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S. T R. NO 568

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE.

REPORT NO. 3.

REVIEW ON Sept. 80

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TORPEDO EXPERIMENTAL ESTABLISHMENT, GREENOCK

S.T.R. No. 568
September, 1950

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE

REPORT NO. 3

(P. T. Corbyn)

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STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE

REPORT NO. 3

(P.T. Corbyn)

List of Contents

Figures /

Figures:

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S.T.R. No. 568
September, 1950

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE

REPORT NO. 3

(P.T. Corbyn)

SUMMARY

Metallic couples, selected from aluminium, two light alloys, three stainless steels and tin, were immersed in T.L. H.T.P. (sodium stannate stabilised) at room temperature for periods of up to eight months. In all cases attack above the surface was initially more marked than below the surface, in which respect aluminium was the least satisfactory. Electrochemical attack occurred below the surface and was very marked in the case of tin and aluminium. The behaviour of the three stainless steels examined under these and also under tropical conditions, suggests that they should not be used as constructional materials for H.T.P. containers.

1. INTRODUCTION

From a study made some twelve months ago of available reports, it appeared that little experimental work had been carried out on metallic couples in H.T.P. Wood and Lovell's comprehensive bibliography (Ref. 1) made no specific reference to work of this nature, but recognised the necessity for such an investigation (Page 12). Occasional tests had appeared in other reports. Board (Ref. 2) referred to a couple between an Aluminium/Magnesium Alloy (F.L. W. 3310) and Birmabright 2 in T.L. H.T.P. and observed evidence similar to that reported below, but over shorter periods. Further results on the same materials have been reported more recently (Ref. 3). Two combinations S.80 (=V.28) with L.34 (commercially pure aluminium) and L.33 (13% silicon alloy) have been examined by Mikolajowski and Murray (Ref. 4). Enhanced decomposition and vapour phase corrosion with T.S. H.T.P. (Phosphoric acid stabilised) was reported. Cooper and Forbes have recently reported (Ref. 5 and 19) the effect of H.T.P. stabilised by various methods (including stannate stabilisation) on couples composed of aluminium with a 7% magnesium alloy and aluminium with F.M.B. (18/8 stainless steel plus molybdenum). Corrosion after 60 days was very slight. Becco (Ref. 6) examined the effect of coupling 99.7% pure aluminium with type 321 stainless steel (19% chromium, 11% nickel) in the presence of unstabilised, and phosphate stabilised, hydrogen peroxide. The aluminium tended to corrode and corrosion of both metals was more noticeable in the presence of unstabilised hydrogen peroxide.

Published information is obviously very limited in scope and refers to only a few specific materials. It has become increasingly clear here and elsewhere (Refs. 2, 3 and Appendix 3 of Ref. 5) that T.L. hydrogen peroxide is probably more corrosive than T.S. hydrogen peroxide, and that a study of vapour phase corrosion and corrosion of metallic couples in T.L. hydrogen peroxide is required. It was indicated at D.A.E.R.'s informal meeting on 8/8/49 (P.G. 2.213, P.G. 2(B) 47 Minute 1.3) that such work was contemplated and the report below reviews the results to date.

As /

As the immediate intention was to obtain data on which to base the design of torpedo components and containers, investigation was limited to the following materials of interest in this respect:-

(a) Aluminium alloys

S.T.A.7/A3 (commercially pure aluminium)

S.T.A.7/AC10 (10% magnesium)

S.T.A.7/AW10 (0.6% magnesium 1% silicon)

(b) Stainless Steels

S.T.A.5/V25 (13% chromium 1% nickel)

S.T.A.5/V27 (18% chromium 8% nickel)

S.T.A.5/V28 (18% chromium 2% nickel)

(c) Pure tin

Analyses of the actual batches of materials employed are given in Table 1 and analysis of the H.T.P. is given in Table 2. The H.T.P. was supplied as T.L. grade, but the tin content was probably very low.

2. EXPERIMENTAL WORK

The general arrangement of the first eighteen couples can be seen in Figure 15. The electrodes consisted of accurately turned $\frac{1}{2}$" diameter rods, with the immersed end hemispherical in shape to eliminate edge effects. The tin electrodes were initially cast in test tubes and then turned to the final diameter. The electrodes were suspended by thick aluminium wires from terminals arranged in pairs, each alternate pair being shorted by an aluminium strip. Each pair of electrodes passed through a pliable P.V.C. cap into a 250 ml. tall form pyrex beaker containing a definite quantity (170 mls.) of T.L. H.T.P. The following volume to surface ratios obtained -

Volume of H.T.P./immersed surface area of specimen = 8.3 cms.

Volume of H.T.P./surface area of specimen exposed to vapour = 9.7 cms.

Area of surface of H.T.P./surface area of specimen exposed to vapour = 1.45

The caps **were** moulded from a P.V.C. paste and fitted tightly over the rim of the beaker and round the electrodes. A third hole loosely closed with a P. V.C. plug was used for sampling. This type of closure is regarded as essential in long term tests to prevent the ingress of air-borne dust and fumes. It was noticeable that, even in the isolated laboratory where the couples were standing, the outside of the beakers became contaminated. The fourth couple developed a split in the P.V.C. cap some time after commencement and, although temporarily covered with a P.V.C. sheet, the early onset of corrosion and the relatively rapid fall in concentration were attributed partly to ingress of air-borne dust.

The following pickling and passivating processes were applied to the various materials before use :-

(a) /

(a) A3 and AW10

Degrease in trichlorethylene vapour. Half minute hot (140°F (60°C)) 2% caustic soda. 24 hours 1:1 nitric acid (1 volume concentrated nitric acid to 1 volume of water). Wash well. Stand in warm distilled water half an hour. Allow to drain.

(b) AC10

Degrease in trichlorethylene vapour. Half minute hot 2% caustic soda. Four hours 1:1 nitric acid. Wash well. Stand in warm distilled water half an hour. Allow to drain.

(c) Stainless Steels

Degrease in trichlorethylene vapour. Half hour boiling 10% caustic soda. 24 hours concentrated nitric acid. Wash well. Stand in distilled water half an hour. Allow to drain.

(d) Tin

Stand in white fuming nitric acid for 16/17 hours. Wash in warm 5% sodium carbonate for three hours. Stand in warm distilled water one hour. Allow to drain.

The appearance of the specimen after pickling was as follows:-

(a) A3

Couples 1 - 6: very pale brown matt surface. Couples 19 and 20: very pale brown in patches, with remainder white matt surface.

(b) AW10

Uniform very pale brown matt surface.

(c) AC10

Couples 7 to 12: matt white surface except for ends showing red-brown streaks. Couples 21, 22: uniform specked red-brown. This speckling is associated with the heat treatment and does not appear to affect compatibility adversely. On the contrary, it appears to improve both compatibility and corrosion resistance. The localisation of the effect in the first group of electrodes was caused by gravitation of "spent" acid to the bottom of the pickling vessel. Subsequently the bath was stirred at intervals.

(d) Stainless Steels

Clear, bright surface.

(e) Tin

Dull surface. Black oxide spots where small pits occurred in the casting. Faint brown film over parts of the surface.

Table 3 gives a complete list of the couples studied. Briefly, the arrangement was as follows:-

A3 /

A3, AW10 and AC10 were each coupled with V25, V27 and V28. Each couple e.g. A3 and V25, was duplicated, one of the duplicates carrying an external connection to complete the electro-chemical circuit. By this means, it was hoped that the unconnected pair would act as a control for the pair with the completed circuit. A later proposal that tin should be used for bursting discs necessitated the study of possible combinations of tin and other structural materials. Accordingly, duplicate pairs of couples were made from tin with A3, AW10, AC10, V25, V27 and V28.

The original physical condition of the materials is of some importance and is given in Table 1. It has been found from other H.T.P. corrosion studies carried out at this establishment - in particular on S.T.A.7/AC8 (5% silicon 0.5% magnesium) - that heat treatment may make a profound difference to the compatibility and corrosion resistance of the alloy. In particular, AW10 should be fully heat treated and AC10 precipitation hardened and solution treated. Attention is drawn to the fact that the carbon content of the stainless steels is somewhat low, a factor which probably also contributes to their corrosion resistance. (Cf ref. .1. Chromium steels). For example, a sample of V25 steel containing 0.28% carbon, pickled and passivated as above, tended to rust superficially during washing after passivation, whereas no trouble was experienced with the V25 steel containing 0.18% and 0.19% carbon.

The beakers were taken from stock, washed and then allowed to stand filled with concentrated nitric acid for several days before use. Over-elaborate surface treatments of glassware appear neither necessary nor desirable for tests of this nature. The plastic caps were allowed to stand in dilute hydrochloric acid for several hours and then in distilled water. Both caps and beakers were oven dried before use, the latter being inverted to prevent ingress of dust.

The tests were carried out at ambient temperatures between 57°F and 72°F (14 to 22°C), averaging about 64°F (18°C). Compatibility and corrosion resistance of aluminium and these light alloys, at elevated temperatures (140°F (60°C)) have been reported previously (Refs. 7 and 8). Tests on stainless steels have also been carried out at these temperatures (see Appendix 1). They show these steels to be virtually useless under certain conditions because of rapid chromium extraction. These results agree substantially with the findings of Beard (Ref. 3 and 20) but extend the study to the examination of various surface treatments. Correct pickling treatment can reduce chromium extraction, but appears unable to eliminate it completely.

Concentration changes in the solution were followed at intervals by removing a small sample and titrating with $\frac{N}{2}$ potassium permanganate. The potential difference between the two electrodes was measured with a valve voltmeter on filling the beakers, 2 hours later, 19 hours later, 26 hours later, after 2 days, 3 days, and 6 days, and thereafter at weekly intervals. It was found in practice that, after removal of a short, the E.M.F. rose relatively slowly and, in time, would probably have reached a value similar to its partner. Accordingly, the E.M.F's of the couples with external connections, i.e. Nos. 1, 3, 5, etc. were taken arbitrarily 30 seconds after removal of the short. The visual appearance of the specimens was also recorded from time to time.

Light was not excluded, but, as far as possible, all beakers in each of the two groups 1 - 18 and 19 - 30 were illuminated equally. The second group received light directly from an East window, whereas the first group was illuminated obliquely. The difference in rate of fall in concentration of the blanks in the two groups probably arises from this cause (Ref. 8).

3. RESULTS

The first 18 couples were immersed for 36 weeks and the remaining 12 (tin couples) for 20 weeks. By this time, the concentration had fallen in several cases to below 10% and there appeared no point in continuing the tests. The appearance of the couples at the ends of these periods can be seen from Figs. 1 - 8 and the associated changes in concentration and potential difference from the graphs (Figs. 9 - 13). Concentration changes in the "blanks" appear in Figure 14.

(a) Concentration Changes

The rate of fall in concentration was initially quite slow in most cases, but gradually accelerated, causing the graph to approach the horizontal axis more rapidly. In the first six couples (aluminium/stainless steels), notwithstanding the considerable sediment, no very rapid increase in decomposition occurred. The corrosion products of pure aluminium are only slightly catalytic. In the case of No. 19, where the solution at the end had the consistency of paste, the rate of fall was naturally very much higher. In Couples 7 to 12 (AC10/stainless steels) and 13 to 18 (AW10/stainless steels) the fall in concentration was usually more rapid as these alloys are not quite so compatible with H.T.P. as aluminium and the corrosion products are probably more catalytic. Generally decomposition at the steel electrode appeared more pronounced than decomposition at the alloy or tin electrode and, in one case where the steel corroded below the surface, (No. 25: a large number of small spots can be seen) concentration fell very rapidly. The rapid fall in concentration of No. 23 (AW10/Tin) commenced when corrosion started below the surface. It is noticeable that all the tin/steel couples (Nos. 25 to 30) lost strength very rapidly and that, as mentioned above, the "blanks", associated with the second group of trials (Nos. 19 to 30), lost strength more rapidly than the first "blank".

(b) Potential Difference

The initial polarity of the couples is indicated in Figs. 9 - 14 and the usual convention as regards sign is adopted. The potentials were measured with a Cambridge Ph meter, used as a millivolt-meter, and the positive sign indicates that this electrode was connected to the positive terminal of the instrument. In drawing the graphs, Nos. 1 to 18 have scales from ±0 to + 0.8 volts, No. 19 and No. 23 (with high negative values) from - 0.8 to ± 0 volts, and the remainder from - 0.4 to + 0.4 volts. In couples 1 to 18, the steels were positive to their partners except for very slight negative values in a few cases (Nos. 7, 8, 11 and 12) near the commencement. In couples 19 to 30, the tin was negative to the other electrode initially (with the exception of No. 19), but polarity later reversed in all couples with light alloys and with certain of the steels (Nos. 25, 26, 29 and 30). The potential difference, where no external connection is made, rises slowly and more or less uniformly throughout the period of test. This gradual rise may possibly be associated with the gradual fall in concentration. More significance can be attached to the potential difference where the external circuit is complete. In this case, a relatively sudden rise occurs when corrosion of the alloy commences below the surface and, although not immediately visible, inspection a few weeks later usually reveals some surface blemish.

If /

If no corrosion of the connected couple occurs, then the potential difference remains low (Nos. 9 and 21). Although the trend is obvious, once corrosion has commenced, individual values of potential difference may vary considerably, which is perhaps not surprising in view of the incrustation of the surface with corrosion products. In addition temperature was not controlled, but the effect would be small. With regard to the three types of stainless steels, it may be observed that V.27 (18/8) remains consistently positive in all cases, whereas, V.25 and V.28 occasionally become negative. This led to the on-set of corrosion in the case of No. 25. (V.25/Tin) From this and other evidence (see Appendix I) it has generally been concluded that the fully austenitic stainless steels are preferable to others. A comparison of the potential difference and concentration curves reveals no evidence of the on-set of corrosion at a particular concentration or, more generally, at a very low concentration of hydrogen peroxide. If potential difference increases and the external circuit is complete, corrosion of the negative electrode occurs,

(c) Appearance

Tables 4 and 5 give details of the appearance of the electrodes after various intervals of time. The steels remained throughout bright and polished below the liquid surface (except No. 25) and oxidised superficially up to 1" above the surface producing the usual range of "temper" colours. The tin electrodes gradually became a light straw colour below the surface and steel grey above. No noticeable corrosion of the tin occurred. The casting flaws in the tin electrodes, e.g. No. 29, occurred at the top and as they were outside the vessel are irrelevant to the present investigation. The aluminium electrodes commenced to corrode above the surface within two months and later below the surface if connected externally to their partners. No.19 began to corrode both above and below the surface within one month and eventually filled the vessel with a gelatinous precipitate. The AC10 electrodes showed very good resistance both above and below the surface for long periods but, if connected externally, pitted seriously once film breakdown had occurred. The AW10 behaved in a similar manner. Both alloys were better than aluminium as regards corrosion resistance, but poorer in respect of compatibility. In addition, the corrosion products of aluminium are relatively innocuous, as can be seen from the comparatively small falls in concentration even where a considerable quantity of gelatinous precipitate had accummulated.

