the sparsely distributed gross pits which form during the anodic polarization of titanium in chloride solutions.

(b) Barrier films formation to high potentials.
60 - 96.5% formic acid, 40 - 50°C.

In this region titanium behaves as a typical 'valve' metal and dielectric oxide films could be formed to high potentials before spark breakdown occurred.

(c) Barrier film formation to low potentials.
0.1 - 96.5% formic acid, 40 - 50°C.

Film formation at temperatures above 40 - 50°C proceeded only to a limiting potential of 20 - 30V when film growth ceased and further passage of charge resulted in the oxidation of the solution at constant potential.

(d) Uniform coffosion with the formation of a loose, non-adherent precipitate. 96.5 - 100% formic acid, 0 - 100°C.

In this region the titanium appeared to corrode uniformly and the titanium hydroxide forms as a loosely-adherent yellowish deposit on the metal surface.

The transition from one zone to another usually occurred over a range of temperature and concentration as indicated by the cross-hatched areas of Fig.2. The transition from barrier film formation to the formation of non-adherent deposits at 96.5% formic acid was, however, quite well defined.

VOLTAGE-TIME CURVES AT CONSTANT CURRENT IN MICROPITTING REGION

Effect of current-density and concentration

Fig.3 shows the V-t relationships for titanium anodically polarized at different current densities in 30% formic acid at 25°C (micropitting zone). At 5 mA/cm^2 the potential increased linearly with charge and interference films formed up to 45V; at O the potential began to oscillate rapidly and with continued passage of charge the amplitude of the oscillations increased, as shown by the magnitude of the arrows. The potential of 45V and the subsequent oscillations of the potential appear to be a characteristic feature of the initiation and propagation of micropits. Subsequent passage of charge resulted in a gradual increase in potential ($\sim$120V after 4h), and an increase in the amplitude of the potential oscillations.

Although the V-t curve at 5 mA/cm^2 was linear up to the potential at which pitting occurred, the curves at lower current densities were non-linear and were characterized by a change of slope (a plateau) in the region 7 - 12V. The significance of this plateau will be discussed in relation to changes in surface topography as revealed by electron microscopy.

Fig.4 shows the effect of concentration within the micropitting zone and comparison with Fig.3 indicates that there is a definite similarity between the effects of concentration and current density. For example, the charge required to attain the potential required for the initiation of micropitting decreases with increase in current density or increase in concentration. It is also evident that plateaux were present only at the lower concentrations of acid.

Fig.5 shows that the potential at which micropitting is initiated varies with concentration of the solution and is a minimum of 30% formic acid indicating that this concentration of acid is most conducive to film breakdown.

Effect of Temperature

Fig.6 shows the effect of temperature on the anodic behaviour of titanium in 30% formic acid at 2 mA/cm^2, and it is evident that the lower the temperature the lower the charge required for micropitting. At 40°C very prolonged times were required for the potential to increase to the value required for micropitting; at 50°C it was not possible to achieve this potential as when the potential increased to about 30V, the ionic current became practically zero.

Region of High Concentration

Fig.7 shows the effect of concentration in the region of concentration where barrier films could be formed to high potentials. The curves are linear initially but at a potential which increases with increase in concentration there is a sudden change in slope. At B breakdown of the oxide film occurs with spark discharge. These curves show that the higher the concentration of the acid the higher the potential before breakdown. At $>$ 96.5% formic acid there was, however, a marked change in behaviour and it can be seen that at this concentration the potential rises to only 60V. At this and higher concentrations the titanium was corroded uniformly with the formation of a yellow non-adherent deposit on the metal surface. At 96.5% formic acid conditions were frequently 'border-line' and in certain cases it was observed that the initial formation of the yellow deposit was superceded by a barrier film which formed underneath the yellow deposit causing it to become detached.

Fig.8 shows the effect of temperature on the V-t curves obtained with 90% acid at 2 mA/cm^2.

Formation of Plateau

Previous results have shown that under certain conditions of anodizing the V-t curves are characterized by a plateau which occurs over the range 7 - 12V. It should be observed, however, that the V-t curves are markedly affected by the nature of the surface of the specimens. Thus, specimens which had been abraded to 1μ diamond and anodized without etching gave linear curves - a marked plateau was evident, however, ifabrading was followed by immersion for 2 min. in the chemical polishing solution.

Fig. 9 shows V-t curves for various concentrations of formic acid and it is evident that only the curve for 50% formic acid is linear - all other concentrations show a change of slope at 7 - 12V. No evidence of plateau formation was observed at higher concentrations of acid, i.e. in the region 60 - 96.5% formic acid. On the other hand, it is evident from Fig.10 that plateau formation is not confined to formic acid and occurs with a wide variety of different electrolyte solutions including dilute solutions of sodium hydroxide. It is apparent from the above considerations that plateau formation at low potentials appears to be a characteristic of the anodic behaviour of titanium.

It is of interest to not that detection of the plateau requires a sensitive recorder and that plateau formation was not observed in earlier studies using a valve voltmeter to measure potential.

Addition of Chloride to Formic Acid

Although the formic acid was of the highest purity it was considered of interest to study the effects of additions of chloride. Additions of 10 p.p.m. Cl^- produced no effect in the micropitting region and very appreciable concentrations were found necessary to lower the breakdown potential below the potential of 45V which characterizes micropitting in formic acid. When 1% NaCl was added to 10% formic acid the breakdown potential was observed to be 23V which is appreciably higher than the breakdown potential in chloride alone.

In the anodizing region (90% formic acid) the effect of chloride was more pronounced and, for example, 40 p.p.m. Cl^- lowered the breakdown potential from 360V to 190V.

OPTICAL MICROSCOPY

Polycrystalline titanium gives rise to multicoloured oxide films which, according to Rivolta,[7] are due to different thicknesses of oxide resulting from the different rates of oxide growth on different crystal faces. The 'as-received' titanium had a grain size of ~ 0.004 mm. but it was possible to increase the grain size to ~ 0.04 mm. by annealing at 750°C for 24 h. in a vacuum of 10^{-6} mm. - the slight oxygen uptake during this procedure was not considered significant as the titanium already contained 0.10% oxygen.

Specimens were anodized under different conditions to a predetermined potential (below that required for pitting) and then examined microscopically. The variation of oxide thickness from grain to grain was estimated to be very much greater in the micropitting region of concentration than in the region where barrier films could be formed to high potentials. Only two interference colours (e.g. red and orange) were present in the case of 96% formic whereas a complete range could be obtained at the low concentrations. In the case of concentrations $>$ 96% the interference films formed initially (i.e. before the formation of the yellow deposit) were uniform.

With 10% formic acid a uniform first order blue film was obtained at 20V but above this potential at least two interference colours were observed, e.g. at 45V there were yellow (2nd order) and grey-blue (just before 2nd order) interference colours. This potential corresponds with the onset of micropitting and it was observed that the pits became initiated on the blue-grey films. In other specimens yellow (2nd order) and red (2nd order) colours were present and pitting was confined to the thinner yellow films. As the potential increased the pits propagated into the film where they initially formed but ultimately pits formed on grains having thicker oxide films. It was concluded from these studies that pits were always initiated on the thinner oxide films.

Identification of Oxides using X-ray and Electron Diffraction

X-ray diffraction was used to identify the white precipitate produced in the solution during micropitting and the yellow adherent deposit formed on titanium in high concentrations (> 96.5% formic acid).

After filtering off the white precipitate, washing and drying, it was examined using bulk anatase (B.D.H. Ltd.) and rutile as comparison standards.

With molybdenum K_α radiation (35 kV, 12 mA) and a zirconium filter it was possible to show that the diffraction lines, although diffuse owing to the small crystallite size, agreed with those obtained with bulk anatase.

The yellow deposit obtained in the high concentration region appeared to be an amorphous form of titanium oxide, although faint lines were observed which indicated that it was probably anatase. Gravimetric studies showed it to be anhydrous.

Electron diffraction studies were carried out using an electron diffraction camera similar to that used by Finch and Wilman. Specimens were prepared metallographically down to 0.25μ diamond using a plentiful supply of paraffin as lubricant to prevent diamond particles becoming embedded in the metal. After degreasing, the specimens were etched in the chemical polishing acid, anodized under pre-determined conditions and the pattern of the oxide was then determined by electron diffraction.

In 95% formic acid it was possible to anodise the specimens to 325V and these films were shown to be crystalline and to correspond with the pattern of anatase. Attempts made to determine the structure of films formed to low potentials (20 - 30V) in this acid were not successful and whether a crystalline oxide forms initially or whether the initial oxide is amorphous and crystallizes at some higher potential could not be established.

Electron Microscopy

The surface topography of films formed to different potentials was studied by electron microscopy using an Akashi Transcope. Specimens were carefully polished and etched, as described previously, and then anodized in a given solution to a predetermined potential.

Replicas were produced by the Bex film technique followed by carbon evaporation at a 30° angle to give maximum contrast. Vaseline was smeared uniformly over the carbon in order to prevent disintegration of the replica when the Bex film was removed by acetone. This took 5 - 6 h. during which time the acetone was renewed two or three times. The Vaseline was then removed by immersion in carbon tetrachloride for 10 h. periodically renewing the solvent to minimize the time of dissolution.

