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Ministry of Supply
DIVISION OF ATOMIC ENERGY (PRODUCTION)

THE EFFECT OF DISSOLVED CHROMIUM ON
THE CORROSION RATE OF TWO CHROMIUM-
NICKEL-AUSTENITIC STEELS IN BOILING
NITRIC ACID

by

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Research and Development Branch, Culcheth Laboratories

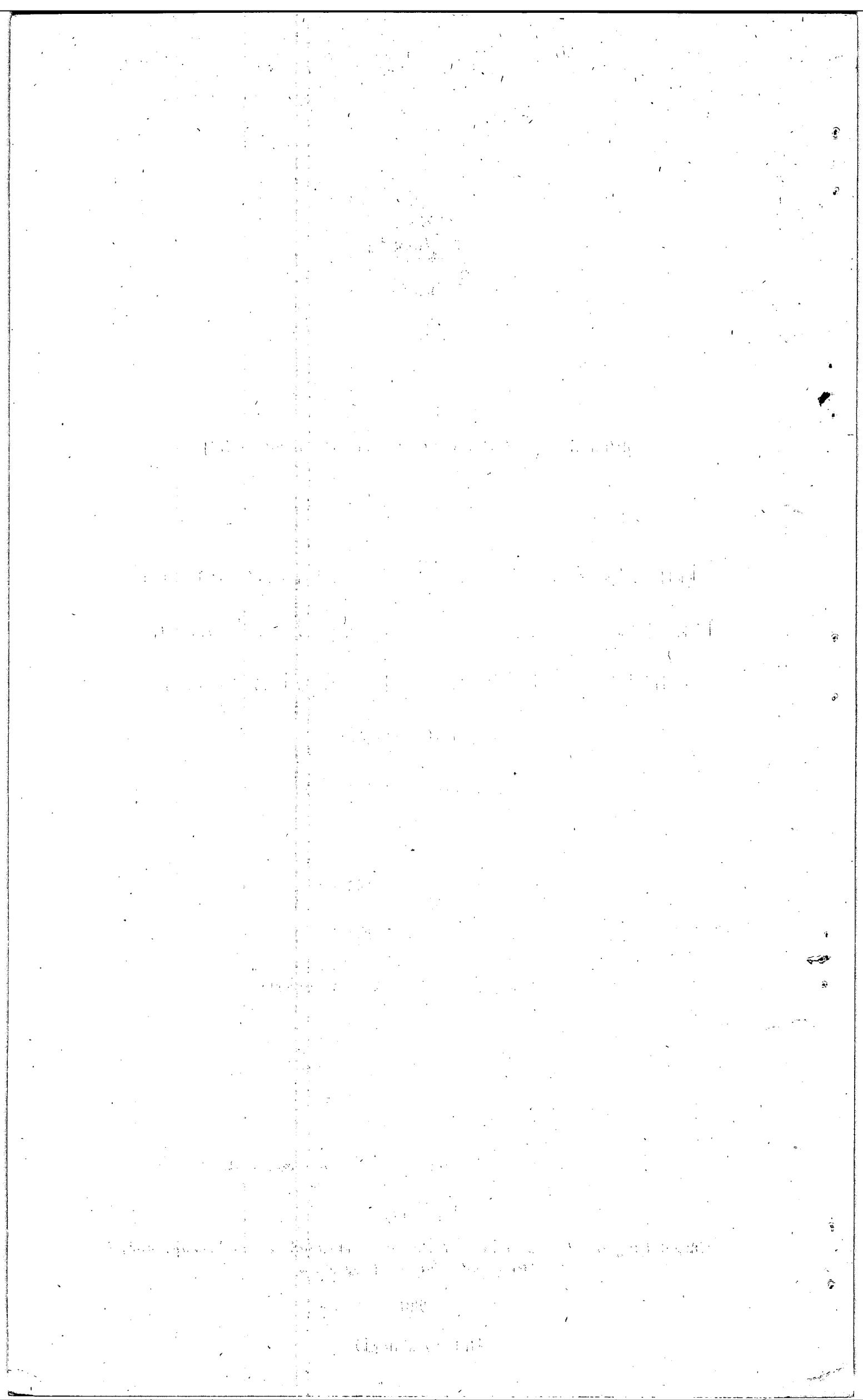
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SUMMARY

The rate of corrosion of chromium - nickel austenitic steels in boiling 70% nitric acid is greatly influenced by certain conditions, e.g.