4. DISCUSSION

It can be seen from the above that corrosive attack above the surface is different in character from corrosion below the surface, due, no doubt, to the nature of the corroding medium. Above the surface, after a relatively short period, the gas phase consists of oxygen saturated with water vapour and hydrogen peroxide vapour. In addition, however, this phase has suspended in it a very fine mist of H.T.P. droplets. The supply of droplets is maintained by the continual gassing of the solution and this type of mist can be seen occasionally like wisps of steam near the access ports of storage tanks.

The liquid phase was nominally T.L. hydrogen peroxide (30 parts per million of hydrated sodium stannate) but probably contained a negligible amount of tin. As a polarograph was not available until the trials were nearly completed, tin could not be determined with any accuracy. Couples

Nos./

Nos. 20 to 30 were however examined polarographically (Ref. 9) for tin in solution at the end of test and, notwithstanding the tin electrodes, no tin was detected (limit of detection under condition of test 1 to 2 parts per million). Samples of T.L. H.T.P. prepared in the laboratory (as described by Wood and Radford (ref. 16)) from unstabilised H.T.P. adjusted with dilute sulphuric acid to an acidity equivalent to 30 mgms. of sulphuric acid per litre have been found to contain no detectable tin after 48 hours in glass containers. (This may be due to insolubility of stannic sulphate see ref. 19 pg. 20). Adjusted with nitric acid in the same manner the tin may or may not remain in solution. Conditions which promote precipitation are not clear, but it seems safer to regard the T.L. H.T.P. used as high purity, stabiliser-free hydrogen peroxide of relatively low acidity and normal nitrate content (10 to 20 parts per million as NO_3). In this respect it may be recalled that both Cooper and Forbes (Ref. 5) and Becco (Ref. 6) found that corrosion of the light alloy component of couples was more pronounced with unstabilised (Becco) hydrogen peroxide than with stabilised samples of peroxide.

(a) Corrosion in the Vapour Phase

Corrosion in the vapour phase has been consistently more marked than corrosion of the fully immersed areas. The atmosphere is not merely oxygenated but is actively oxidising more noticeably up to approximately 1" above the surface. The steels, for example, show a whole series of interference tints, due to oxide film formation (Ref. 10) ranging from yellow, through brown and mauve, to deep blue. As the liquid level falls, rapidly to begin with, then more slowly, due to decomposition, the series may be repeated; compare, for example, the steels in No. 9 (36 weeks) and No. 27 (20 weeks). Normally, these interference colours are not observed at low temperatures on iron. Oxidation in this temperature range probably occurs (Ref. 11) predominantly by diffusion of the oxygen to the substrate, through the initially formed oxide layer, rather than by diffusion of the metal ions outwards to the oxygen, which would thus cause external thickening of the oxide film. At a later stage in these trials bronzing of some of the steels below the surface (notably Nos. 4, 9 and 10) also occurred, presumably due to thickening of the oxide film in contact with the liquid taking place at a much slower rate than in the gas phase.

This heavy and continuous oxidation of the steel suggests a possible mechanism of attack on the aluminium surface. Vernon has shown (Ref. 12) that oxidation of aluminium occurs by periodic rapid increases followed by intervals of very slow change. The oxide film builds up rapidly and then cracks as the volume of the oxide is greater than the volume of the parent metal and the oxide layer, anchored to the substrate, is therefore under compression. Recently Bradshaw and Clarke (Ref. 13) have demonstrated the incidence of this stress in anodised aluminium after sealing (but not before) and suggests that hydration and "plugging" of the pores causes its development. Vapour phase corrosion of the aluminium would appear to occur, therefore, by oxide film formation, "plugging", cracking, followed by further oxidation and a repeat of the cycle. The exfoliated appearance of the corrosion products would tend to support this view. The vapour phase attack on the alloys was of the same general character but was much more localised and appeared to follow definite paths along the surface. As corrosion progressed on the aluminium the

corrosion/

corrosion products reached the peroxide surface, absorbed liquid and became swollen and gelatinous. Eventually the products fell into the liquid and formed a gelatinous layer on the bottom of the container (see Fig. 1, couples 1, 3, 4 and 6, reading from left to right). Corrosion is certainly accelerated by this absorption process, probably by electro-chemical action within the gelatinous layer.

If the above mechanism is correct, the high concentration of oxygen in the gas phase plays a major role in corrosion. Under torpedo conditions, the containers will, in addition, be under slight pressure due to spring loading of the vent valve and conditions could be worse than those obtaining during these trials. In order to test this hypothesis, it is intended to carry out trials in which the atmosphere above the solution is continually purged with filtered air in order to maintain only a low concentration of oxygen.

(b) Corrosion in the Liquid Phase

Corrosion in the liquid phase, when it does occur, is more of an electro-chemical nature. Normally the protective oxide films on both electrodes would offer very high resistance to current flow and the high specific resistance of H.T.P. would also limit its magnitude.

Local surface defects, which are probably always present even in the most carefully prepared specimens, develop, the protective skin is broken and a pit begins to form (see, for example, couples 1, 7 and 13 in particular). At this stage the effect of completing the external circuit becomes very apparent. A glance at the left-hand couple in each of Figs. 1-8 show that breakdown below the surface has only occurred where the circuit is complete. Even in No. 20 where the pickling procedure left a (visually) non-uniform surface, no attack below the surface has occurred, whereas, this non-uniformity almost certainly contributed to the rapid corrosion of No. 19. In a qualitative manner, the incidence of corrosion below the surface is indicated by a rise in the potential difference to a high value. The relatively sudden rise in certain cases is probably due to breakdown of the protective film at that particular time. There is thus little doubt that coupling of different metals in H.T.P. can lead to serious corrosion. Coupling of tin and aluminium is particularly objectionable and the casual observation that unprepared tin and aluminium electrodes left in contact in H.T.P. rapidly produce a jelly of aluminium hydroxide was one of the factors which suggested the necessity for this investigation. Tin bursting discs in aluminium or light alloy casings are therefore not recommended. An aluminium bursting disc should be insulated as far as possible from its holder and the employment of a thin P.V.C. disc backed by an aluminium disc is recommended.

(c) Direct Chemical Attack

Some mention appears appropriate of possible corrosion by direct chemical attack on the individual uncoupled metals by H.T.P. In general, an inactive oxide layer appears to be formed, or is formed in the initial pickling and then maintained. In the special case of chromium steels at tropical temperatures, however, direct solution of chromium in the H.T.P. as a deep purple compound is observed (see Appendix I). This purple compound has been the subject of considerable research over a period of years and the latest contribution appears to be that of Bobtelsky, Glasner, and Bobtelsky-Chaikin (Ref. 14). They suggest that the violet compound is the anion of the well known blue compound produced from chromates and hydrogen peroxide and that it only occurs if the Ph is greater than 4.5. Their conclusions refer to dilute solutions but the appearance of the violet colour in concentrated hydrogen peroxide is in agreement, in as much as the Ph of the solutions is usually greater than 4.5.

Compatability work with T.S. hydrogen peroxide (Phosphoric Acid stabilised) has not been continued here since the decision to use T.L. hydrogen peroxide for torpedoes. Corrosion of certain light alloys in T.L. has occurred, but no comparison has been made with T.S. peroxide. Published information on corrosion is virtually limited to phosphate stabilised (T.S.) peroxide, stanuate stabilised (T.L.) peroxide and unstabilised peroxide, the overall picture appearing to be that the latter two are more corrosive than the former. Beard (Ref. 2) specifically states that he has found T.L. more corrosive to aluminium than T.S. and that the addition of nitrate does not inhibit this corrosion (Ref. 3). Cooper has shown (Ref. 15) that the nitrate, however, does inhibit corrosion caused by chloride ions. He also points out that "There is some evidence to suggest that stannate tends, other things being equal, to enhance corrosion of aluminium in H.T.P. and this is confirmed by other tests not reported". This remark is repeated in Ref. 5.

Published evidence of corrosion is difficult to assess for a number of reasons. The length of time and temperature of the tests varies (present work - 8 months at room temperatures; Ref. 15 - up to 4 months at 122°F (50°C); Ref. 2 and 3 - 2 months at room temperatures; Ref. 6 - up to 4 weeks at 151°F (66°C) and up to ? months at 86°F (30°C)). The actual analysis of the materials tested is frequently not stated and some of the characteristics of the H.T.P. employed are unknown. As regards T.L. H.T.P. small supplies received here in alumiuium tanks have generally been found to have more than 10 ppm. nitrate, very small amounts of the specified impurities and high stability. Acidity however, has usually been low (less than 15 ppm. as sulphuric acid by titration at 10-fold dilution in the specified manner), and the tin content has probably been low although until recently this has not been accurately determined. Information regarding tin content is extremely scanty. Normally the tin, added as stannuate, is precipitated (Ref. 16 Page 13) and the practice has been to allow these precipitations to occur over a few days before decanting the T.L. H.T.P. (Ref. 15). The remaining tin may be negligible (Wood and Radford (Ref. 16) quote a single figure for T.L. of 1.8 ppm. (Spectroscopic)) and, due to the alkalinity of the stannate, the acidity is also slightly lowered. Precipitation does not necessarily occur at the same rate (refer above to the difference between samples acidified with sulphuric acid and nitric acid) and since the dispersion is colloidal may be influenced by peptising agents in one direction and polyvalent ions in the other. The Japanese practice of stabilising by adding stannic oxide gel peptised with ammonia (ref. 12) may be mentioned in this connection, and may, in fact, be a more satisfactory method than adding sodium stannate.

Hence although tin compounds in solution might be expected to corrode aluminium and its alloys, there seems little evidence that they can be present in any quantity under normal conditions. The only other relevant features in T.L. appear to be low acidity and absence of phosphate. It is suggested that low acidity may favour the formation of aluminium hydroxide or possibly an ion pair complex (Al^{+3}) (OOH^{-1}) analogous to the complex (Fe^{+3}) (OOH^{-1}) formed by iron in hydrogen peroxide solutions (Ref. 18).

Phosphates/

Phosphates are well known for their protective action and phosphoric acid would both maintain acidity and protect the metal.

(d) Hydrogen Peroxide Concentration

One aspect of the present work which is somewhat unsatisfactory is that hydrogen peroxide concentrations in the later stages of the trials are very far removed from concentrations ever likely to occur in practice. It may be that dilute solutions promote corrosion and that, if the concentration is maintained at a high level, corrosion will not occur. Again although the pairs without external connections appear to act quite effectively as "controls" for the connected pairs it would be desirable to know whether the individual members of the controls behave in the same way if placed separately in H.T.P. To examine these possibilities, trials are in progress with single electrodes immersed as before but in separate beakers. In a proportion of these beakers the H.T.P. will be renewed monthly to maintain concentration at a level found in practice. Super purity aluminium (99.9% +) has also been included to examine whether the 0.5% impurity in commercial aluminium contributes to the vapour phase corrosion. Surveillance trials on small (15 litres) aluminium lined containers with stainless steel exit pipes are also in progress.

5. CONCLUSIONS

1. The coupling of different metals in H.T.P. can produce serious corrosion. If two metals are employed, they should be electrically insulated from one another.

2. Vapour phase corrosion of aluminium was very marked, whereas the two light alloys showed only slight corrosion of this type. The stainless steels were heavily oxidised immediately above the surface.

3. Tin is not recommended for bursting discs, especially in the presence of aluminium.

4. Stainless steels are not recommended for storage tanks or parts thereof. If used, V.27 (18/8) is to be preferred and should be electrically insulated from aluminium or light alloy components. Carbon content should be low.

5. T.L. H.T.P. appears to be more corrosive than the T.S. variety and its contamination resistance may become low due to the precipitation of the stabiliser. As phosphates are known to confer definite protective action, it would seem worth while ascertaining what quantity of phosphate could be added, in conjunction with stannate, without unduly shortening the life of the catalyst.

REFERENCE

(L. and R. Numbers are T.E.E. Internal Markings)

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TABLE 1

NOMINAL AND ACTUAL COMPOSITIONS OF ALLOYS USED FOR COUPLES IN H.T.P.

Alloy Specification	Nominal Composition	Actual Batch Composition	Condition	Remarks
STA.7/A.3	Al 99.6%	Fe 0.22, 0.26 Si 0.16, 0.16 Mn < .02 Mg < .02 Zn < .05 Cu 0.05, 0.05	Fully Softened	Couples 1-6 T.E.E. Reg. No. S.S.471
		Fe 0.21 Si 0.19 Mn < .01 Mg < .01 Zn < .02 Cu < .01 Sn < .04	Fully Softened	Couples 19, 20 T.E.E. Reg. No. 202
STA.7/A.C.10	Mg 9.5/11.0 Si 0.25 Fe 0.3 Cu 0.15 Mn -	Mg 10.00 Si 0.18 Fe - Cu 0.07 Mn 0.25	Fully Heat Treated	Couples 7-12 T.E.E. Reg. No.43
		Mg 9.84 Si 0.16 Fe 0.23 Cu < .10 Mn < .10	Fully Heat Treated	Couples 21-22 T.E.E. Reg. No. 166
STA.7/A.W.10	Mg 0.5/1.25 Si 0.75/1.3 Fe 0.6 Mn 1.0	Mg 0.59 Si 1.06 Fe 0.27 Mn 0.03	Fully Heat Treated	Couples 13-18 and 23, 24 Note: low manganese T.E.E. Reg. No. 167
STA.5/V.25	C 0.18/0.25 Si 0.50 Mn 1.0 Ni 1.0 Cr 12.0/14.0	C 0.18 Si - Mn - Ni 0.60 Cr 13.2	Hardened and Tempered	Couples 1,2,7,8, 13,14 T.E.E. Reg. No.17
		C 0.19 Si 0.58 Mn 0.53 Ni 0.53 Cr 13.1	Hardened and Tempered	Couples 25, 26 T.E.E. Batch No. G.P.4
STA.5/V.27	C 0.20 Si 0.20 Mn 1.00 Ni 8.0/10.0 Cr 16.0/20.0	C 0.12 Si - Mn - Ni 9.6 Cr 18.3	Fully Softened	Couples 3, 4, 9 10, 15, 16 T.E.E. Reg. No. 17
		C 0.08 0.15 Si - Mn - Ni - Cr 17.1 17.1	Fully Softened	Couples 27, 28 T.E.E. Batch No. G.P.10

contd.