Fig. 11(a) - (h) shows replicas which have been obtained by anodizing titanium to different potentials in the micropitting region (10% formic acid, 2 mA/cm^2). Below 9V the surface appeared to be smooth and featureless but at this potential there was some evidence of the formation of small mounds on the surface. This effect was quite distinct at 15V (Fig. 11(a)) and Figs. 11(b) - (d) show that as the potential is increased the mounds appear to become larger and more extensive. At 50V (Fig. 11(d)) smaller mounds appear to form on the surface of the larger mounds.

At 55V (a potential which corresponds approximately with the micropitting potential) a change in the surface topography was observed and it would appear from Fig. 11(e) that the mounds have ruptured and that each mound has formed four segments - a similar effect is shown at 60V (Fig. 11(f)). At 65V the surface shows evidence of marked pitting (Fig. 11(g) and (h)) and presumably pitting is initiated as soon as the mounds rupture.

Fig. 11(h), which was obtained in 90% formic acid, shows that mound formation occurs in the region of concentration where films can be formed to high potentials. It should be noted, however, that these mounds appear to be larger and smoother than those obtained in the micropitting region (c.f. Fig. 11(d)). Formation of films at 75V and 150V in 90% formic acid followed by anodizing in 30% formic acid resulted in micropitting at ∼ 60V - a value only slightly higher than that required for micropitting of unanodized specimens in this concentration of acid.

It appears from these results that the formation of mounds occurs in both the micropitting and anodizing regions of concentration but mound rupture, at least at comparatively low potentials, occurs only in the micropitting region.

DISCUSSION OF RESULTS

The results obtained in the present work have shown that the anodic behaviour of titanium in formic acid is markedly dependent on the concentration and temperature of the acid and that these factors will determine the nature of the electrode reactions. Slight changes in conditions have been shown to affect anodic behaviour to a marked extent and, for example, although micropitting occurs at 45°C, increase of temperature to 50°C results in passivity. Barrier films will form to high potentials in the region 60 - 96.5% formic acid, the maximum potential increasing with increase in the concentration of acid - but uniform corrosion will occur at concentrations slightly greater than 96.5%. Depending on concentration and temperature it is possible to obtain four different types of behaviour:

(a) micropitting (localized attack and simultaneous film formation)

(b) passivity (limited formation of oxide film followed by gas discharge)

(c) uniform corrosion

(d) film formation to high potentials.

Although some consideration will be given to all types of behaviour, emphasis will be placed in this discussion on the mechanism of micropitting.

Elevated temperatures

Titanium dioxide is non-stoichiometric and can be represented by $TiO_{1.91-2.0}$. Hauffe[16] and Grunewald[16a] have shown that WO_3 dissolved in TiO_2 raising the electrical conductivity while additions of Ga_2O_3, Al_2O_3 or NiO lower it - on this basis these workers consider the oxide to be an n-type conductor with oxygen defects and interstitial electrons.

On the other hand, Hurlen[17] has argued that sufficient space is available in lattice to accommodate Ti^{4+} interstitially. It is well known that the conductivity of semi-conductors is predominantly electronic and that the temperature dependence is positive, i.e. $K = A.\mathrm{expt} - Q/TR$. Charlesby[18] showed during studies of the anodic behaviour of zirconium that the conductivity at 100°C was 33 times the conductivity at 19.5°C. Nevertheless, the pronounced increase in conductivity of titanium oxide with temperature appears to be unusual, and it may be possible that this is associated with a change in thestoichiometry or nature of the oxide at elevated temperatures. An increase in the number of oxygen defects would increase the conductivity.

Since passivity at elevated temperatures occurred in the majority of electrolyte solutions studied, it is evident that this phenomenon is due entirely to the properties of the oxide film. The fact that micropitting does not occur at elevated temperature follows, however, from Fig.5 where it is evident that micropitting is initiated only at potentials $>$ 45V as at elevated temperatures film formation ceases when the potential reached 20 - 25V. Although micropitting in formic acid does not occur at elevated temperatures, it can be predicted and demonstrated that pitting will occur in hot chloride solutions as the potential for pitting is only 12 - 14V - a value which is appreciably lower than that required for micropitting.

Micropitting Region

The formation of very fine pits uniformly and densely distributed over the metal surface with simultaneous growth of the oxide film which occurs when Ti is anodically polarized in concentrations of formic acid $<$ 50%, appears to be a unique characteristic of this particular system. Attempts to find other acid solutions which produce a similar effect on titanium have been unsuccessful - on the other hand it has not been found possible to produce micropitting on zirconium using formic acid or any other acid.

It is evident, therefore, that micropitting results from some unique properties of the system Ti/formate anion, as it has been shown that sodium formate in the range of concentration from 0.1% to saturated will produce micropitting even at pH 14. It should be observed, however, that the depth of the pits is less and surface attack is greater than with comparable concentrations for formic acid. (The barrier films obtained in 60 - 96.5% formic acid could not be obtained with sodium formate owing to solubility considerations). The fact that micropitting can be achieved in formate solutions over a range of pH precludes any mechanism based on the formation of acid and it is evident, therefore, that this phenomenon results from the specific property of the formate anion c.f. theories to explain pitting by chlorides in neutral solutions.[19]

There are many examples which can be quoted which show that the corrosion rate of a given metal frequently shows maxima and minima in certain ranges of acid concentration. Ma and Peres[20] have studied the Ti/H_2SO_4 system and have observed an increase in the rate to a maximum at 40% and then a fall to a minimum at 65% which is then followed by a rapid increase. They suggest that corrosion in the low concentration region is probably due to the formation of complex anions $[Ti(SO_4)_{2x}]^{-2x}$ and that the rate of formation of these complexes increases with acid concentration reaching a maximum at 40%. In the range 40 - 65%, the complex anions are considered to decompose giving titanium dioxide, which passivates the titanium, and sulphuric acid. The increase in rate at concentrations greater than 60% is explained by the formation of another complex $[TiO_2(SO_4)_x]^{-2x}$. There is no definite evidence of complex formation to support this view although it should be observed that the detection of complexes in solutions of this nature is extremely difficult.

Lane, Golden and Acherman[13] have studied the corrosion behaviour of titanium in various concentrations of formic acid at 35, 60 and 100°C in aerated and non-aerated solution. They have shown that at 35° the rates in aerated solutions are negligible and at the higher temperatures the rates are appreciably less in oxygenated solutions. From their results it would appear that the rate increases with concentration to a maximum at 50% and then falls rapidly with concentration and reaches a very low value at 90% formic acid. Corrosion rates at higher concentrations were not studied. In many cases 'borderline passivity' occurred and the corrosion behaviour under unaerated conditions appeared to depend on such factors as the thickness and continuity of the air-formed film, smoothness of the surface, etc., so that whereas certain samples corroded, others remained passive.

A consideration of the V-t curves (Fig.3) shows the following characteristics:

(a) a rapid initial increase in potential to $\sim$9V,
(b) a slower rate of increase of potential extending over 9 - 15V,
(c) a rapid increase in potential to $\sim$ 50V,
(d) slight fluctuations in the potential corresponding to the initiation of micropitting,
(e) a gradual increase in potential as the pits propagate into the metal,
(f) an increase in the magnitude of the fluctuations of potential as the potential increases.

A characteristic feature of the anodic behaviour of titanium is the formation of different interference colours on different grains. This is possibly due to epitaxy between the grain and the oxide resulting in oxide films of different orientations and growth rates. This phenomenon has been studied extensively by Rivolta[7] who showed that different interference colours on titanium could be obtained in a variety of electrolyte solutions providing the potential was greater than 10V - he concluded that the colours were due to different thicknesses of oxide on grains of different orientation. It should be observed that beryllium gives different interference colours when anodized in chromic acid + nitric acid solutions and Young[21] has suggested that this may be due to local variations in temperature at the high temperatures used or to a variable ohmic p.d. at different parts of the surface. Cadmium behaves similarly when anodized in potassium hydroxide solution at low current densities and it may be significant that c.p. hex metals are particularly prone to show this behaviour.

For the purpose of the present discussion it is assumed that the interference colours are a manifestation of oxides of different thicknesses on different grains. If this phenomena is due to epitaxy it is also likely that the oxide thickness is variable even when the film is colourless, i.e. at potentials $<$ 10V.

The presence of 'mounds' on the surface of the oxide at potentials $>$ 9V has been demonstrated by electron microscopy and it would appear that mound rupture occurs at a potential which corresponds with the initiation of micropitting ($\sim$45V). Presumably each ruptured mound is the site of an extremely small pit and with passage of charge these pits coalesce to give micropits. No evidence can be submitted at

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There can be no doubt that most oxide films on metals are under stress and the Pilling and Bedworth rule postulates that the nature of the stress (lateral compression or lateral tension) will depend on the volume ratio. Although there have been numerous studies of stress in oxides produced by high temperature oxidation there is little information on stresses in anodic oxides. The volume ratio for TiO_2 (anatase) is 1.78 and studies of anodic oxide formation of titanium by Hass[22] has shown that oxygen ions diffuse inwards to the metal oxide interface so that the new oxide builds up at the metal/metal oxide interface. Under these circumstances, and providing the oxide is uniform in thickness, the oxide will be in lateral compression. If the plasticity of the oxide is insufficient to relieve these stresses, film cracking or void formation is to be anticipated. Several workers have observed that films produced anodically on titanium are cracked.

Cathcart, Campbell and Smith[23] have observed blister formation during oxidation of niobium at 400°C - at this temperature breakdown occurred after 300 min. and the rate changed from parabolic to linear. Marker studies showed that the oxide formed at the oxide/metal interface and it was concluded that oxygen ions diffused inwards. They considered that when a segment of the metal lattice at the interface was converted to oxide, a 3-dimensional expansion of the metal lattice was required to bring metal ions into the oxide lattice, and this was resisted by the overlying layers of previously formed oxide with consequent blister formation. Thus oxidation continually produces stresses in the oxide.