- (1) The frequency with which the nitric acid is renewed.
- (2) The ratio of specimen surface area to volume of nitric acid.
- (3) The type of condenser employed.

It is shown that these factors all operate by modifying the concentration of hexavalent chromium which tends to build up in the corroding solution and rapidly accelerates corrosion. The presence of hexavalent chromium can easily be prevented by ensuring the presence of nitrogen peroxide thereby decreasing the corrosion rate, and improving the deviation of results in the boiling nitric acid test.

A suggested mechanism for the formation of hexavalent chromium is put forward, and the effect on the electrode potential of the specimen in the acid is demonstrated.

1. INTRODUCTION

During the corrosion testing of 18/13/1 austenitic steel in boiling 70% nitric acid, considerable variation was found in the results from various makers' laboratories, between which there was no standardisation of the conditions of testing. It was believed that the chief cause of variation might be contamination of the acid by the products of corrosion, mainly iron, chromium and nickel nitrates, and experiments were carried out to devise a suitable standard test.

1. Method of Test

Almost all the early experiments were carried out in the apparatus shown in Diagram 1(a) consisting of a 500 ml conical flask with a ground glass neck, into which was fitted a vertical reflux condenser. The specimen was held vertically in a glass chair shaped to serve also an "anti-bump" device. Heating in an oil bath was found to cause excessive bumping, so that heating by hot plates was adopted as an anti-bump.

The acid used was 70% weight/weight strength and of practically A.R. purity. There was no significant variation from batch to batch. In the course of experiments, there was a small volume loss between acid changes, but the acid strength remained remarkably constant.

All specimens were prepared in a similar manner. After machining to size they were heated at 1100°C. for 15 minutes in a muffle furnace, withdrawn and air cooled. They were then pickled free from scale and hand polished down to No.1 emery paper. So far as possible all specimens were actually cut from the same sheet and in the same direction.

While an endeavour was always made to achieve a similar boiling rate in all flasks, there was no evidence that small variations had any appreciable effect.

2. Acid Volume

In Table I are set out the results of corrosion experiments in which specimens $1" \times \frac{1}{2}" \times \frac{1}{8}"$ were immersed in volumes of boiling acid varying from 100 ml. to 450 ml. In all cases the acid was renewed every two days. It is apparent that solution volume has a most marked effect on corrosion rate, the penetration in mm/year being nearly 10 times as great for 100 ml. as for 450 ml. As would be expected, the effect becomes greater as the solution volume is decreased. On the other hand, with volumes exceeding 350 ml. the effect is decreased.

3. Frequency of Acid Changes

Exactly the same effect can be shown by keeping the volume constant and varying the frequency of solution change. Table II shows the progressive penetration rates of $1\frac{1}{2}" \times 1" \times \frac{1}{8}"$ specimens in 450 mls of acid. They have been divided into three sets in which the acid was changed at 24, 48 or 96 hour intervals. The corrosion of specimens with 96 hour acid changes was exceedingly rapid - about $2\frac{1}{2}$ mm/year, whereas with 48 hour changes it was about 0.70 mm/year and with 24 hour changes about 0.62 mm/year at the same period. The results for 48 and 24 hour acid changes have been examined in detail, corrected for diminishing surface area and the initial period of slow corrosion, and set out in Fig. 1. Test Nos. 198 - 201 incorporated 24 hour acid changes and Tests Nos. 202 - 205, 48 hour acid changes. Tests Nos. 569 - 580 refer to tests which had acid changes on Monday, Wednesday and Friday, but as the specimen size was different they were not strictly comparable.