TABLE 1 (continued)

Alloy Specification	Nominal Composition	Actual Batch Composition	Condition	Remarks
STA.5/V.28	C 0.25 Si 0.1/1.00 Mn 1.00 Ni 1.0/3.0 Cr 16.0/20.0	C 0.14 Si - Mn - Ni 2.57 Cr 16.4	Hardened and Tempered	Couples 5,6,11, 12,17,18 T.E.E. Drg. No. 17
		C 0.19,0.21 Si - Mn - Ni 1.82, 1.84 Cr 16.9 17.2	Hardened and Tempered	Couples 29, 30 T.E.E. Batch No. G.Y.14
TIN	Sn 99.9 +	Not less than 99.9%	Block tin cast	Couples 19-30 T.E.E. Reg. No. 91

TABLE 2

COMPOSITION OF T.L. H.T.P.

T.E.E. BATCH NO. 2 RECEIVED 12.7.49

Concentration	% w/w	85.6	85.4
Acidity	mgms H_2SO_4 per l	-	13
Nitrate	mgms NO_3 per l	11.4	10.5
Tin	mgms Sn per l	-	-
Chloride	mgms Cl per l	0.5	-
Sulphate	mgms H_2SO_4 per l	1.0	-
Iron	mgms Fe per l	0.04	-
Copper	mgms Cu per l	0.03	-
Phosphate	mgms PO_4 per l	0.4	-
Stability	ccs oxygen/cc/24 hrs. at 60°C	1.3	2.2

NOTE: 1st results October, 1949
2nd results February, 1950.

TABLE 3

METALLIC COUPLES IN H.T.P.

FIRST GROUP

1	2	3	4	5	6	7	8	9
A.3. V.25 External Connection	A.3. V.25 No external Connection	A.3. V.27 External Connection	A.3.V.27 No external Connection	A.3. V.28 External Connection	A.3. V.28 No External Connection	A.C.10 V.25 External Connection	A.C.10 V.25 No external Connection	A. C.10 V.27 External Connection

SECOND GROUP

10	11	12	13	14	15	16	17	18
A.C.10 V.27 No external connection	A.C.10 V.28 External Connection	A.C.10 V.28 No external Connection	A.W.10 V.25 External Connection	A.W.10 V.25 No external Connection	A.W.10 V.27 External Connection	A.W.10 V.27 No external Connection	A.W.10 V.28 External Connection	A.W.10 V.28 No external Connection

THIRD GROUP

19	20	21	22	23	24	25	26	27	28	29	30
Tin A.3. External Connection	Tin A.3. No external connection	Tin A.C.10 External Connection	Tin A.C.10 No external Connection	Tin A.W.10 External Connection	Tin A.W.10 No external Connection	Tin V.25 External Connection	Tin V.25 external Connection	Tin V.27 External Connection	Tin V.27 No external Connection	Tin V.28 External Connection	Tin V.28 No external Connection

F2-797-51

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AEC
Air War College
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BAR ________
BuAer-TD-412
BuDocks
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BuShips
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CinCNELM
CinCPac
ComPhibGrpOne
ComServPac
ComSixthFlt
ComSubLant
ComSubPac
DTMB Aero Lab
DTMB Tech Library
EngnrCenFtBelvoir
EODS Indian Head
Hydrographic Office
MID
Munitions Board
NACA
NADC Johnsville
NAMC Phila
NAMTC Pt Mugu Calif
[✓ NARTS Lake Denmark]
NAS Johnsville
NATC Patuxent
NATU NAS Quonset Pt
NTS Newport
NBTL Phila
NEES Annapolis
NEL San Diego
NGF Washington
NMCS Panama City Fla
NMRI NNMC Bethesda
NOL
NOP Indianapolis
Norf Nav Shpyd
NORTLO MIT
NOTS Inyokern Calif
NOU Key West
NPF Indian Head
NPG Dahlgren
NRDL San Francisco
NRL
NUSL New London
N Y Nav Shpyd
OCSigO
ONR
ONR Boston
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ONR New York
ONR Pasadena
ONR San Francisco
OpDevForLant
Ord Tech Museum
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SPIA APL JHU
TRDS Ft Eustis Va.
USAF
UndSecNavAsstR&D
USCG
USMC
WSEG
CIA
Op-________

SECRET

REMARKS:

Underscore Addressee -- Reference to the right.

Appearance of electrodes Nos. 1-18 at different times after commencement of test

No.	Couple	4 Weeks	11 Weeks	20 Weeks	26 Weeks	30 Weeks	36 Weeks (see Figs. 1-8)
1	A.3 V.25	A.3 No change	Considerable corrosion above surface.	Corrosion continued. Products floating on surface.	Thick gel above surface of liquid. Ppt in vessel.	Gel dried out. Ppt increased.	As before above surface Pits at surface and just below.
	External connection	V.25 Bronzed just above surface with faint spots.	Purple-blue fading to yellow up to $\frac{1}{2}$" above surface with darker rings.	As before. Mottled above yellow area.	As before, deep blue.	Few rusty spots on steel above surface. Bronzed below.	As before
2	A.3 V.25	A.3 No change	As 1 (see above)	As 1 (see above)	Dry flaky corrosion. Slight precipitate.	As before	As before. No attack below surface.
	No external connection	V.25 Bronzed just above surface with faint spots.	As 1 (see above)	As before. No mottled surface.	As 1 (see above) + few black spots.	As before	As before
3	A.3 V.27	A.3 No change	As 1 (see above)	Corrosion continued. Better than 1. Similar to 2.	As 2 (see above)	As before	As before above surface Numerous black spots below. Thick gelatinous ppt.
	External connection	V.27 Bronzed as above.	As 1 (see above)	As before	As before. Blue colour relatively slight.	As before	As before. Bronzing relatively slight.
4	A.3 V.27	A.3 No change	As 1 (see above)	Corrosion very marked. Ppt. in liquid.	Thick gel above surface. Considerable Ppt.	As before	Gel dried out. No attack below. Thick gel. ppt.
	No external connection	V.27 Bronzed as above	As 1 (see above)	As before with additional mottling. (As 1 - see above)	As before + bronzing below. One relatively large spot on steel above.	As before. Noticeably bronzed below.	Bronzed below. Usual rings above.
5	A.3 V.28	A.3 No change	As 1 (see above)	As 1 (see above)	As 2 (see above)	As 3 (see above)	Dry flaky corrosion. Slight ppt. No attack below.
	External connection	V.28 Bronzed as above. Large black spot above surface	As 1 (see above)	As 1 (see above)	As before	As before	Usual colours well marked.
6	A.3 V.28	A.3 No change	As 1 (see above)	As 1 (see above)	As 2 (see above) but lower corrosion becoming gelatinous.	Dry flaky corrosion. Thick gel ppt.	Partly gelatinous corrosion above. Thick gel. ppt. No attack below.
	No external connection.	V.28 Bronzed as above.	As 1 (see above) Two small spots below surface.	As 1 (see above)	As before	As before	Usual colours well marked.
7	AC 10 V.25	AC 10 No change	No change	No change	Slight localised attack. above liquid surface	As before. One small spot gelled. (above liquid surface)	Slight attack above except for 1 spot much enlarged and black. Corroded below on domed end. Thick ppt.
	External connection	V.25 Bronzed above surface with faint spots.	Purple-blue fading to yellow up to $\frac{1}{2}$" above surface with darker rings.	As before	As before, deep blue	As before	Usual colours well marked.
8	AC 10 V.25	AC 10 No change	No change	No change	As 7 (see above)	As before	Slight attack along lines above surface. Good below
	No external connection	V.25 Bronzed above surface with faint spots.	As 7 (see above)	As before	As 7 (see above)	As before	Very blue. Thick brown film just above surface.
9	AC 10 V.27	AC 10 No change	No change	No change	Very slight attack above liquid surface.	As before	Slight attack along lines above. Good below.
	External connection	V.27 Strong bronzing above surface with faint spots	As 7 (see above) Some bronzing below surface.	As before	Well defined sequence of coloured rings above surface.	As before	Intensity of rings relatively slight. Well bronzed below.
10	AC 10 V.27	AC 10 No change	No change	No change	As 9 (see above). One spot with long corrosion "whisker".	As before. "Whisker" fallen into solution.	Only slight attack above. Good below surface.
	No external connection	V.27 Bronzed above surface with faint spots.	As 7 (see above) Some bronzing below surface.	As before	As before	As before	Usual rings more pronounced than 9.

TABLE 4 (Contd.)

Appearance of electrodes Nos. 1-18 at different times after commencement of test

No.	Couple	4 Weeks	11 Weeks	20 Weeks	26 Weeks	30 Weeks	36 Weeks (see Figs. 1-8)
11	AC 10 V.28	AC 10 No change	No change	No change	Slight localised attack.	As before. Spots becoming "whiskery".	Slight attack above. Black areas below. Fine gelatinous deposit.
	External connection	V.28 Bronzed above surface. Few spots above & below surface	Purple-blue fading to yellow up to ½" above surface, with darker rings.	As before	As before	As before	Strong coloured rings above. Few spots below.
12	AC 10 V.28	AC 10 very slight attack. 1 spot below surface.	No change	No change	As 11 (see above)	As before	Attack along lines above surface. 1 small spot below.
	No external connection	V.28 Bronzed above surface. Large spot above & another below surface.	As 11 (see above)	As before	As before	As before	Strong coloured rings above.
13	AW 10 V.25	AW 10 No change	No change	Very slight attack Above liquid surface.	As before Attack high above liquid surface.	As before. Attack along definite lines.	Long black pit at water-line. Pitted on domed end. Slight attack above. Fine gelatinous Ppt.
	External connection	V.25 Bronzing above surface with faint spots.	Purple-blue fading to yellow up to ½" above surface with darker rings.	As before with few black specks.	As before, deep blue	As before	Bronzed with coloured rings.
14	AW 10 V.25	AW 10 No change	No change	Slight attack above liquid surface	As 13 but attack more noticeable & lower.	As 13 (see above)	Attack along lines above. Good below.
	No external connection	V.25 Bronzing above surface with faint spots.	As 13 (see above)	As 13 (see above)	As before	As before	Bronzed with marked coloured rings.
15	AW 10 V.27	AW 10 No change	No change	Very slight attack above liquid surface.	As before	Slight attack high up. One black spot ($\frac{1}{8}$") below surface.	Very bad pits at surface and on domed end. Slight attack above. Fine gel Ppt.
	External connection	V.27 Bronzing above surface with faint spots.	As 13 (see above)	Bronzed & mottled with colours as before.	As before	As before rings relatively pale.	Only relatively slight colouring.
16	AW 10 V.27	AW 10 No change	No change	Very slight attack above liquid surface.	As before	As before) Best condition	Very slight attack above only.
	No external connection	V.27 Bronzing above surface with faint spots.	Bronzing only slight. Two dark spots above surface.	As before	As before	As before) of all	Only relatively slight colouring.
17	AW 10 V.28	AW 10 No change	No change	Very slight attack above liquid surface	As before	Slight attack along definite lines above surface.	Slight attack above. One small black area below.
	External connection	V.28 Bronzing above surface with faint spots above & below.	As 13 (see above)	As before	As before	As before, deep blue.	Colours well marked.
18	AW 10 V.28	AW 10 No change	Very slight attack at one spot above surface.	Very slight attack above liquid surface.	As before	As 17 (see above)	Slight attack above only.
	No external connection	V.28 Bronzing above surface with faint spots above & below.	As 13 (see above)	As before	As before	As before, deep blue.	Colours well marked.

[illegible]C/EGT

TABLE 5A

Appearance of couples Nos. 19-30 at different times after commencement of test

No.	Couple		5 weeks	9 weeks	13 weeks	20 weeks (see Figs. 1 - 8)
19	Tin A.3	Tin	No change	No change	No noticeable effect on areas visible above sediment	As before. Dark above surface & straw coloured below
	External connection	A.3	Gelatinous layer above & below surface. Foam on liquid. Ppt. in vessel	Very severe corrosion above & below surface vessel half full with sediment	As before. Vessel 2/3 full of gelatinous sediment	Very severe corrosion above & below liquid surface. Thick paste left in vessel
20	Tin A.3 No external connection	Tin	No change	No change	No change	Dark above surface. Straw colour below.
		A.3	No change	Gelatinous corrosion products above surface	Corrosion above continues. Ppt. in vessel. Satisfactory below surface	Corrosion above surface. Ppt. in vessel. Below surface satisfactory.
21	Tin A.C.10	Tin	No change	Slight darkening	As before	As 20 (see above)
	External connection	A.C.10	No change	No change	No change	Very slight attack above surface along definite lines
22	Tin A.C.10	Tin	No change	No change	No change	As 20 (see above)
	No external connection	A.C.10	No change	No change	No change	As 21 (see above)
23	Tin A.W.10	Tin	No change	No change	No change	As 20 (see above)
	External connection	A.W.10	No change	No change	No change	Bad attack on lower end of electrode below surface. Fine gelatinous suspension. Very slight attack above liquid surface.
24	Tin A.W.10	Tin	No change	No change	No change	As 20 (see above)

	No external connection	A.W.10	No change	No change	No change	No change except for very slight attack above surface
25	Tin V.25	Tin	No change	No change	No change	As 20 (see above)
	External connection	V.25	Few scattered rust spots above & below surface	Scattered, but numerous spots below liquid surface. Sl. mottling above. Rapid gassing at V.25.	Mottling above liquid surface more prenounced. Gassing rate slower. Liquid level fallen.	Very spotted below surface Yellow & purple above surface. No gassing.
26	Tin V.25	Tin	No change	No change	No change	As 20 (see above)
	No external connection	V.25	Mottled above surface Few small spots below	As 25 (see above) but less marked.	As 25 (see above). Gassing rate increased. Liquid level fallen.	Mottled but not coloured. Very slight spots below liquid surface
27	Tin V.27	Tin	No change	No change	No change	As 20 (see above)
	External connection	V.27	Slight bronzing above surface	Mottled above liquid surface. 1 small spot below	Mottling & bronzing more pronounced. One or two spots above & below. Gassing quite fast.	Mottled & bronzed. Colours not so pronounced & bands narrow.
28	Tin V.27	Tin	No change	Small pits (in casting) blackened - below liquid surface.	No change	As 20 (see above)
	No external connection	V.27	As 27 (see above)	Bronzed as before	As 27 (see above) but without spots	Pronounced "blueing" with purple & then yellow bands above. No spots below liquid surface
29	Tin V.28	Tin	No change	No change	Fine "crazed" pattern on tin above liquid surface	As 20 (see above)
	External connection	V.28	As 27 (see above)	Bronzing marked above liquid surface. 1 spot below liquid surface.	Bronzing & colouring (deep blue) very pronounced	Pronounced bands as for 28 above liquid surface. Satisfactory below except one spot.
30	Tin V.28	Tin	No change	No change	No change	As 20 (see above) but difference between upper & lower surfaces slight.
	No external connection	V.28	As 27 (see above)	Bronzing marked above liquid surface	As 29 (see above)	As 29(see above) but no spots

Table 5b


No. 1
A3 V25
External Connection
No. 2
A3 V25
No external connection
No. 3
A3 V27
External connection
No. 4
A3 V27
No external connection

FIG. 1.

FIG. 2.