Jenkins[24] has suggested a similar mechanism to explain a change from a decreasing rate to a linear rate at 650° when the oxide was found to consist of layers which had been twisted and shattered. This transformation was considered to be due to growth stresses which, when the oxide had attained a certain thickness, partially shattered the outer layers.

From the above discussion it is possible to suggest a mechanism for micropitting based on film rupture of the thinner layers of oxide due to unequal growth rates of oxide on different grains.

Fig.12(a) represents three grains of different orientation with a very thin air-formed film (this is not necessarily uniform) and Fig.12(b) shows the different thicknesses of oxide after anodizing to the potential where different interference colours become evident. Fig. 12(c) shows that any expansion of the thinner oxide is constrained by the more rapidly growing oxides. Although the orientation of the grain will be the dominating factor in the initial growth of the film it will become of less significance as the films thicken owing to the higher ohmic p.d. through the thicker oxides. This will result in a higher ionic current through the thinner oxide which will now start to grow more rapidly. The combined effect of the concentration of the current on g_B and the constraint produced by the surrounding thicker oxide will result in the development of a high stress in the oxide on g_B and eventual detachment of the oxide from the metal surface with the formation of a blister, (Fig.12(d).

This mechanical interpretation of the mechanism of blister formation is in accord with the observations that pitting occurs initially on the thinner grains. It also explains the random and uniform distribution of the pits resulting from the random distribution of grains of different orientation.

In considering the reason for the ultimate rupture of the blisters (Fig.12(e) it should be noted that blister formation occurs in the anodizing region, but even at elevated temperatures there is no evidence of blister rupture. This suggests that blister formation depends on the concentration of formic acid. It is possible that micro-fissures form when the blisters attain a certain size, which corresponds with the breakdown potential of $\sim$ 45V, and that acid is drawn into the void so that it comes into contact with the underlying metal surface (which may be bare of filmed with a very thin oxide). In the micropitting region this will result in reaction with the metal and the gas pressure may be sufficient torupture the blisters. In the anodizing region, although the blisters may be penetrated by the acid, contact with the underlying metal will result in further oxide formation.

V-t Curves in the Micropitting Region

Plateau formation (7 - 12V) A change in the slope or a plateau in the V-t curve at constant current usually represents a change in the magnitude of the ionic current which results from some chemical or physical transformation of the oxide. Thus in the case of niobium there is a slight change of slope at 20V (probably due to a change in chemical nature) and a pronounced plateau at ∼75V which is due to the field crystallization of the initially-formed amorphous oxide.[25]

It has been shown that providing the rate of formation of the oxide is slow, the V-t curves for titanium are characterized by a sudden decrease in the rate of oxide formation and that this persists over 7 - 12V (Figs.3 and 4). This phenomenon is not confined to formic acid and occurs with the majority of the solutions studied (Fig.10). No definite evidence can be submitted to explain this change in rate as identification of the nature of the oxide at this thickness is extremely difficult. It may, however, be significant that blister formation on the surface is first observed at ∼9V so that it is possible that the plateaux may be connected with this phenomenon.

Oscillations of potential and propagation of pits
Above the breakdown potential the V-t curves are characterized in all cases by oscillations of potential and a gradual increase of potential and as the pits propagate into the metal, the amplitude of the oscillations increases. Oscillations of potential were observed by Muller[26] during the anodic oxidation of formic acid on a platinum anode and more recently by Buck and Griffith[27] using chronopotentiostatic techniques. The latter were able to postulate a mechanism for the oxidation of formate in basic solutions but not in acid or neutral solutions.

The mechanism of pitting by chlorides is still not fully understood, but many theories postulate specific adsorption followed by complex formation. There is no information on the nature of titanium/formate complexes and in any case it would appear from the present study that complexes formed at the metal/solution interface within the pits are immediately hydrolysed when the complex diffuses into the bulk solution.

The stability of titanium is due to passivity and an all-important effect of the adsorbed formate anion may be to prevent adsorption of water or hydroxyl - there is considerable evidence for the adsorption of formic acid and formate on metal surfaces and, in particular, on specific crystal faces. There are certain resemblances between the behaviour of formic acid and formates in cathodic processes and some of the phenomena observed in the present work. Thus Prall and Shreir[28] have shown that formates and formic acid reduce the activation overpotential for discharge of copper from copper sulphate solution and modify the crystal structure giving pronounced platelets. This may result from specific adsorption of formate ions on the (111) plane - a plane which requires the highest activation energy for the discharge process - so that no deposition occurs on this plane. Crocker and Robertson[29] have shown the activation energy for decomposition of formic acid on faces of single crystals of copper is greatest on the (111) face.

It is possible, therefore, that within the pit the formate anion adsorbs on specific crystal faces (possibly (111)) and prevents adsorption of water or hydroxyl - a step which is a necessary perequisite for oxide formation.

Although the oxidation of formic acid on platinum is accompanied by oscillations in potential this is unlikely to be a major cause of the oscillations observed in the present study. Oscillation of potential have been observed to occur during the anodic polarization of titanium in chloride solutions and it is considered, therefore, that these result from the geometry of pit rather than from the specific nature of the anion. The fact that the magnitude of the oscillations of potential increases as the pits propagate into the metal gives support to this view.

The ohmic potential of the solution permeating the pit will be markedly increased by the presence of gas bubbles (carbon-dioxide from the oxidation of formic acid and oxygen from the oxidation of water) and by the presence of precipitated titanium hydroxide resulting from hydrolyses of complexes - dispersal of these species into the bulk solution will result in a fall in potential. In addition, fluctuations of concentration polarization are likely under the conditions prevailing within the pit. It is apparent that as the pit length increases the effect of these factors will become more pronounced with a consequent increase in the magnitude of the oscillations. It should be noted that actual oscillations recorded must be regarded as a statistical integration of the changes of the ohmic potential and concentration polarization occurring at the individual pits.

<u>Nature of formic acid in relation to micropitting, anodizing and uniform corrosion</u> The relationship between the nature of the electrolyte solution and the anodic behaviour of a metal is not fully understood so that the following discussion must be largely speculative. The different effects observed are clearly dependant on changes in the nature of formic acid solutions in water at different concentrations of acid. As the concentration of acid increases it is apparent that the concentra-

tion of undissociated molecules (or ion pairs) will increase and that, in addition, there will be a pronounced tendency for the molecules to form dimers - it also follows that the concentration of water will decrease.

At low concentrations, complex formation rather than oxide formation may be the energetically and kinetically favourable process - it is highly probable that this is preceded by adsorption of formate onto the metal surface (or metal surface filmed with a thin oxide) so that adsorption of water (the oxide favouring species) is prevented. These complexes diffuse away from the metal/solution interface and then react with water giving a precipitate of titanium hydroxide in the bulk solution. The formate anion appears to be the species that is active in complex formation as it has been shown that micropitting occurs over a range of pH. It should also be noted that the minimum breakdown potential occurs at 30% formic acid - a concentration which has the highest conductivity. At 50% formic acid the acid may be predominantly in the form of diners which do not adsorb so readily on the metal surface so that adsorption of water and the subsequent direct transfer of metal ions onto the lattice of the oxide (anodizing) is the preferred process.

At very high concentrations of acid (general attack) the activity of water is so low that preferential adsorption of diners of formic acid is now possible. In this case it would appear that the complex is hydrolysed as soon as it is formed giving a loosely adherent precipitate on the metal surface.

FUTURE WORK

The mechanism of micropitting of titanium is still not fully understood and further studies are in progress in which use will be made of capacity measurements. The metal will be anodically polarized to a predetermined potential and changes in capacity with time will be measured to detect formation of cracks or discontinuities in the film.

Further studies of blister formation in the anodizing region will be of interest and electron micrographs will be prepared over a range of potentials. It would be of interest to determine the potential at which the oxide crystallizes. Previous studies using electron diffraction have not been successful, but this aspect justifies further study.

No further work is contemplated on formic acid but additions of formaldehyde to sulphate solutions would be of interest. There is some evidence that traces of methane might produce micropitting under anodic conditions.