4. Addition of Metal Ions

Specimens were next corroded in boiling 70% nitric acid to which additions of chromic, ferric, or nickel nitrates were made, and the results are given in Table III, from which it can be seen that by far the greatest accelerating influence was that of chromium. Iron had a small accelerating effect when added in large quantities, but nickel showed little action. The same results were obtained when these experiments were repeated on an 18/8 type of steel, and are reported in Table IV. It therefore appeared that the ratio of volume to surface area and the frequency of acid changes on the corrosion of austenitic steels might be due to their influence on the chromium concentration built up in the corroding solution.

II. THE MECHANISM OF CORROSION ACCELERATION BY CHROMIUM

1. General

The first indication that the role of chromium was complex arose during an experiment in which a specimen was corroded in 70% nitric acid containing added chromium nitrate, and maintained a few degrees below the boiling point. It was found that under these conditions, chromium did not act as an accelerator, and that the specimen lost weight at the same rate as a specimen held at a similar temperature in pure 70% nitric acid. The amount of chromium nitrate added, $0\frac{1}{2}$ gm/litre, was more than had been previously used. It was also found that, at this temperature, 110°C , a specimen could be held for over 100 hours in unchanged 70% acid without accelerated corrosion occurring.

Previous work had shown that the presence of alkali dichromates in dilute nitric acid at room temperature produced corrosion of the same order as that normally occurring in the boiling concentrated acid; at the boiling point even 1.56 N nitric acid containing 0.25 molar sodium dichromate dissolved the specimens at the rate of 12 mm/year.

2. Solution Colour

During this period, tests in acid containing chromic nitrate were still proceeding, and it was noticed that the original strong blue-green colour of a fresh solution changed, after roughly 24 hours boiling, to orange-yellow. This change was found to occur even in the absence of a specimen in the solution, and analysis of the solution showed the presence of chromate ions. After 48 hours boiling, almost all the chromium originally added as nitrate could be precipitated as chromate.

Further investigation revealed that chromate also occurred in nitric acid in which 18/13/1 austenitic steel had been corroded at the boiling point, and that the percentage of the chromium in the hexavalent form increased as the time between acid changes increased. This is illustrated by the following results, obtained with the standard 18/13/1 steel specimens, 1" x $\frac{1}{2}$ " x $\frac{1}{8}$ ", in 350 ml. of boiling 70% nitric acid in the times stated.

Time (hours)	Solution Analysis			
	Chromium as Chromate (grms.)	Total Chromium (grms.)	Iron. (grms.)	Nickel (grms.)
48	0.0013	0.0088	0.032	0.0078
48	0.0019	0.0100	0.035	0.0110
72	0.0047	0.0154	0.044	0.0084
72	0.0064	0.0165	0.050	0.0119

It will be seen that not only did the total chromium in solution increase when the period was extended from 48 to 72 hours, but that the percentage of chromium present in the hexavalent form rose from 17% to 35%.

These results led to the hypothesis that the corrosion accelerating effect of chromium was due to the presence of chromate ions. Further work, described in later sections, confirmed this view, but in the first instance experiments were designed to illustrate the mechanism of chromate formation. Chromate was also found in solutions after corrosion of 18/8/1 steel, and it is probable that all high chromium steels are susceptible to this type of corrosion.

3. Effect of Adding Gases, Oxidising and Reducing Agents and Acid Strength

(a) Liquid - Gas Interface

An indication of the mechanism of chromate formation was given by the discovery that chromic nitrate was perfectly stable in 70% nitric acid unless the solution was actually boiling (boiling point of 70% nitric acid 123°C.). No change of colour was observed after a week at 110°C. This suggested that the liquid gas interface might be concerned but it was found that by bubbling argon through a boiling solution of chromic nitrate in 70% nitric acid, the change to chromate was only slightly accelerated. Carbon dioxide gave similar results.

(b) Treatment with Oxidising Agents

Oxygen and ozonised oxygen were also bubbled through a similar solution with results comparable to those with argon

/and

carbon dioxide. The addition of large quantities of 40% H_2O_2 had no noticeable effect, but a small quantity of ceric sulphate immediately changed the chromic nitrate to chromate. Potassium permanganate produced a similar result but larger quantities were necessary. It was also found possible to oxidise cold chromic nitrate at the anode of an electrolytic cell provided that the nitric acid present did not exceed 5% weight/weight.