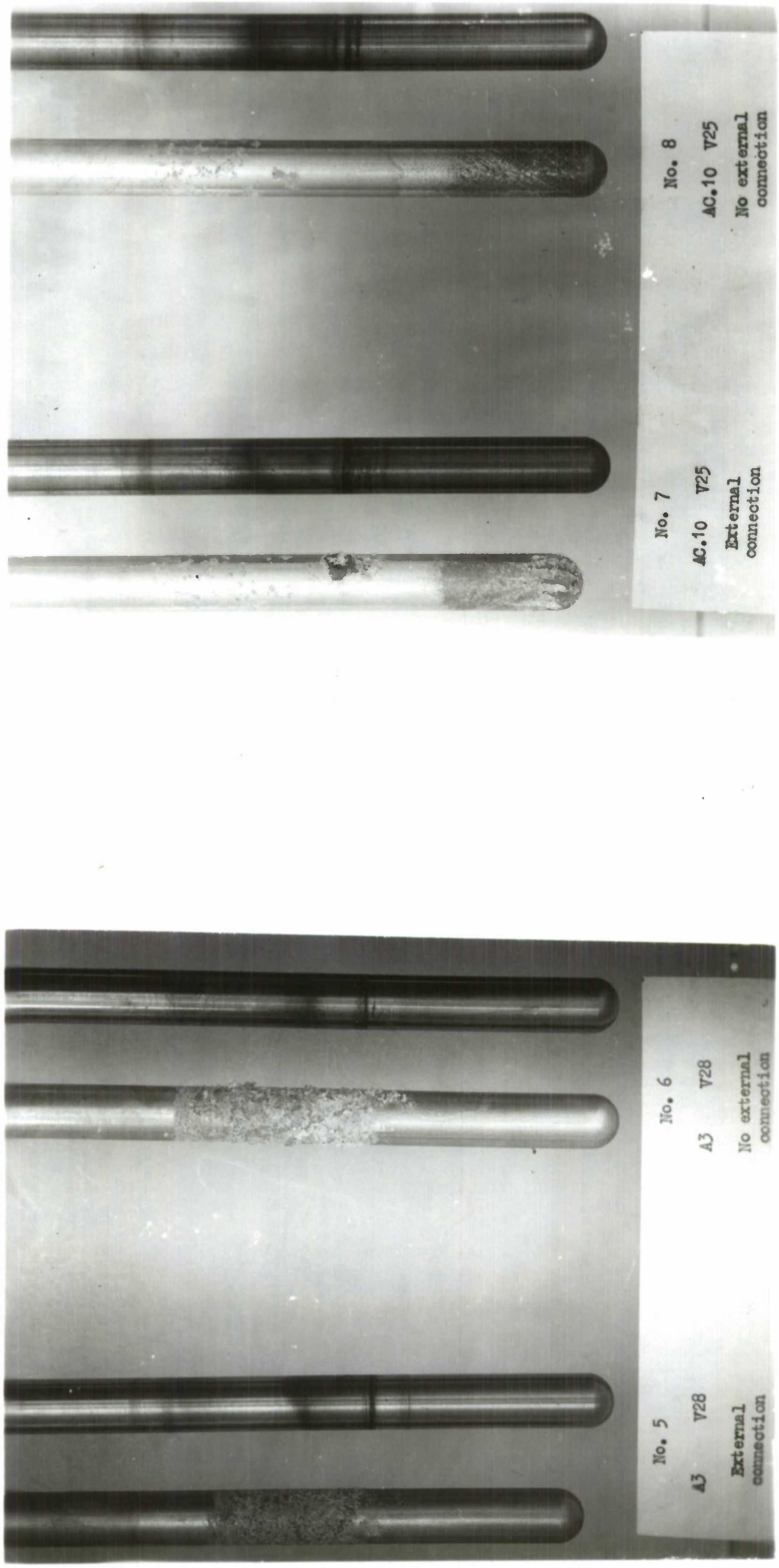

No. 7
AC.10 V25
External connection
No. 8
AC.10 V25
No external connection
No. 5
A3 V28
External connection
No. 6
A3 V28
No external connection

FIG. 3.

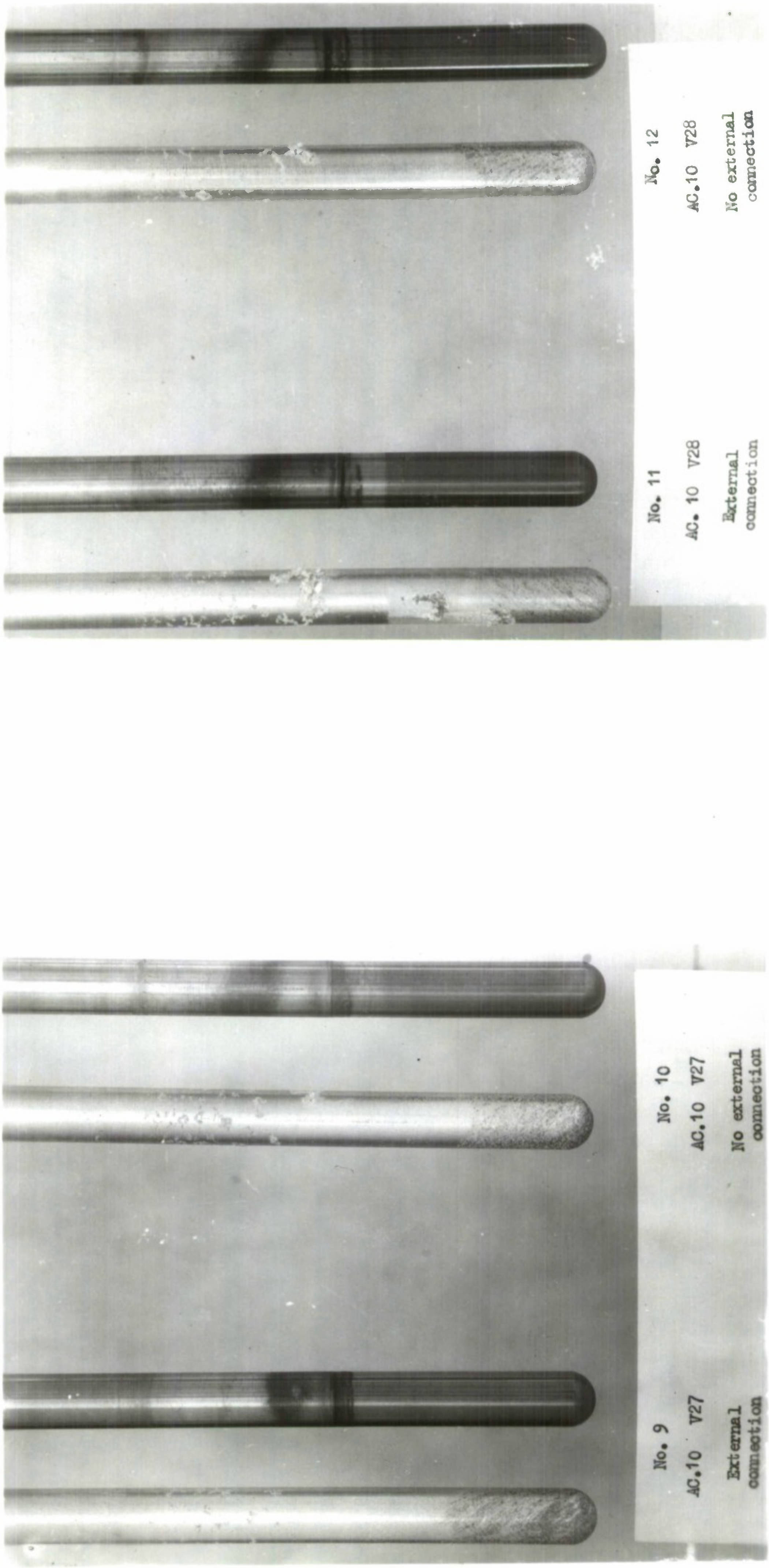
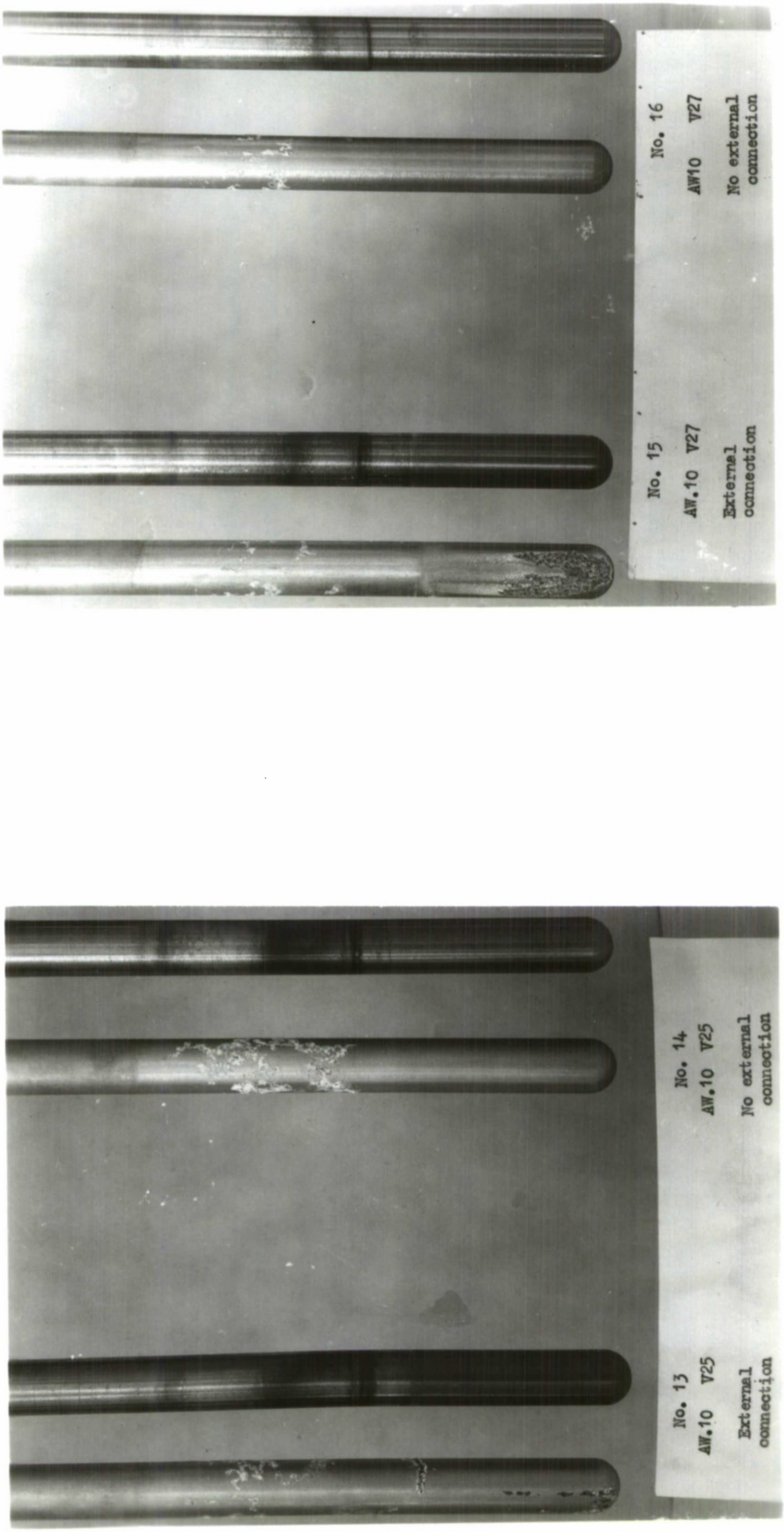

No. 12
AC.10 V28
No external connection
No. 11
AC. 10 V28
External connection
No. 10
AC.10 V27
No external connection
No. 9
AC.10 V27
External connection

FIG. 4.


No. 16
AW10 V27
No external connection
No. 15
AW.10 V27
External connection
No. 14
AW.10 V25
No external connection
No. 13
AW.10 V25
External connection

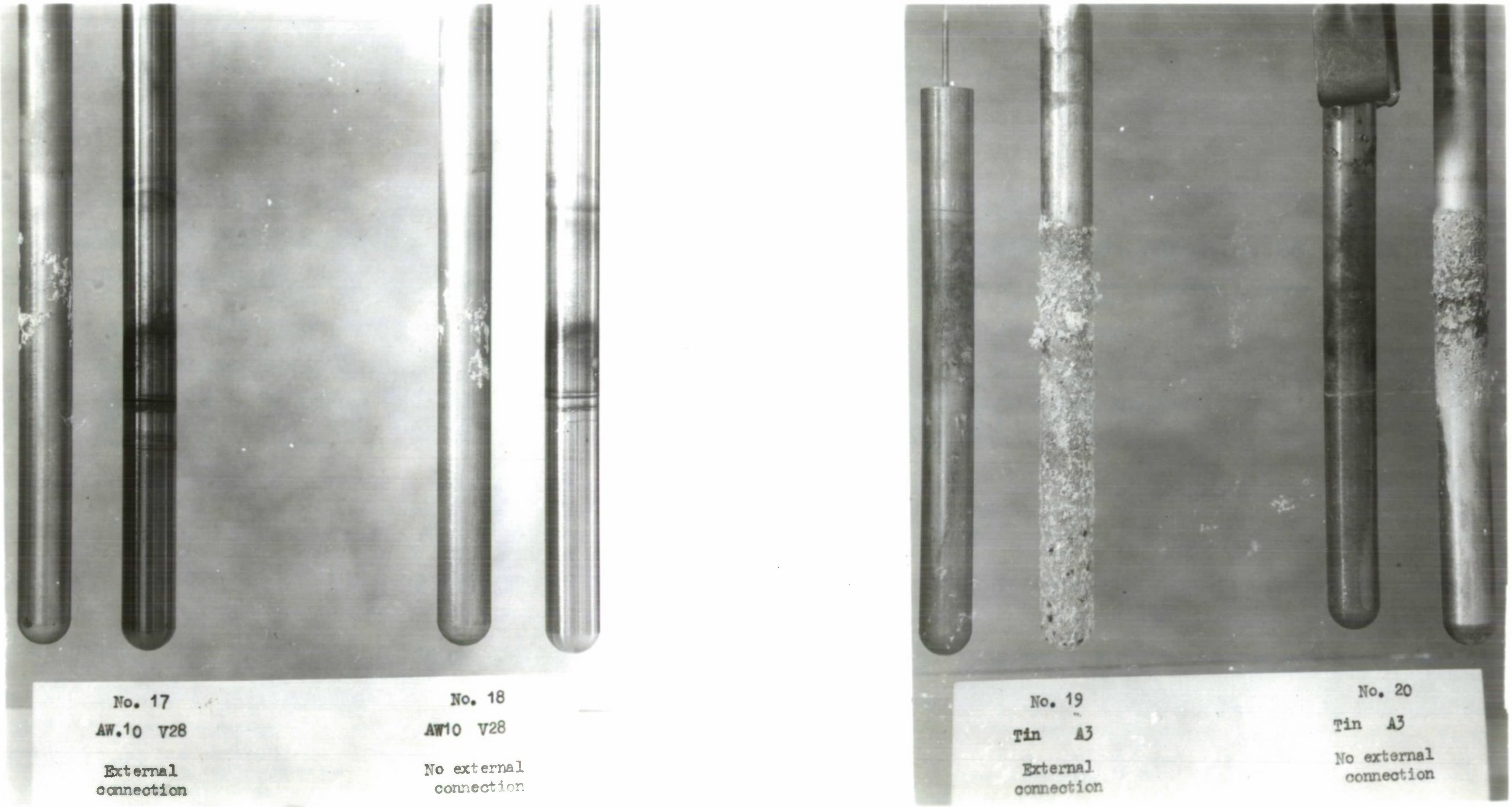

No. 17
AW.10 V28
External connection
No. 18
AW10 V28
No external connection
No. 19
Tin A3
External connection
No. 20
Tin A3
No external connection

FIG. 5.