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FIG. 1 Cell used for anodizing

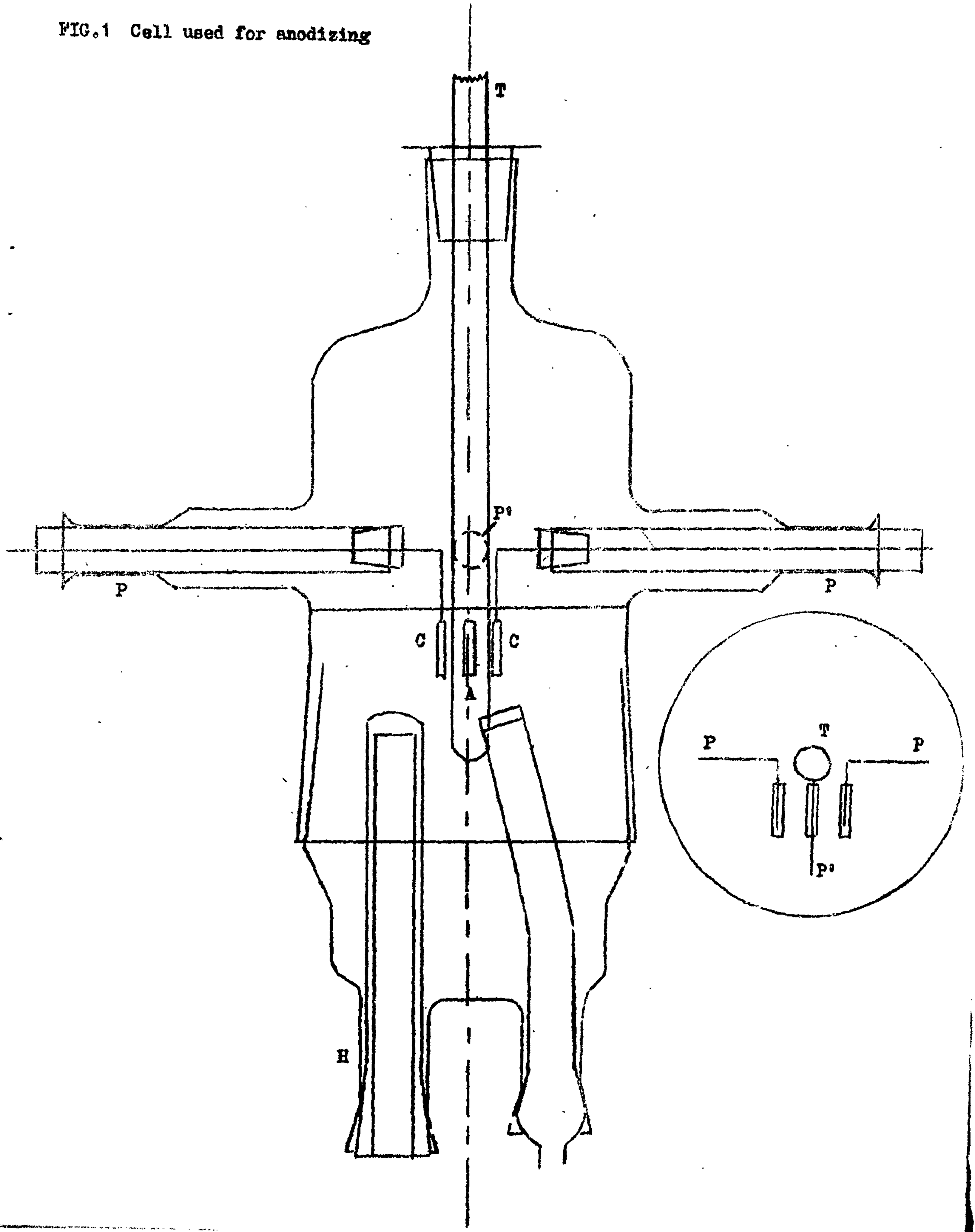
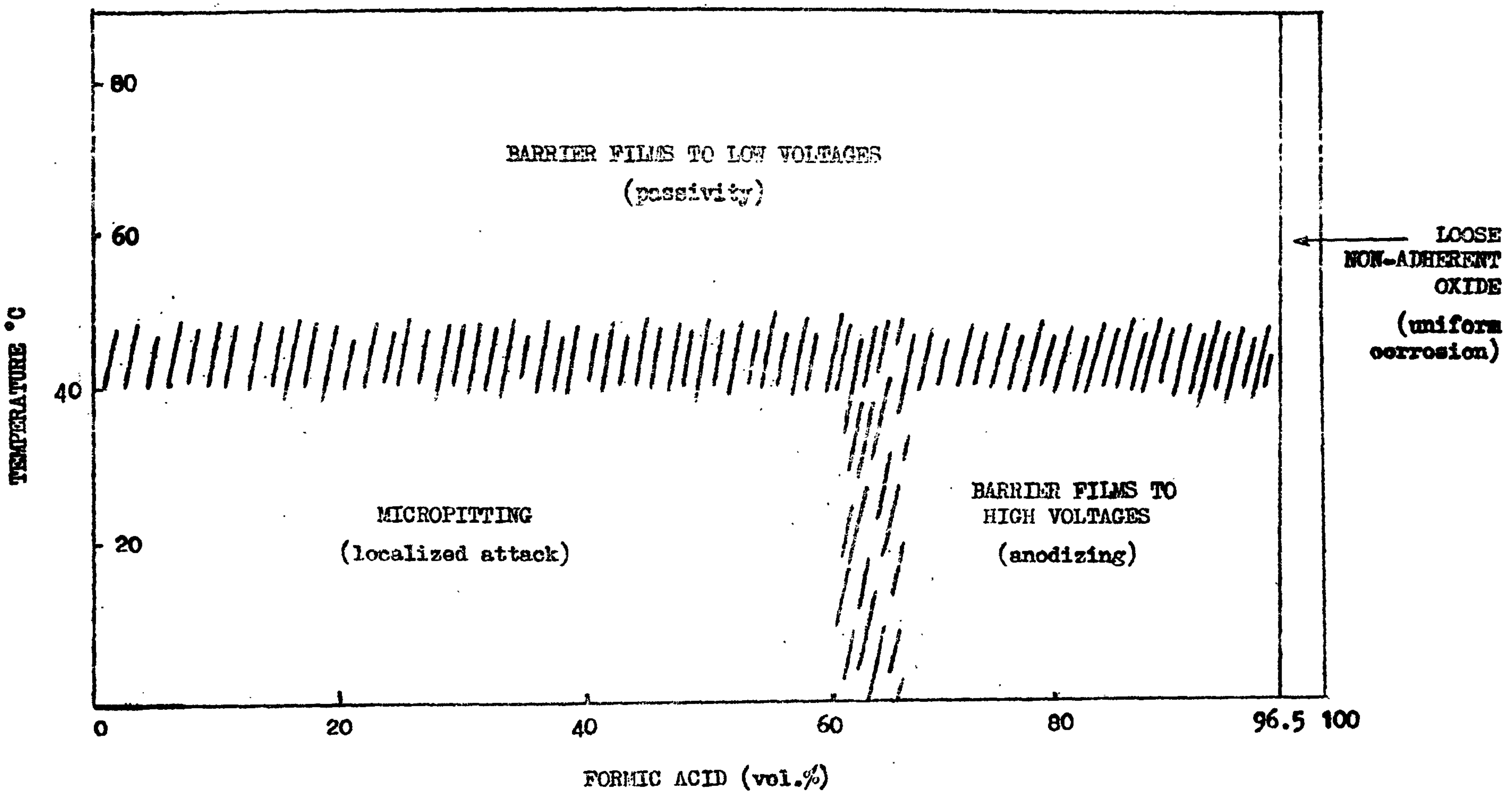