(c) Treatment with reducing agents and with oxides of nitrogen

The effect of certain reducing agents on chromate ions in boiling 70% nitric acid was also investigated. Hydrazine sulphate caused immediate reduction to chromic nitrate and hydroxylamine hydrochloride caused reduction when large quantities were added.

N_2O , NO and NO_2 gas were generated in an argon atmosphere and bubbled through a boiling solution of chromate in 70% nitric acid. N_2O and NO had no effect, but NO_2 caused reduction to nitrate. The action of NO_2 was much quicker when the solution was just off the boil. A little cellulose added as filter paper to a boiling solution caused copious evolution of NO_2 and the solution changed to the green colour of chromic nitrate instantly. The addition of the nitrite radicle as sodium nitrite also brought about the evolution of NO_2 , with the consequent reduction of the chromate to chromium nitrate. On the other hand, the addition of urea to a boiling solution of chromic nitrate in 70% nitric acid, to remove the nitrous acid initially present, caused the change to chromate to occur in a shorter time.

When chromic nitrate is boiled under a "cold finger" type of condenser, NO_2 is always present immediately above the solution and the solution itself is coloured brown. Under these conditions no chromate has been found, and corrosion is correspondingly reduced. (See II. 7)

It appears, therefore, that NO_2 must be concerned in the conversion of chromic nitrate to chromate.

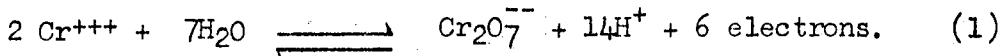
(d) Effect of Nitric Acid Strength

The strength of the nitric acid was found to be important. Below 40% wt/wt. of acid, chromic nitrate was stable at boiling point, and at 50% strength, the change was slow and incomplete. At 60% and upwards there was a complete colour change in about 18 hours of boiling, though traces of nitrate might be present for 48 hours (with a specimen in the solution there was always some nitrate present).

4. Valency Changes in the Chromium Ion

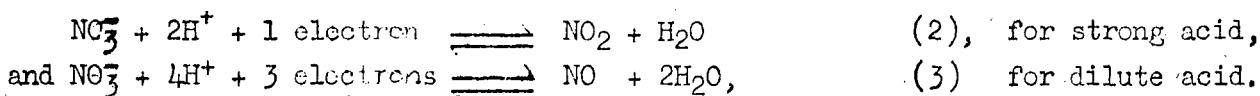
The term "Chromate" has been used in a general sense. From a study of the literature it seems probable that chromium is oxidised and then undergoes a condensation to di-chromate, in boiling nitric acid, but it has not been possible as yet to obtain experimental proof, as chromates, di-chromates, trichromates and tetra-chromates, are all precipitated as chromates by lead, silver or barium. Further work is being carried out.

The partial ionic equation for dichromates is given as -

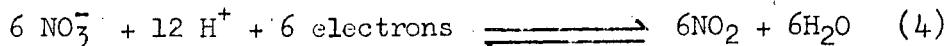


For oxidation these electrons must be supplied by the nitric acid, for which two partial ionic equations are given -

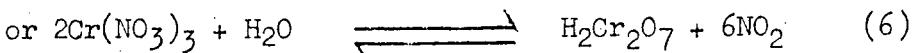
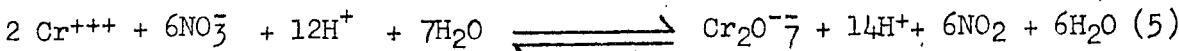
$/NO_3^-$



Equation (2) satisfies the conditions, and multiplying, we obtain -



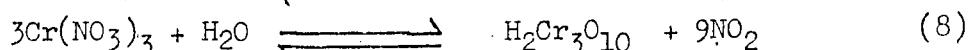
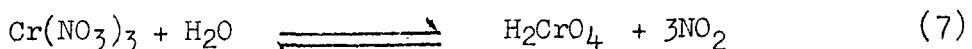
Adding equations (1) and (4)



Equation (6) is an over simplification, as obviously the presence of strong nitric acid is necessary, although none is used up.