FIG. 6.

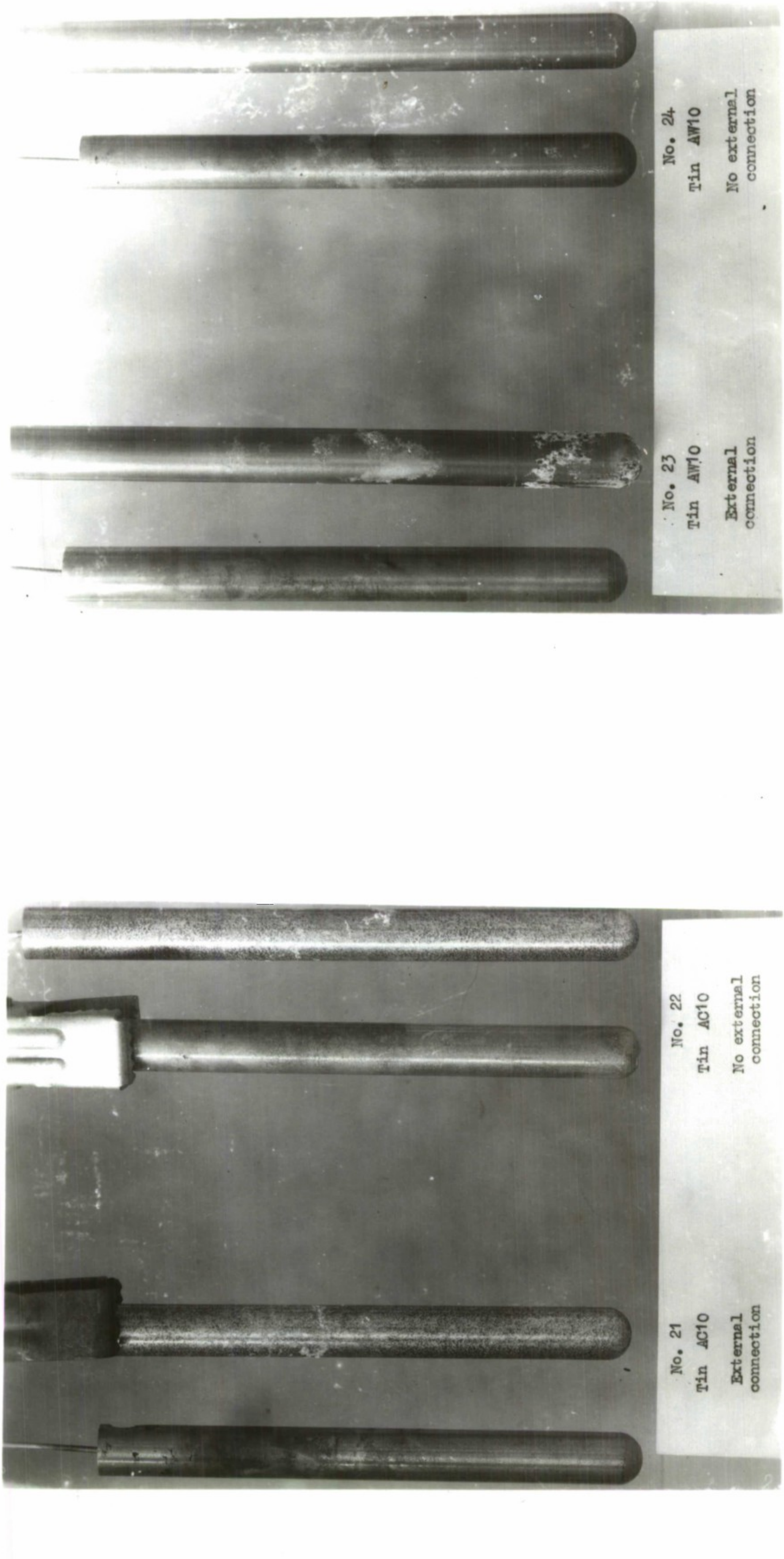
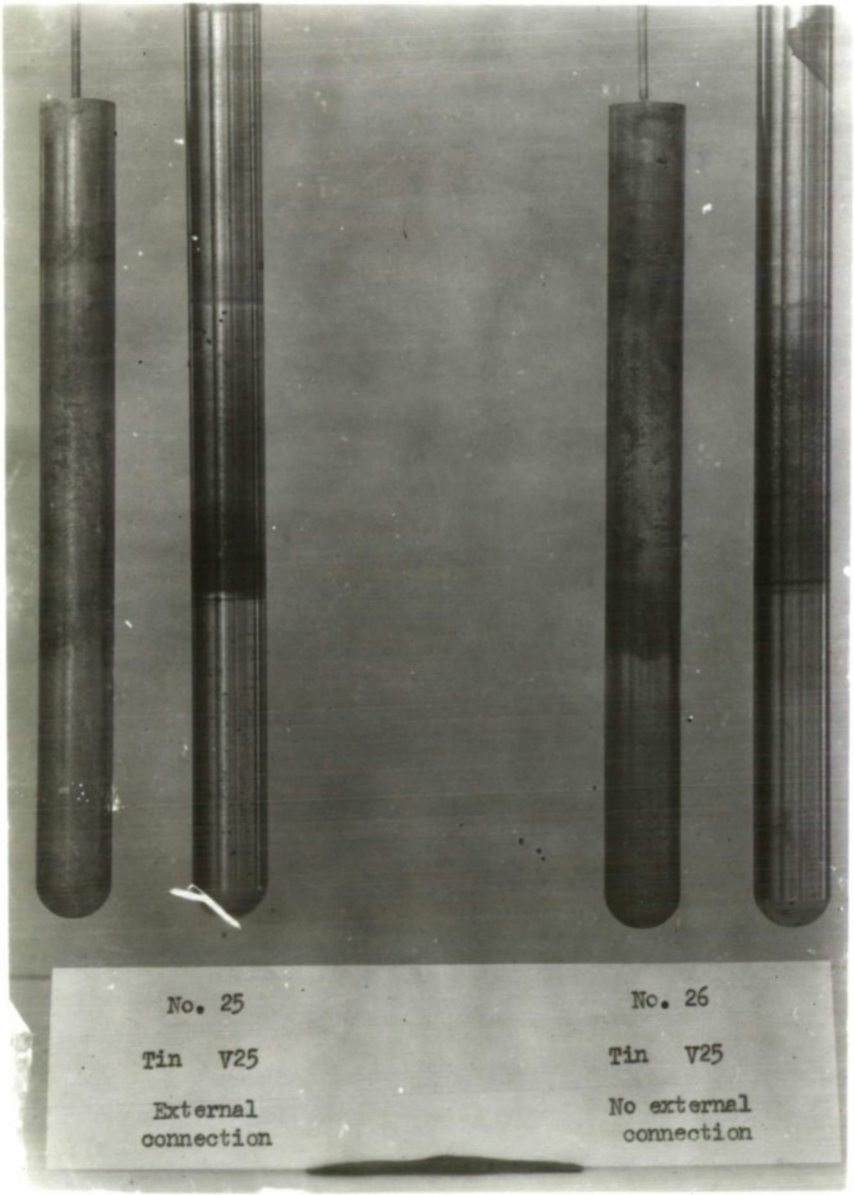

No. 21
Tin AC10
External connection
No. 22
Tin AC10
No external connection
No. 23
Tin AW10
External connection
No. 24
Tin AW10
No external connection

FIG. 7.


No. 25
Tin V25
External connection
No. 26
Tin V25
No external connection

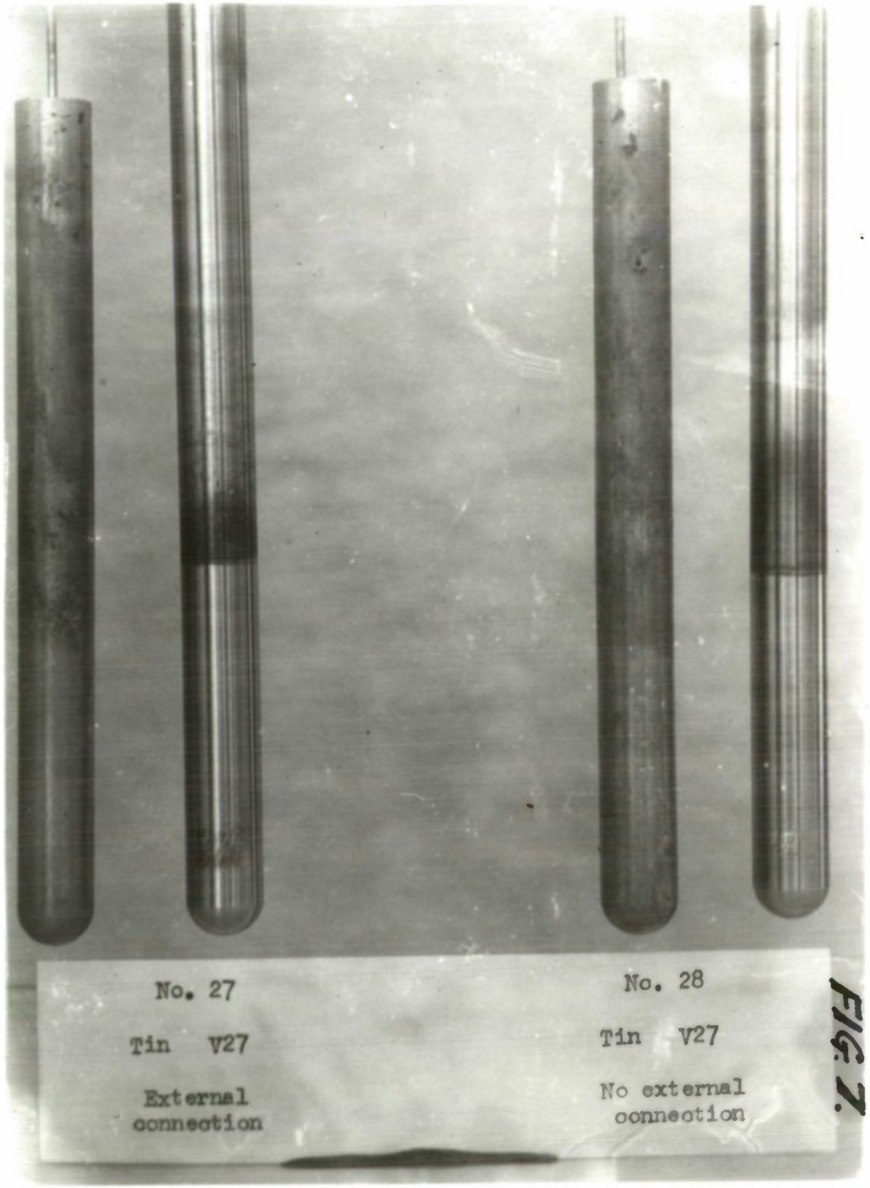
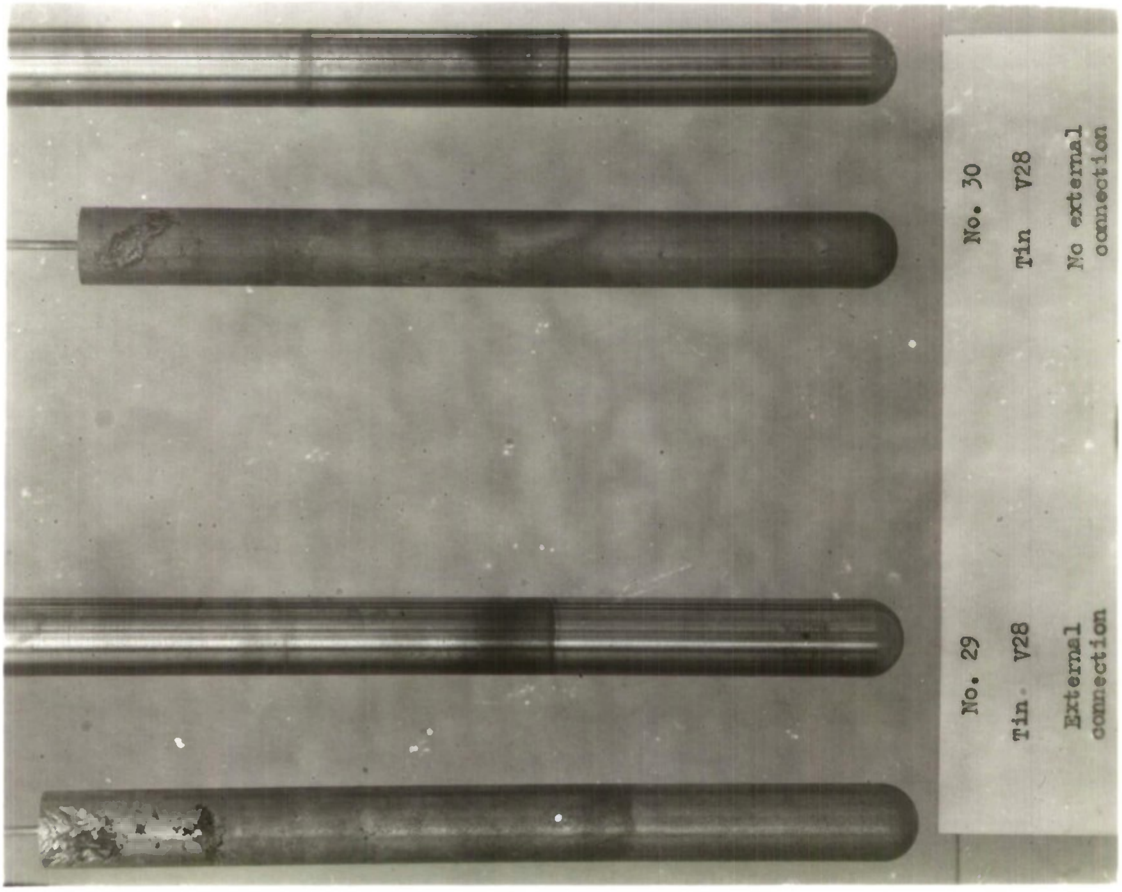

No. 27
Tin V27
External connection
No. 28
Tin V27
No external connection

FIG 8


No. 29
Tin V28
External connection
No. 30
Tin V28
No external connection

T.E.E.
S.T.R. No. 568.