FIG.2 Effect of concentration and temperature



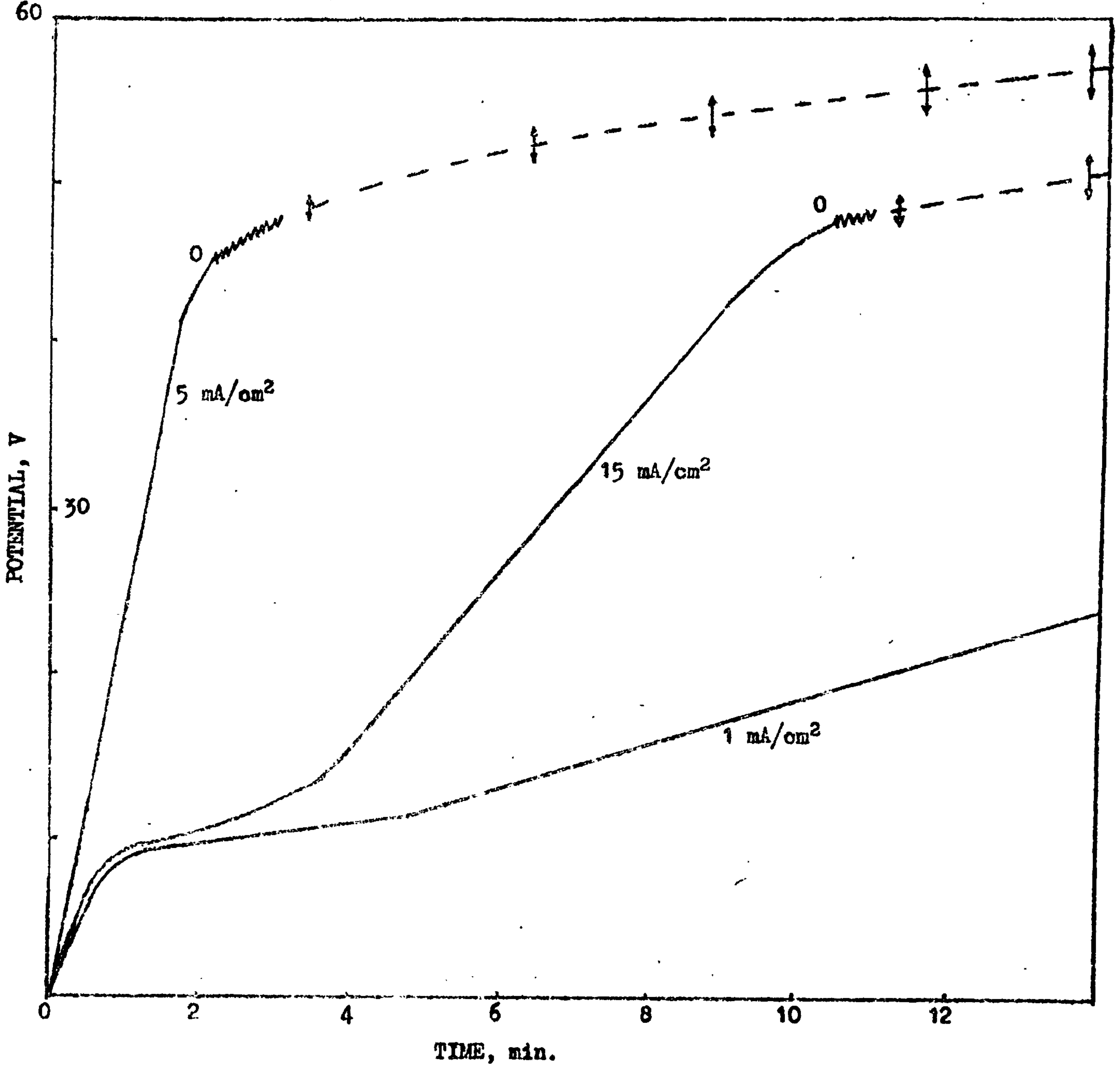


FIG.3 V-t curves at different current densities

FIG.4 V-t curves at different concentrations of acid

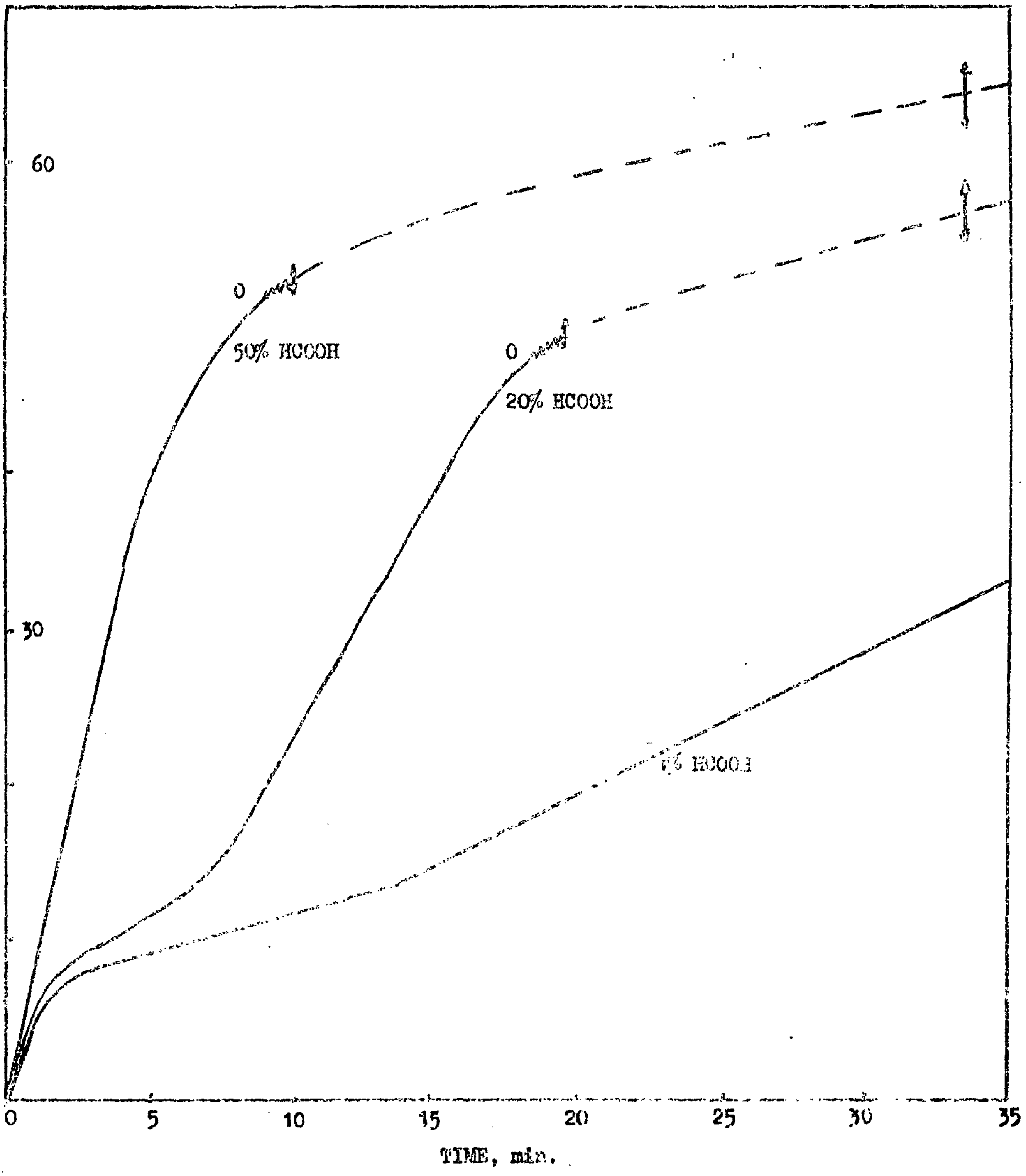


FIG.5 Breakdown potential at different concentrations of acid

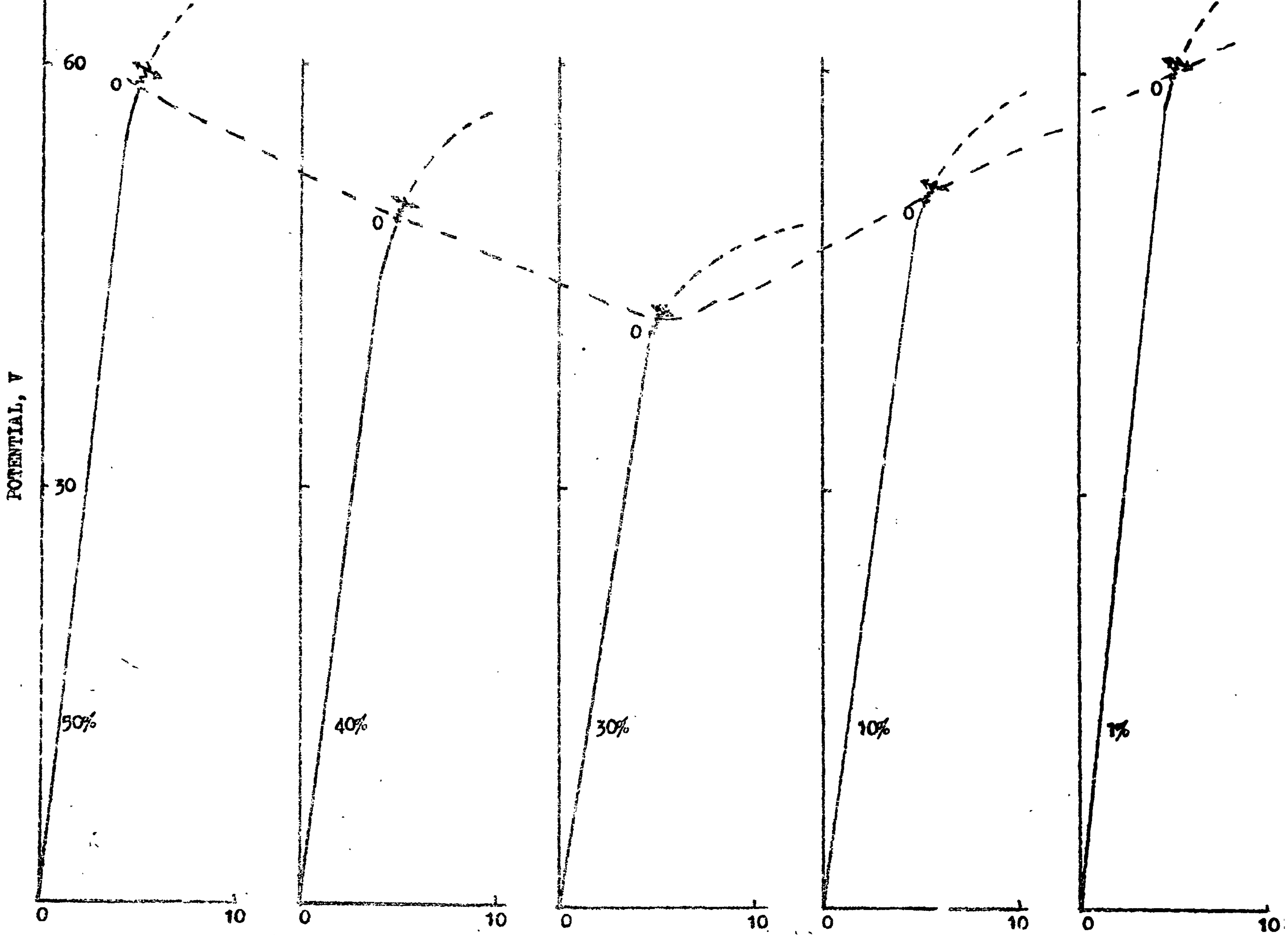


FIG.6 Effect of temperature

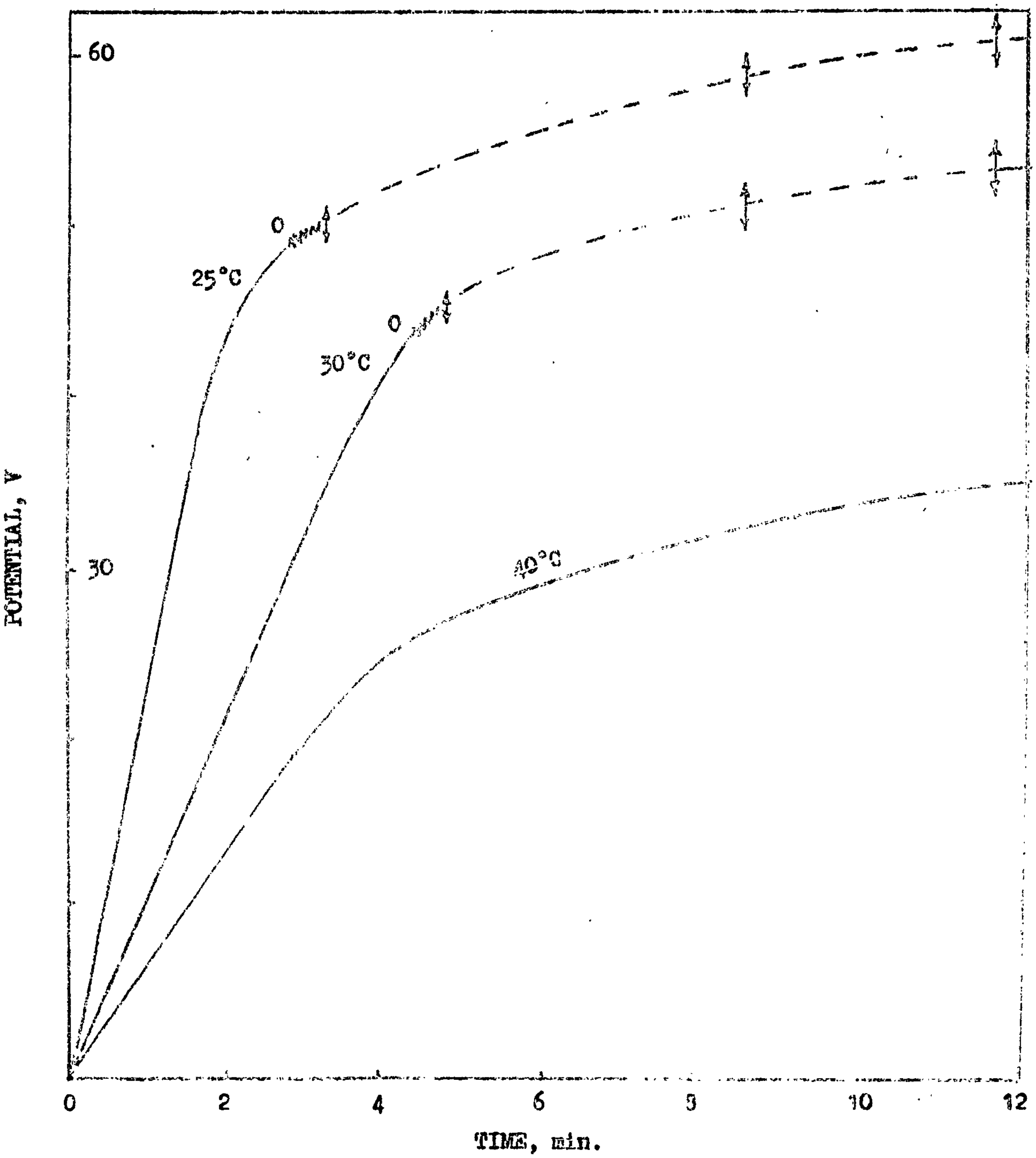


FIG.7 V-t curves in the anodising region

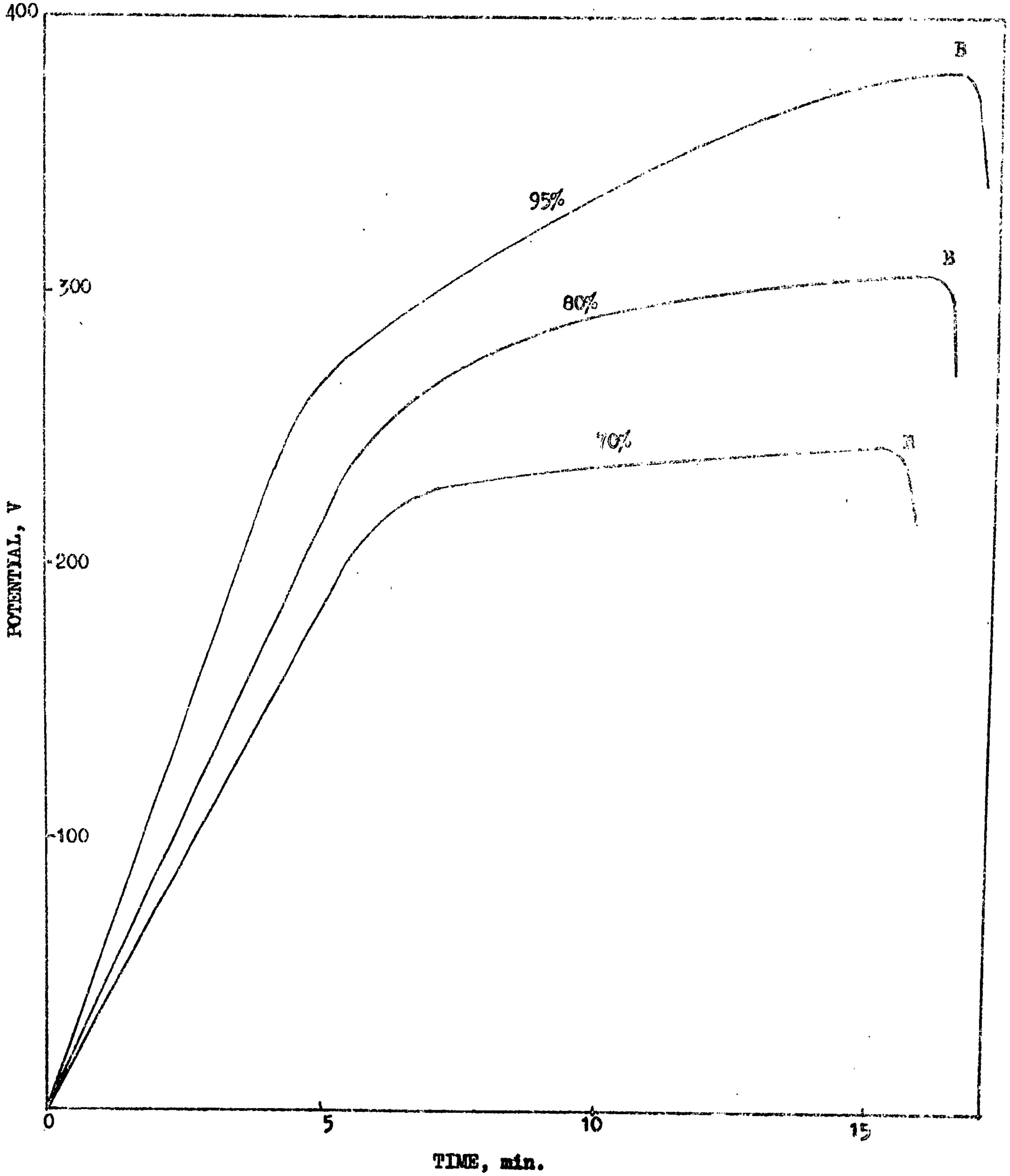


FIG.8 Effect of temperature on V-t curves in anodising region