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE.

REPORT No. 3.

FIGURES 9-10.

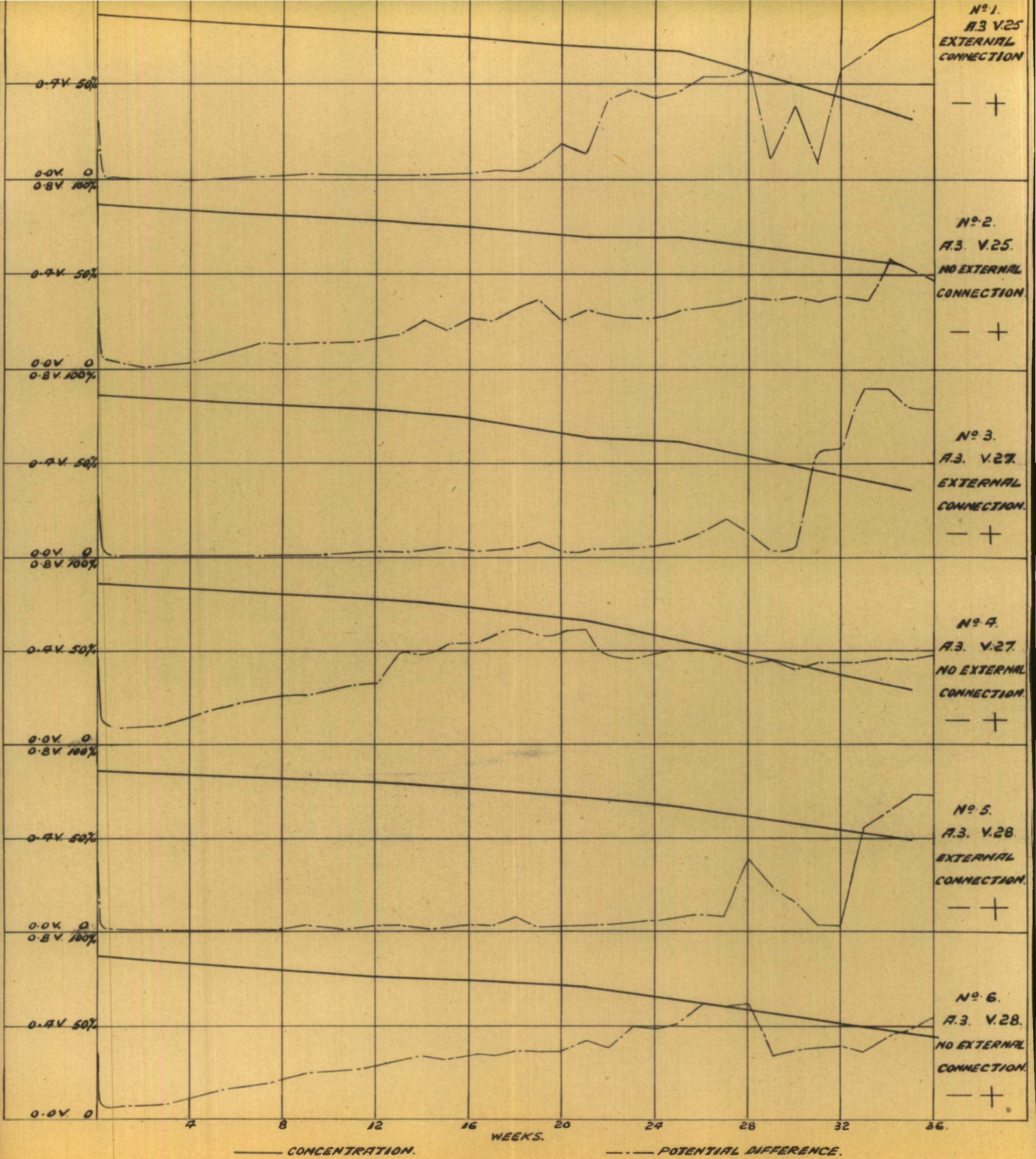


FIG. 9. CHANGES IN CONCENTRATION AND POTENTIAL DIFFERENCE WITH TIME.

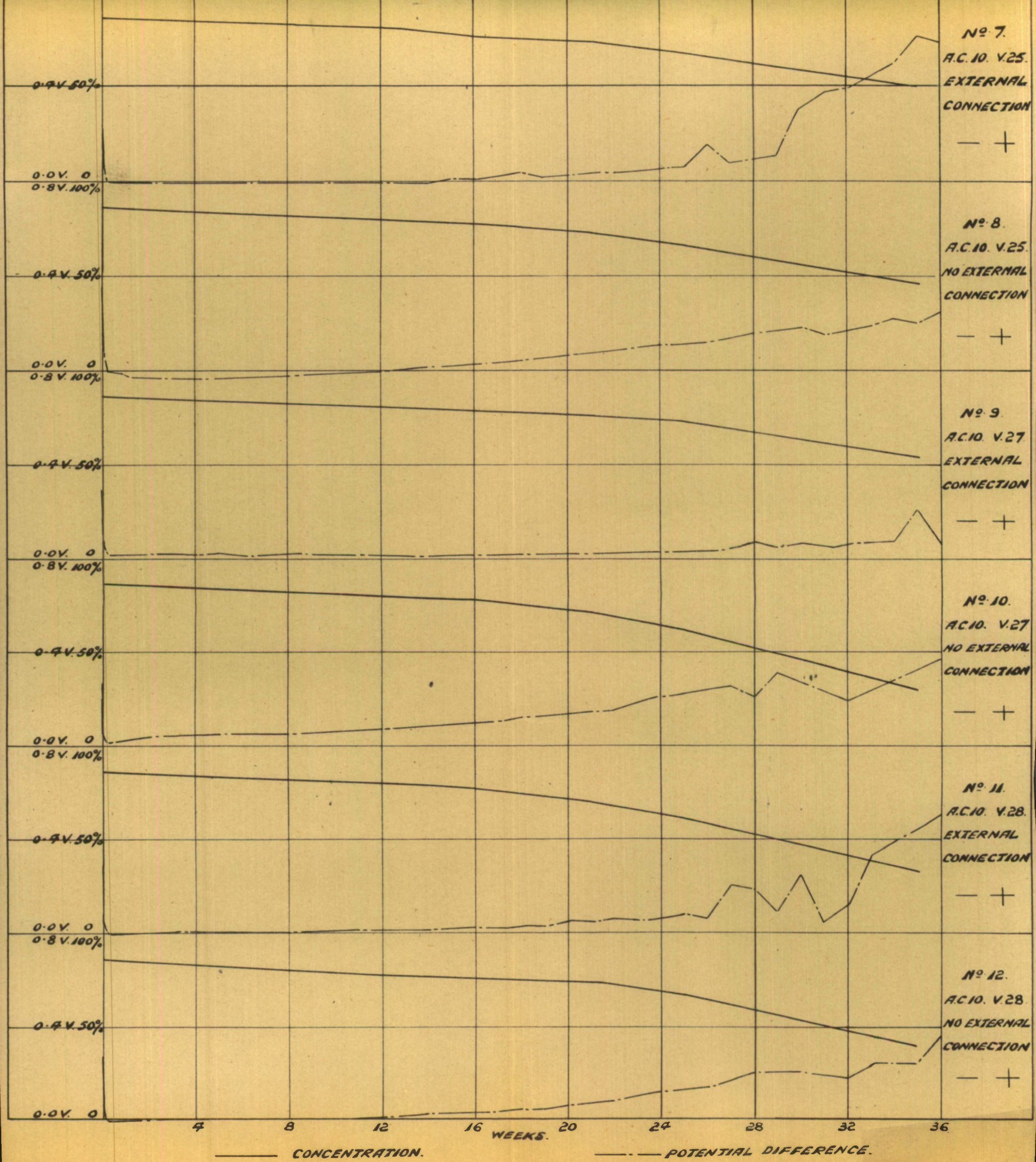


FIG. 10. CHANGES IN CONCENTRATION AND POTENTIAL DIFFERENCE WITH TIME.

I.E.E. TAB. Nº 1175/L.

T. E. E.
S.T.R.No.568.

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE.
REPORT No. 3.

FIGURES 11-12.

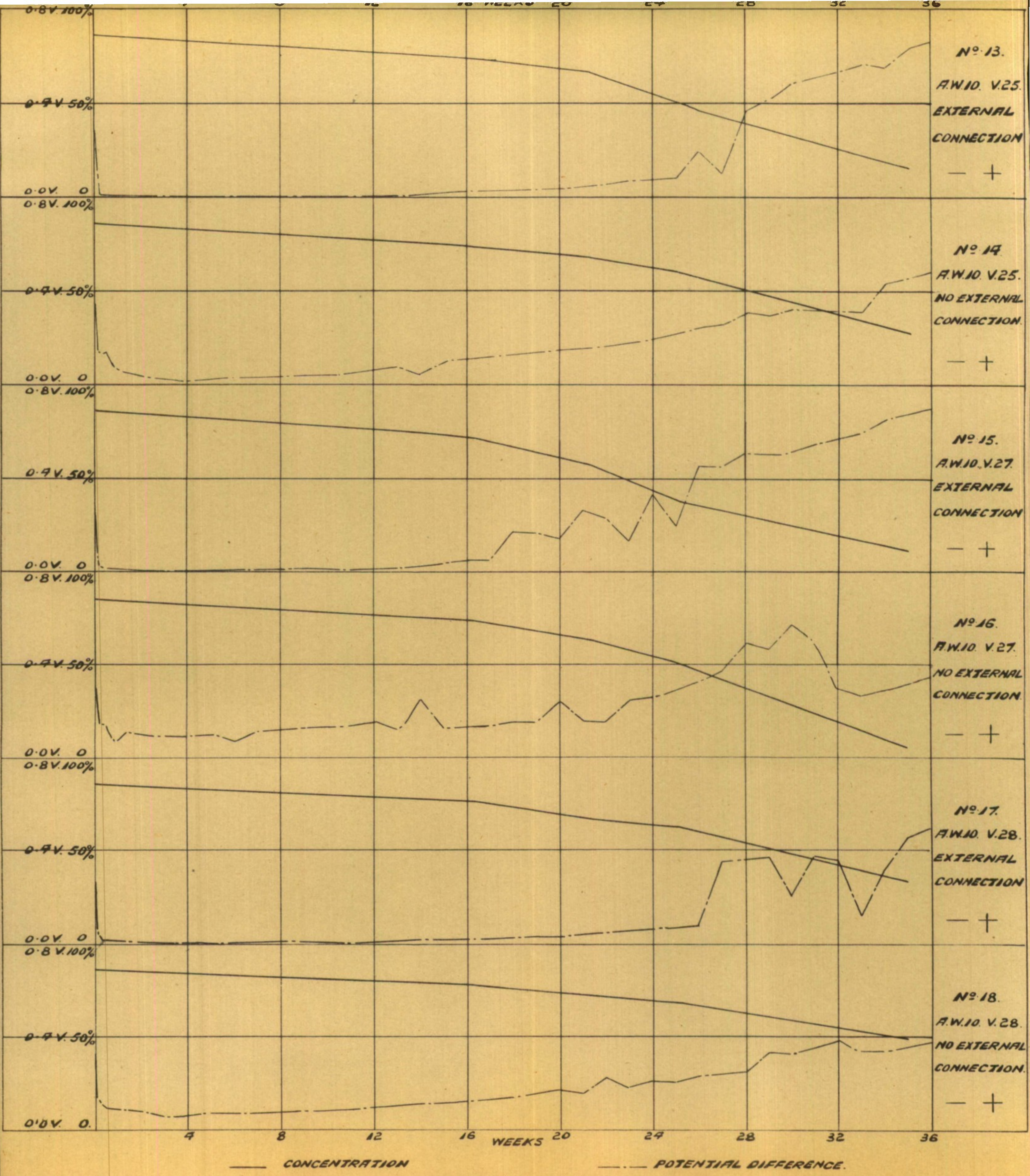


FIG. 11. CHANGES IN CONCENTRATION AND POTENTIAL DIFFERENCE WITH TIME.

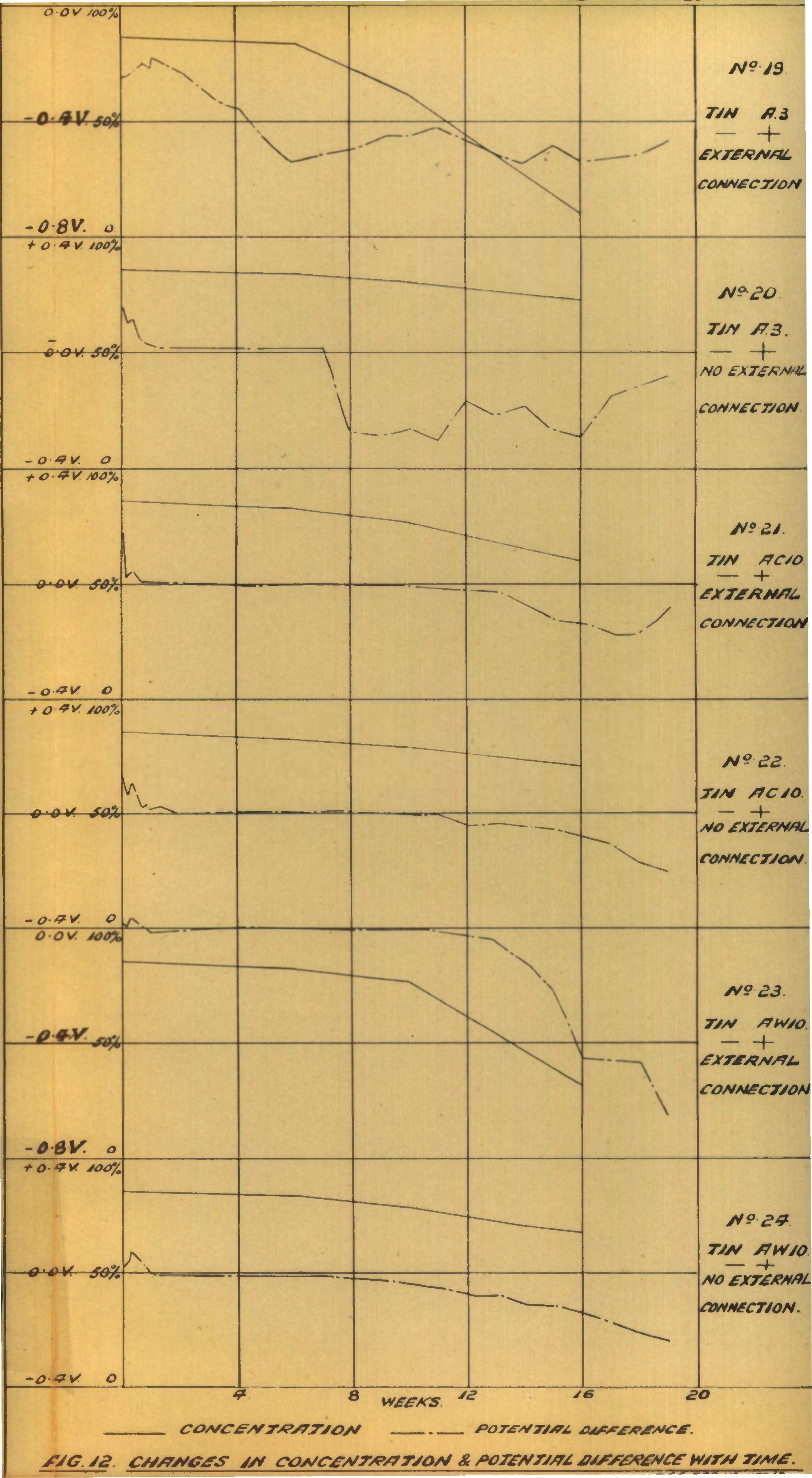


FIG. 12. CHANGES IN CONCENTRATION & POTENTIAL DIFFERENCE WITH TIME.

T.E.E.
S.T.R. No. 568.

STABILITY AND COMPATIBILITY TESTS WITH HYDROGEN PEROXIDE.

REPORT No. 3.

FIGURES 13-14.

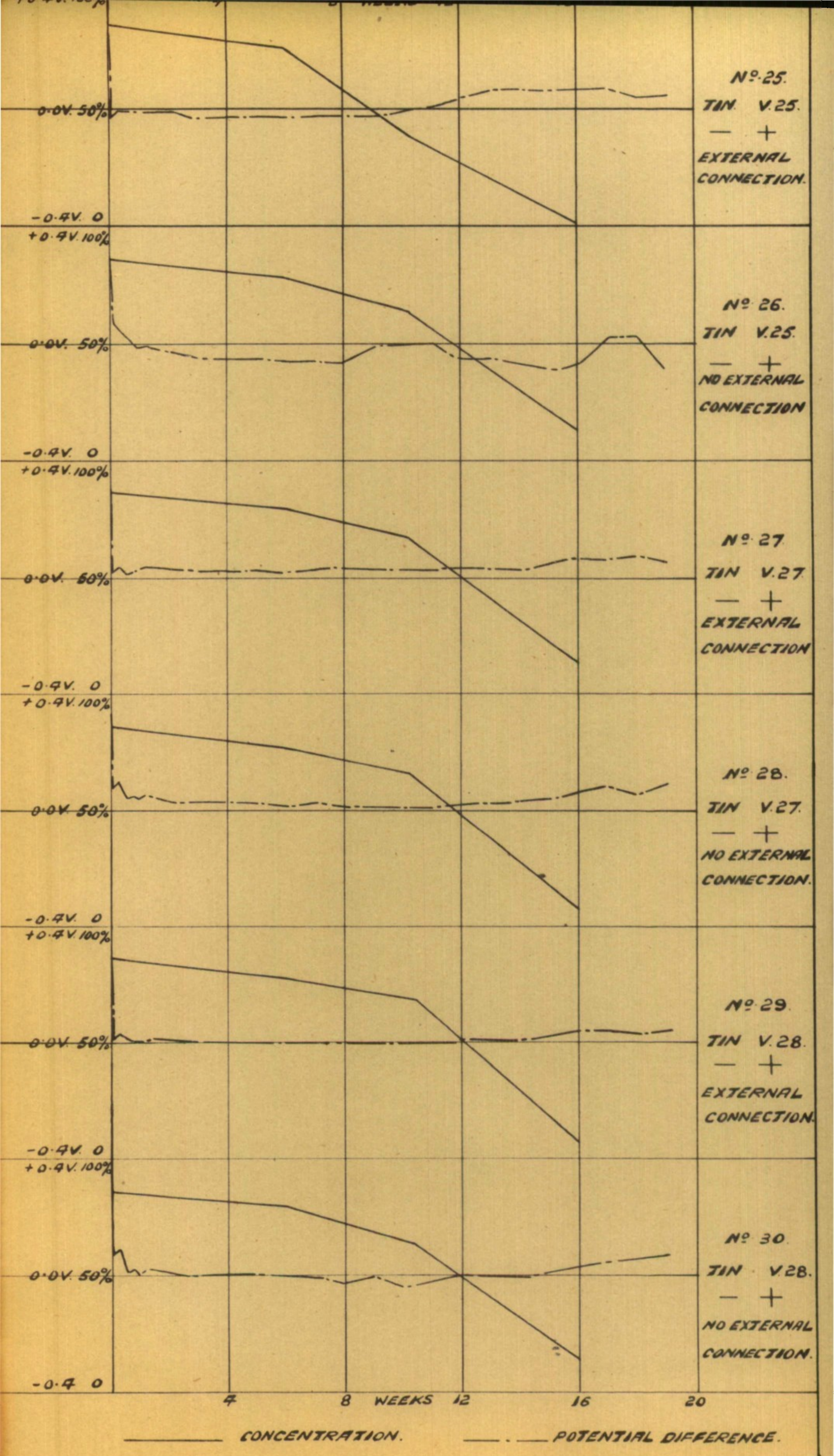


FIG. 13. CHANGES IN CONCENTRATION AND POTENTIAL DIFFERENCE WITH TIME

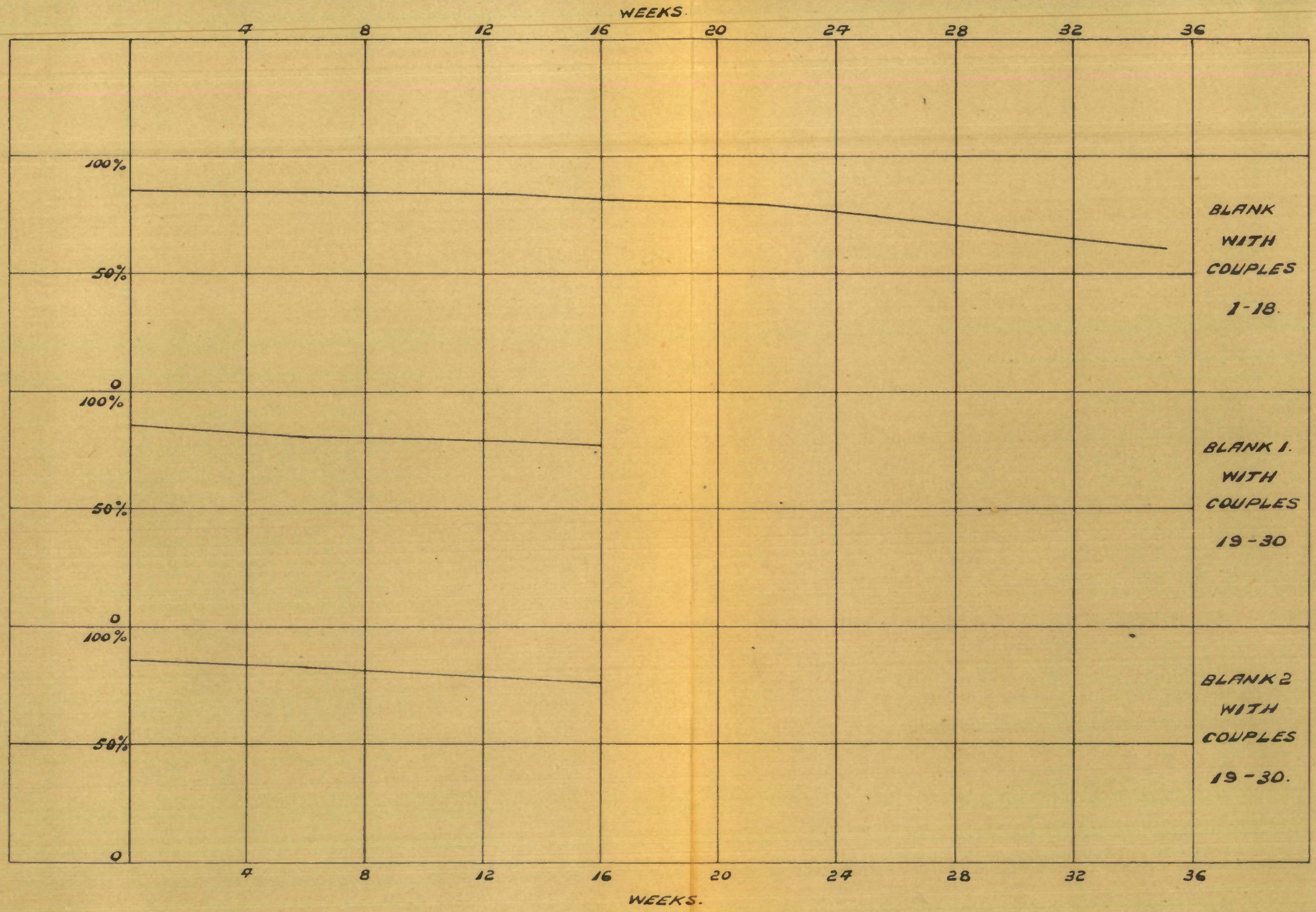
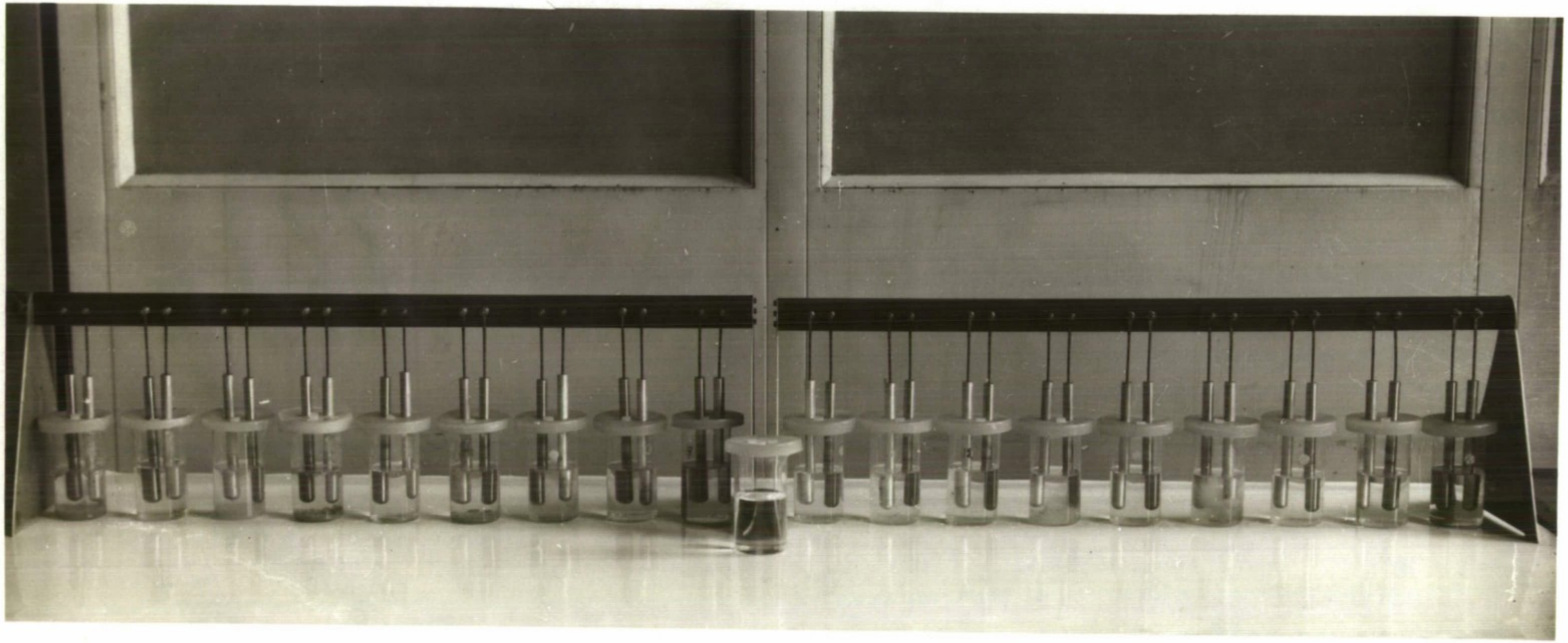


FIG. 14. CHANGES IN CONCENTRATION IN THE BLANKS WITH TIME.

TAB DRG. 1175/3.

FIG. 15



METALLIC COUPLES IN H.T.P... Nos 1 - 18

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TORPEDO EXPERIMENTAL ESTABLISHMENT, GREENOCK

T.N. No. 75
September, 1950

THE COMPATIBILITY OF STAINLESS STEELS WITH HIGH TEST PEROXIDE

(P.T. Corbyn, T. Keir)

LIST OF CONTENTS:

SECRET

APPENDIX I SECRET

TORPEDO EXPERIMENTAL ESTABLISHMENT, GREENOCK.

T.N. 75
September, 1950

THE COMPATIBILITY OF STAINLESS STEELS WITH HIGH TEST PEROXIDE

(P. T. Corbyn, T. Keir)

Summary

Three stainless steels were found to have poor compatibility with stannate stabilised H.T.P. (T.L.) at tropical temperatures (140°F. (60°C)) due to extraction of chromium. Phosphate stabilised H.T.P. (T.S.) showed better resistance than T.L.. Pickling with sulphuric acid or hydrochloric acid enhances chromium extraction and a method of pickling which reduces extraction to a minimum is given. Polishing (followed by pickling and passivating) appears to enhance this extraction.

1. INTRODUCTION

The extraction of chromium from stainless steels by H.T.P. has occasionally been observed (ref. 1 - stainless steels and chromium steels). Usually room temperature tests have been carried out and, as extraction is slow, the full effect is missed. Beard, however, (ref. 2) has recently carried out tests at 140°F (60°C) and reported extremely serious decomposition due to chromium extraction. The catalytic effect of Cr ions at a concentration of 1 gm atom per litre has been shown to be even greater than iron, copper, lead and silver at similar concentrations (ref. 3).

Chromium ions in solution produce a deep purple colour observable above a concentration of about 3 mgms/litre. It was first noticed at T.E.E. when attempting to condition a pickled stainless steel spring in T.L. H.T.P. Previous short term tests (not reported here) on polished specimens had shown no such extraction with T.S. H.T.P. When using a new pickling procedure prior to attempting long term tests on stainless steels this colour was again observed and the investigation which followed is given below.