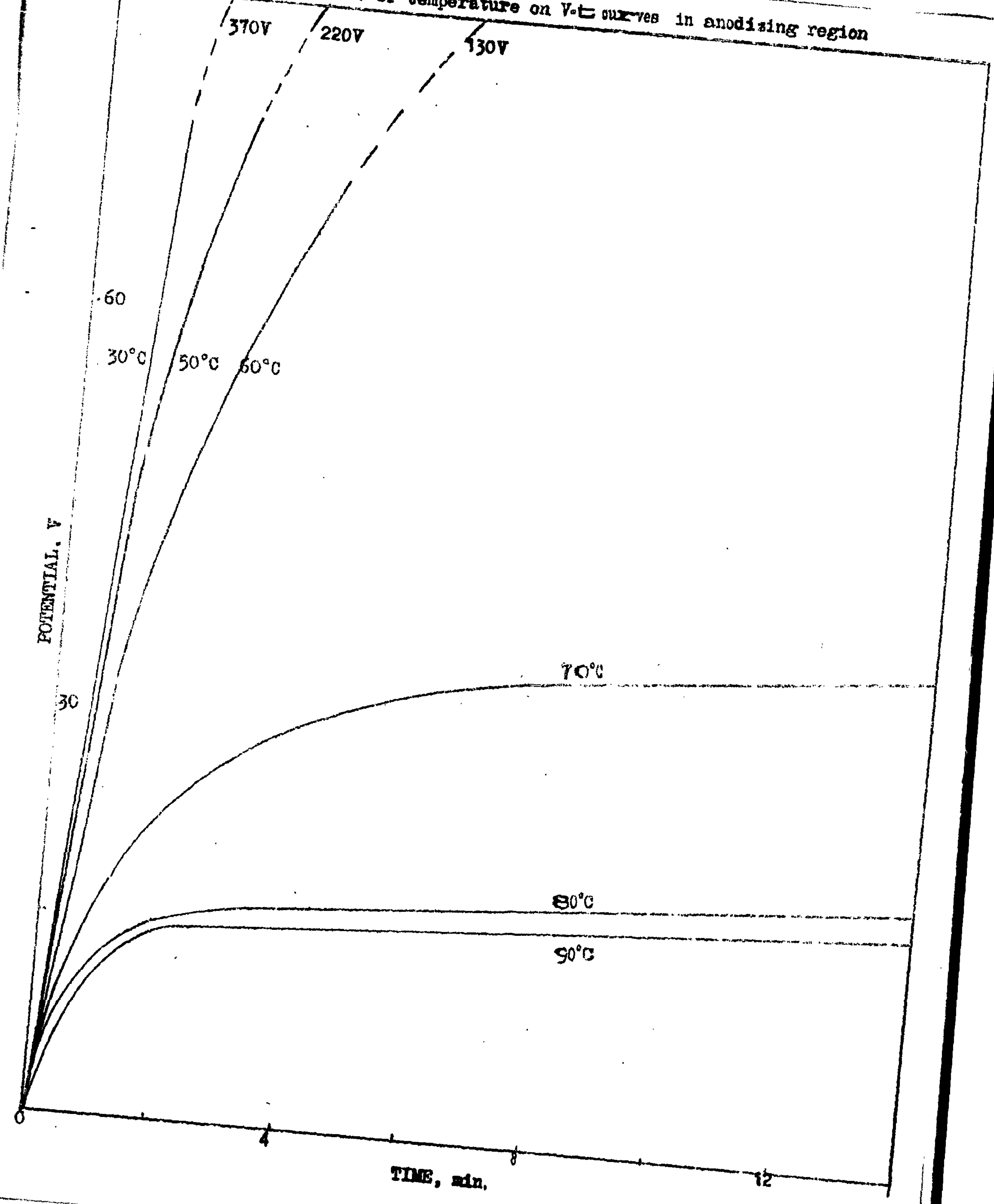


FIG.9 Plateau formation in formic acid

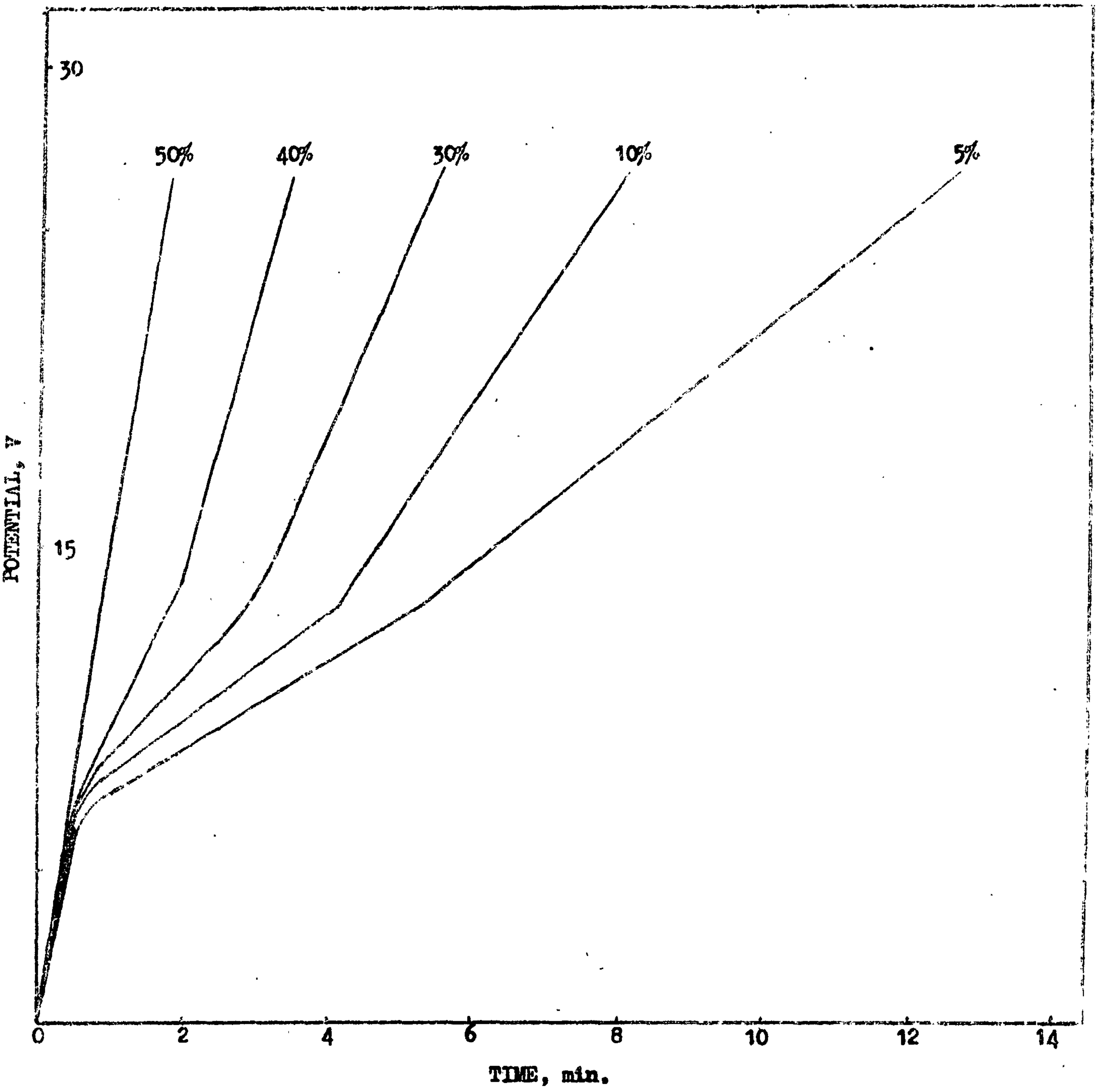


FIG.10 Plateau formation in different solutions

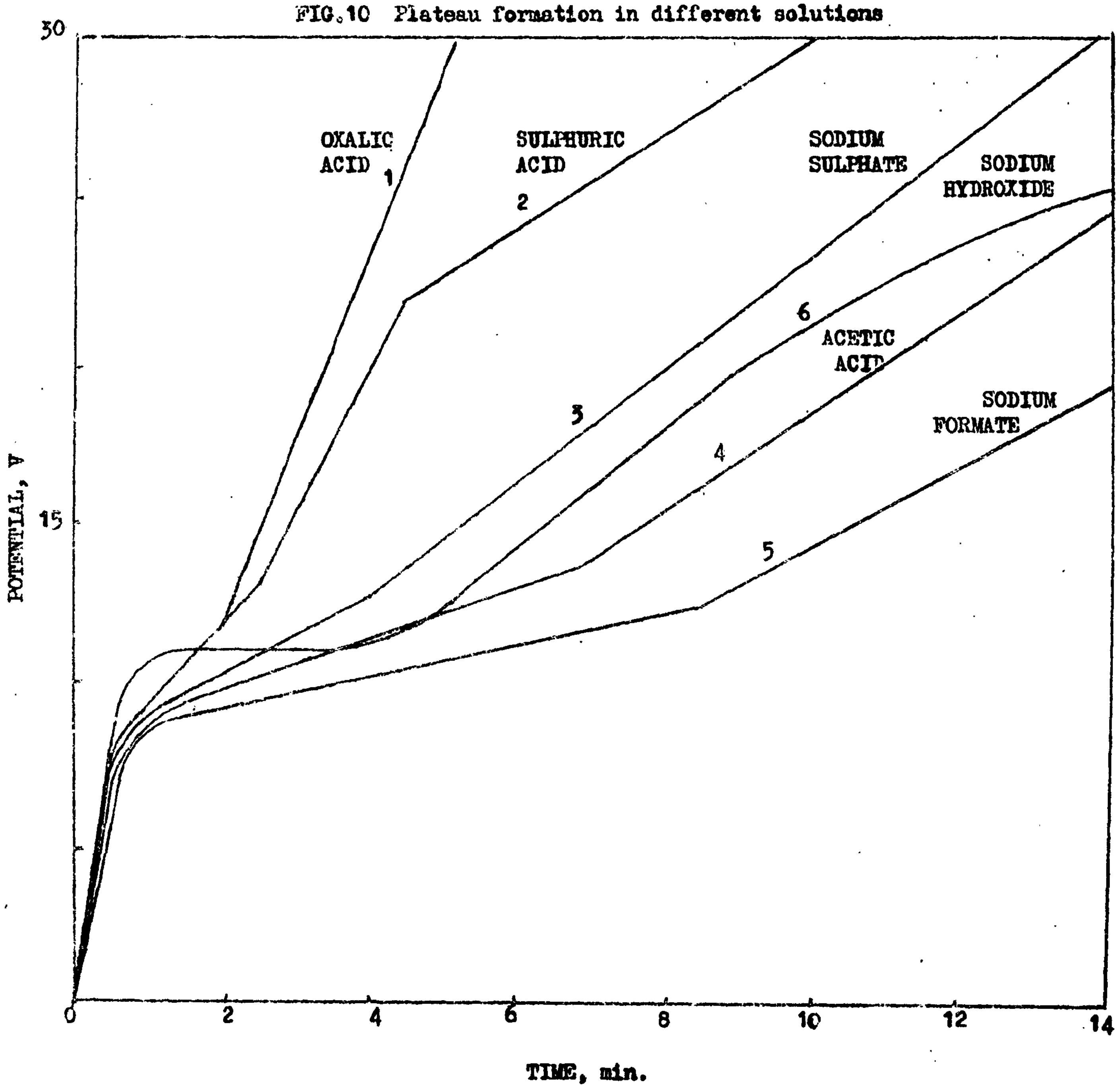
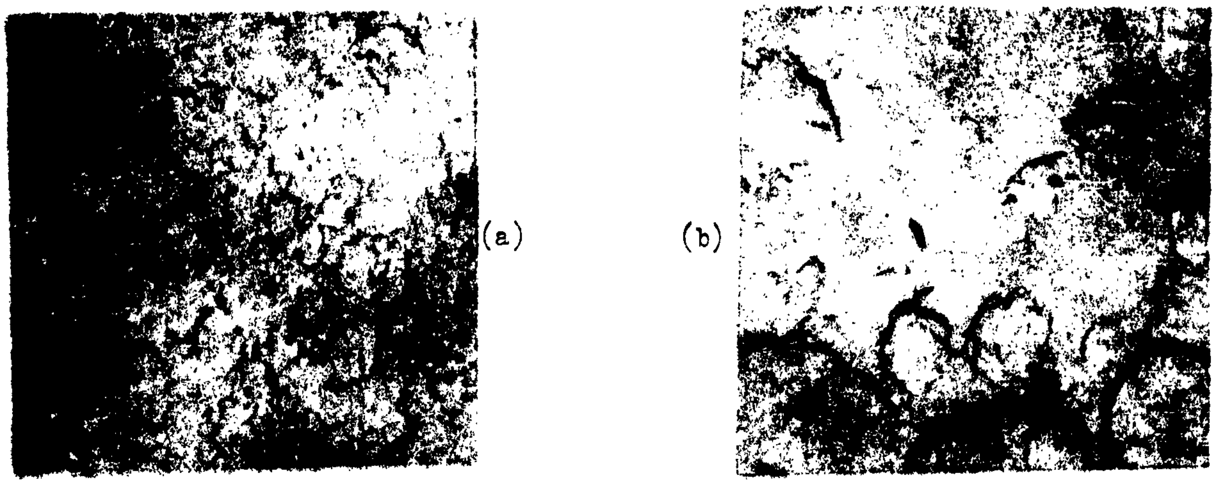


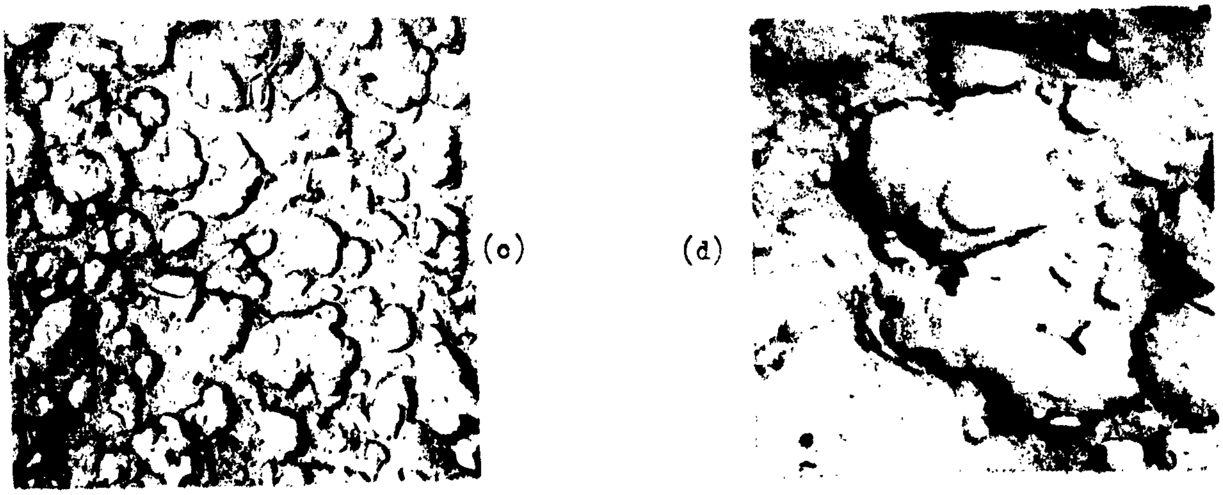
FIG.11

ELECTRON MICROGRAPHS OF THE ANODIC FILM FORMED ON TITANIUM IN 10% FORMIC ACID SOLUTION.



15V FILM X 12000

30V FILM X 12000



50V FILM X 4000

50V FILM X 12000

FIG.11


(e)

55V FILM X 12000


(f)

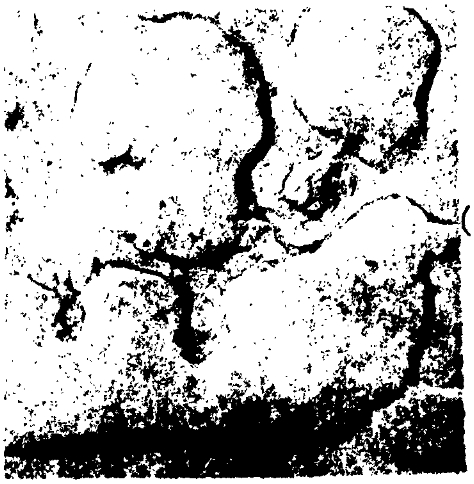
60V FILM X 12000


(g)

PIT FORMED AT 65 V X 12000

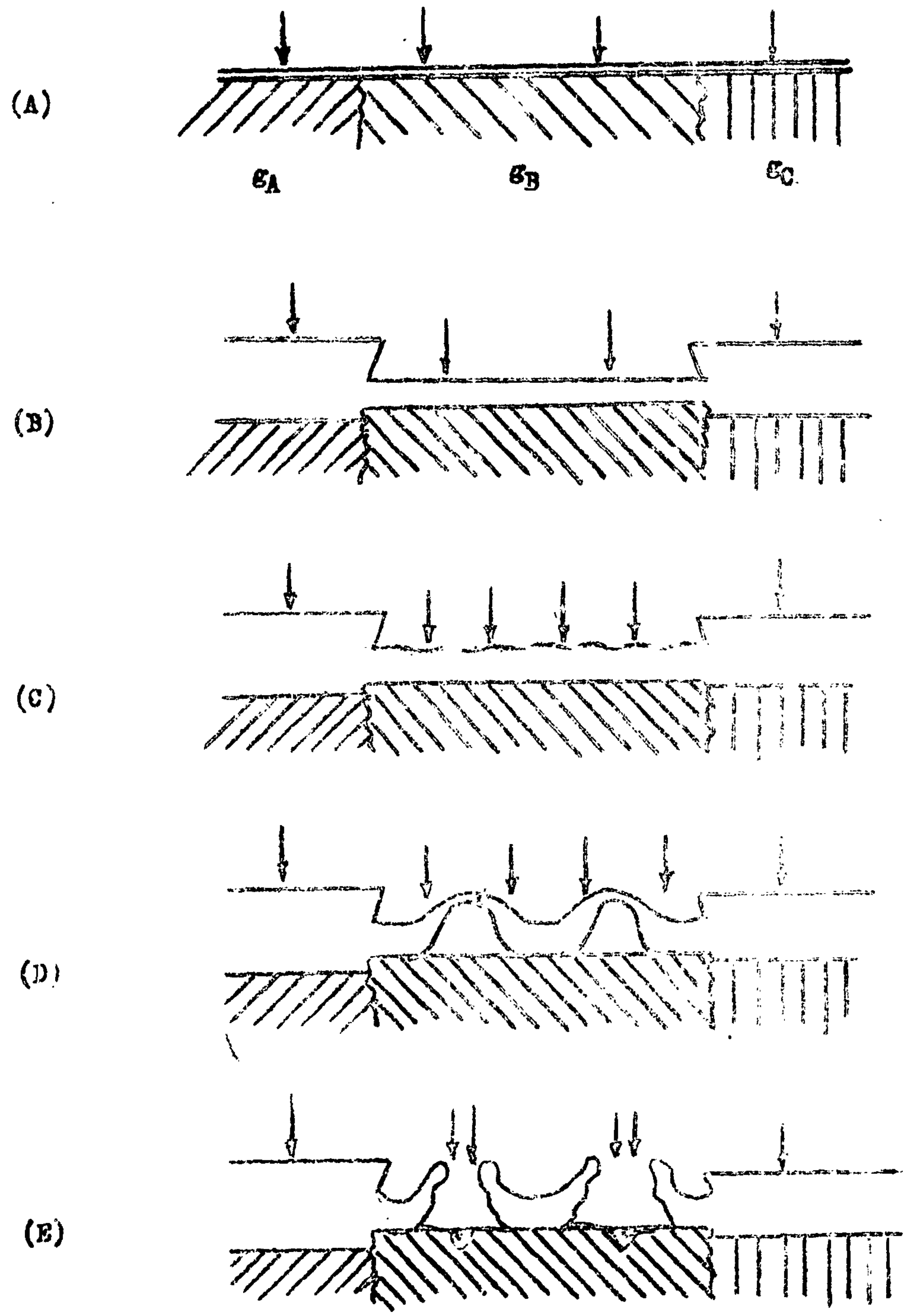

(h)

PIT EDGE AT 65V X 12000


(i)

75V FILM IN 90% HCOOH X 12000

FIG.12 Mechanism of blister formation and pitting



EXPENDITURE

Personnel:	H. LECKIE	(not supported by Contract)	
	K. MONDEL	(Laboratory Assistant)	£500

Apparatus:	Power unit	£ 50
	Recorder	£200
	Valve Voltmeter	£100