2. EXPERIMENTAL WORK

Compatibility tests were carried out at 140°F (60°C) as described in S.T.R.'s 549, 557 (refs. 4 and 5). A pyrex tube containing 30 mls. H.T.P. is heated in a thermostat and the gas evolved is collected and measured in a Lunge nitrometer. The connection is then broken, a test piece $1\frac{1}{2}$" x $\frac{1}{2}$" x .05" (11 sq. centimetres) is dropped into the H.T.P. and the test is continued for any desired length of time. Rates of gas evolution are measured at intervals. For the H.T.P. alone gassing rates are quoted as cubic centimetres of gas evolved per hour per cubic centimetre of solution i.e. the observed hourly rate divided by 30. For the test pieces the rates are given as cubic centimetres of gas evolved per hour per square centimetre of surface i.e. the observed hourly rate divided by 11. Normal practice is to deduct the hourly rate for the H.T.P. alone from the hourly rate for the H.T.P. containing the test piece and then divide by the surface area. This deduction is quite negligible in most of the cases quoted here and accordingly, the results are given without this correction. In a particularly bad case for example the actual rates were H.T.P. 0.9 ccs/hr., H.T.P. + test piece 1540 ccs./hr.

The ratio ... /

The ratio of volume to surface area was in all cases 2.7 cms.

The following steels were examined:-

Specification STA.5/V.25 - nominally Cr 13% Ni 1%
STA.5/V.27 - nominally Cr 18% Ni 8%
STA.5/V.28 - nominally Cr 18% Ni 2%

Actual compositions were unknown. The surface condition is stated in the various tables and the five pickling methods employed were as follows:-

Procedure 1. ½ hour in boiling 10% caustic soda.

16 hours in cold 1:1 nitric acid (1 vol. of concentrated nitric acid to 1 vol. of water) with 3 mls of H.T.P. added per 100 mls. Wash well with warm distilled water. Rinse in H.T.P. before placing in tube.

Procedure 2. Cold conc. hydrochloric acid + conc. nitric acid in ratio by volume 17:3 - 3 minutes. 16 hours in cold 1:1 nitric acid + 3 mls H.T.P./100 mls. Wash well with warm distilled water, etc.

Procedure 3. Hot (60°C) conc. hydrochloric acid + conc. nitric acid + water in ratio 10:1:10 - 3 minutes. 16 hours in cold 1:1 nitric acid, etc.

Procedure 4. Hot (60°C) conc. sulphuric acid + conc. hydrochloric acid + water in ratio 3:1:16 - 3 minutes. Warm (40°C) 20% $\frac{v}{v}$ nitric acid + ½ cc (per 100 mls) of hydrofluoric acid - 3 minutes. 16 hours in cold 1:1 nitric acid, etc.

Procedure 5. Procedure 2 but with 1% antimony trichloride added as inhibitor.

Each pickling procedure was followed by the passivating treatment in 1:1 nitric acid. Concentrated nitric acid may also be used without any apparent advantage. No. 1 is normally adopted at T.E.E. No. 2 is recommended by H. Walter (ref. 6). Nos. 3 and 4 are recommended by Firth Vickers - the former with proprietary inhibitors. As the constitutions of these inhibitors were unknown they were not employed. No. 5 was an inhibited modification of No. 2.

The T.S. H.T.P. employed was several years old and of rather low stability. Its analysis (given in S.T.R. 549) shows 9 mgms. PO_4 per litre and acid number 0.35 (mls $\frac{N}{100}$ NaOH per 10 mls H.T.P.). Two batches of T.L.H.T.P. were used, both of very similar composition but differing by a few per cent. in concentration. The analysis of one of these batches is given in S.T.R. 568.

3. RESULTS

Short term tests (8 hours) carried out some two years ago on specimens of the above mentioned steels, together with the special Firth Vickers steels F.S.L., F.D.P., F.M.B., showed moderate compatibility (Similar to the results in table 6). Tests were carried out in T.S. H.T.P. on highly polished specimens, pickled by Procedure 1. Machined surfaces are encountered normally, however, and at a later date machined specimens of V.27 and V.28 were prepared for long term compatibility tests. The pickling treatment recommended by H. Walter (Procedure 2) was employed and the results are given in Table 1. Extremely high decomposition rates were observed (N.B. Satisfactory materials give rates of about 0.2 - 0.5 ccs./hr./sq. cm. under the conditions of test) and the solution containing V.28 became purple.

As these ... /

As these results disagreed with earlier figures pickling procedure was suspected and the five different procedures mentioned above were applied to the third of the three stainless steels V.25. Tables 2(A) and 2(B) show clearly that pickling with sulphuric or hydrochloric acid (Procedures 2 - 5) promotes chromium extraction causing relatively enormous increases in rate of decomposition. Procedure 1 reduces this effect but compatibility is rather poor and may deteriorate (see below). Chromium extraction probably causes this poor compatibility but the colour is not observable below about 3 mgm/litre.

Tables 2A and 2B refer to T.L. H.T.P. and it was thought probable that T.S. H.T.P. would show a better performance. Table 3 indicates that in fact T.S. H.T.P. is very much better than T.L. in this respect, but none the less decomposition rates gradually rise as chromium is extracted.

Although the purple colour had now been observed several times, the causitive agent was still unknown. Chromium was suspected and additions of quantities up to 13 mgms/l were made to both T.L. and T.S. peroxide. The resulting decomposition rates are given in Tables 4(A) and 4(B) and show, together with the colours observed, that chromium extraction is indeed one of the causes of poor compatibility of stainless steels with H.T.P. The rate of decomposition, at any particular concentration, rises gradually with time and then drops rapidly to zero as near complete decomposition is reached. The solution at the same time changes from purple to yellow. The T.S. showed no improvement over T.L. peroxide when chromium was added directly which suggests that the phosphoric acid tends to repress the <u>extraction</u> of the chromium from the steels.

On the assumption that residual acidity causes this extraction an alkaline wash after passivation was suggested as a remedy. Table 5 shows that this was ineffective and again points to the fact that Procedure 1 is the most satisfactory.

Accepting Procedure 1 for further surface treatment of stainless steels attention was turned to the <u>mechanical</u> preparation of the steel surface. Buffed surfaces are compared with machined surfaces in table 6A and highly polished surfaces (finished with "blue back" emery) are compared in table 6 (B). Rather unexpectedly it was found that chromium extraction was enhanced to some extent by highly polishing the surfaces. This has also been observed by Beard (ref. 7) in tests at room temperatures.

In the above tests V.25, V.27 and V.28 were used more or less indiscriminately, as interest centred on chromium extraction rather than on their respective compatibilities. In point of fact there is little to choose between them at tropical temperatures as chromium extraction can occur in all cases. V.27 (18/8) is probably preferable to the other two for applications in temperate climates.

Although chromium extraction occurs rapidly at high temperatures it has also been observed here after long periods at room temperatures (ca 60°F.) Beard (ref. 7) has also observed chromium extraction in the cold.

4. <u>CONCLUSIONS</u> ... /

4. CONCLUSIONS

1. Stainless steels V.25, V.27, and V.28 are not suitable for prolonged contact with H.T.P. under tropical conditions. High decomposition rates are caused by solution of chromium ions.

2. If employed the stainless steel should be smooth turned and not highly polished. It should be pickled with hot 10% caustic soda for half an hour followed by 1:1 nitric acid (or concentrated nitric acid) for about 24 hours.

3. T.S. H.T.P. appears to be more compatible with stainless steels than T.L. H.T.P. at 140°F. (60°C.) but confirmation is required.

PTC/JS.

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TABLE 1

COMPATIBILITY TESTS ON STAINLESS STEELS

Gas evolution in ccs at N.T.P./hr./sq. centimetre
Total immersion in 81.8% TL H.T.P. at 140°F. (60°C.)

Material	Surface Condition	Surface Treatment	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq. cm.			
				Hour 1	Hour 2	Hour 3	Hour 7
V.27	Machined Sharp edges	2	.016	11	16.8	17.4	19.7
V.28	Machined Sharp edges	2	.017	11	15.6	19.4	26.4

V.27 Bright surface initially. Bronzed finally. No noticeable colour in solution after 24 hours.

V.28 Grey-black surface initially. Dulled and rusting slightly after 24 hours. Solution purple.

TABLE 2A

COMPATIBILITY TESTS ON STAINLESS STEELS SURFACE TREATED BY DIFFERENT METHODS

Gas evolution in ccs at N.T.P. per hour per sq. centimetre.
Tptal immersion in 81.8% T.L. H.T.P. at 140°F. (60°C.)
Material: V.25. Machined surface.

Surface Treatment	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq. cm.				
		Hour 1	Hour 19	Hour 20	Hour 23	Hour 25
1	.010	2.0	7.3	-	-	-
2	.037	6.7	45	-	65	-
3	.035	7.8	90	-	-	-
4	.030	11	-	66	110	140
5	.052	17	-	-	Nil	-

Treatment 1 Solution very slightly purple
Treatment 2 Solution purple
Treatment 3 Solution purple. Decomposition complete by 22 hours, leaving yellow solution.
Treatment 4 Solution purple
Treatment 5 As for 3 (above)

TABLE 2B

(REPEAT OF TESTS IN TABLE 2A)

Surface Treatment	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq. cm.					
		Hour 1	Hour 2	Hour 3	Hour 4	Hour 5	Hour 22
1	.048	2.3	2.6	3.3	3.4	3.6	2.8
2	.060	7.0	7.1	10	12	12	31
3	.029	16	16	17	17	20	100
4	.103	7.0	12	14	15	17	65
5	-	7.4	-	10	11	21	45

Treatment 1 No colour. Metal showed faint signs of corrosion after 24 hours but remained bright.

Treatment 2 Purple solution. Faint signs of corrosion but remained bright.

Treatment 3 Solution purple initially. Yellow after 24 hours. Metal as 2 above.

Treatment 4 Solution purple initially. Yellow after 24 hours. Metal as 2 above.

Treatment 5 Purple solution. Dark deposit after pickling remained throughout.

TABLE 3

COMPATIBILITY TESTS ON STAINLESS STEELS SURFACE TREATED BY DIFFERENT METHODS

Gas evolution in ccs at N.T.P. per hour per square centimetre.
Total immersion in 84% TS H.T.P. at 140°F. (60°C.)
Material V.25. Machined surface.

Surface Treatment	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq. cm.			
		Hour 1	Hour 3	Hour 5	Hour 24
1	.19	1.9	2.1	2.2	4.3
2	.21	1.8	1.8	1.9	3.6
3	.27	1.7	2.1	2.3	5.6
4	.22	1.0	-	1.6	-
5	-	1.4	2.2	-	4.5

PTC/EGT

TABLE 4A

EFFECT OF ADDING CHROMIUM TO H.T.P.

Gas evolution in ccs at N.T.P. per hour per cc. of H.T.P.
81.8% T.L. H.T.P. at 140°F. (60°C.)
Cr added as solution of chrome alum. (Analar)

Amount added	Concentration of Cr mgms/1.	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/cc of H.T.P.			
			Hour 1	Hour 4	Hour 24	Hour 28
1 ml water	0	.07	.41	.43	.41	.41
0.9 ml water 0.1 ml soln.	1.3	.08	1.8	1.6	2.5	2.5
0.7 mls water 0.3 mls soln.	4	.08	1.5	1.4	2.3	2.4
1 ml soln.	13	.04	3.5	3.5	6	6

TABLE 4B

(REPEAT OF TESTS IN 4A BUT USING 84% T.S. H.T.P.

Amount added	Concentration of Cr mgms/1	H.T.P. ccs/cc/hr	Gassing rate ccs/hr/cc of H.T.P.			
			Hour 1-2	Hour 4	Hour 24	Hour 48
1 ml water	0	.21	0.32	0.37	-	0.51
0.9 mls water 0.1 mls soln.	1.3	.18	1.1	1.4	1.9	3.1
0.7 mls water 0.3 mls soln.	4	.19	1.6	2.0	2.9	6.1
1 ml soln.	13	.22	5.3	9.3	13	2.2

Note: Solution containing 13 mgs/1 Cr nearing complete decomposition in 48 hours.

TABLE 5

COMPATIBILITY TESTS ON STAINLESS STEELS SURFACE TREATED BY DIFFERENT METHODS BUT WASHED IN HOT CAUSTIC SODA AFTER PASSIVATION

Gas evolution in ccs at N.T.P. per hour per square centimetre.
Total immersion in 81.8% T.L. H.T.P. at 140°F. (60°C.).
Material V.28. Machined surface.

Surface Treatment	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq.cm.			
		Hour 2	Hour 4	Hour 6	Hour 23
1	.06	1.7	2.1	2.1	2.6
2	.15	7.0	8.0	8.5	-
3	.11	11	14	15	21
4	.05	8.2	9.2	8.7	21
5	.05	-	9.9	11	28

Treatment 1	No colour
Treatment 2	Solution purple
Treatment 3	Solution purple
Treatment 4	Solution purple
Treatment 5	Solution purple

SECRET

TABLE 6A

COMPATIBILITY TESTS ON STAINLESS STEELS WITH DIFFERENT SURFACE FINISHES

Gas evolution in ccs at N.T.P. per hour per sq. centimetre.
Total immersion in 85.2% T.L. H.T.P. at 140°F. (60°C.)
Material: V.28. Surface treatment No. 1 with
caustic soda wash after passivation.

No.	Finish	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq.cm.			
			Hour 1	Hour 2	Hour 20	Hour 24
1	Buffed rounded edges	.034	6.9	7.3	6.5	7.2
2	"	.040	3.6	3.9	3.4	3.5
3	"	.055	2.8	3.0	2.9	2.9
4	Machine finish square edges	.049	1.1	1.2	1.3	1.0
5	"	.025	1.0	1.0	1.2	1.0
6	"	.029	2.2	2.5	2.6	2.5

Test piece, 1-2 slightly discoloured after pickling and showing slight incipient corrosion after 24 hours. No solutions coloured.

TABLE 6 B

(REPEAT OF TESTS IN TABLE 6A)

No.	Finish	H.T.P. ccs/cc/hr.	Gassing rate ccs/hr/sq.cm.				
			Hour 1	Hour 4	Hour 25	Hour 49	5 days
1	High Polish Rounded edges	.048	2.9	3.5	3.9	5.6	6.8
2	"	.038	2.7	3.2	3.6	5.1	13.3
3	"	.067	2.9	3.5	4.2	6.1	2.3
4	Machine finish square edges	.043	1.3	1.2	1.0	3.4	2.6
5	"	.051	1.5	1.5	1.2	1.7	4.1
6	"	.041	1.2	1.3	1.1	1.7	2.9

Concentrated nitric acid used for passivating.
Test pieces 1-3 slightly dulled at end of test and the solutions became slightly tinged with purple. No. 3 solution after 5 days was pale yellow indicating near complete decomposition.
Test pieces 4 - 6 were unaltered.

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