Equation (6) does, however, represent the end reaction

If the other chromates were involved, then the appropriate end equations would be -



It will be seen that the amount of NO_2 given off by the oxidation of a molecule of chromic nitrate is the same in all cases.

This conception of a reversible oxidation - reduction reaction, in which the oxidation is performed by the nitric acid itself, and which is controlled by the rate of removal of NO_2 , provides one explanation for the observations outlined above.

5. Electrode Potentials in Chromic Nitrate and Chromate Solutions

The measurement of potentials in boiling nitric acid presented considerable difficulty; the apparatus is illustrated in Diagram II. The liquid interface potentials were not known and were assumed constant. All readings recorded are relative to the saturated $\text{KCl}/\text{calomel}$ half cell. Potentials were measured on a Cambridge Electrometer Valve pH meter.

The KCl bridge was refilled for every reading, and was then immediately removed.

In Fig. 2, the potential of a platinised platinum electrode versus calcamel has been plotted against time; the flask contained 400 mls. of boiling 70% nitric acid to which 1.347 gms. $\text{Cr}(\text{NO}_3)_3$, $9\text{H}_2\text{O}$, ± 0.175 gm. Cr were added. The immediate effect of the chromium addition was to lower the potential, but it then rose sharply, and continued to rise, though at a decreasing rate and asymptotically, for the duration of the experiment. During this time, there had been a noticeable change in solution colour in about 5 hours, and the change was visually complete in about 18 hours. In 45 hours the change to chromate was practically complete. There was a little loss of solution by evaporation during the run, and a constant level device feeding fresh acid would have been an improvement, but it is clear that the method is suitable for following the oxidation of chromium.

In other experiments an 18/13/1 austenitic steel electrode was used. This was in the form of the usual $1" \times \frac{1}{2}'' \times \frac{1}{8}''$ specimen, except that a projection was left to make a connection. This projection was swaged down to about $1/16''$ dia. $\times 4"$ long, and the whole annealed, pickled and polished. Before using it was

/boiled

boiled for 24 hours in 70% nitric acid.

Fig. 3 shows the potential of this 18/13/1 electrode (against calomel) in a similar solution to that used for the previous experiment. The potential obtained was, of course, different, but it will also be noticed that the maximum occurred in a much shorter time. This was because it was not possible to completely oxidise the chromium in the presence of the steel. The latter would be slowly dissolving to give more nitrate, and forming some nitrous acid in the process. For this reason actual corrosion solutions only contain a proportion of the total chromium as chromate.

At the point marked on the figure, NO_2 gas was blown through the solution, and the potential immediately dropped towards the original value. At the same time the colour reverted to blue-green. (This colour change was somewhat masked by the presence of excess NO_2 and was only properly shown by quenching the solution and purging with argon). The erratic nature of this part of the curve was thought to be due to an uneven gas flow.

Figure 4 shows the potentials obtained with the 18/13/1 austenitic steel electrode when chromium was added in various forms to boiling 70% nitric acid. Boiling was carried out for 10 minutes before the reading, long enough to remove NO_2 in the acid, but not to make a significant change in nitrate concentration. A fresh solution was used for each reading. The difference between the chromates and the nitrate is very striking, and the higher potential of the former gives the probable reason for their greater rate of attack on austenitic steel. The curves for dichromate and chromate are very similar, as would be expected, since the anions will finally exist in the same form in solution, and any difference would be due to the presence of potassium.

Electrode - potentials have also been measured in boiling 70% nitric acid to which nickel nitrate and ferric nitrate additions were made and the results are shown in Figs. 4A and 4B. The effect of nickel was to depress the potential almost proportionally, but the effect of iron additions was very erratic. The maximum potential recorded with iron in solution was 905 millivolts, well below the values obtained when chromate ions were present.

Results in Figure 5 were obtained by employing actual corrosion solutions. Standard 18/13/1 specimens were boiled in 70% nitric acid under reflux condensers for the times stated, after which the solutions were transferred to the potential measuring apparatus. An 18/13/1 austenitic steel electrode was used. The analysis of some of the solutions was as follows:-

Hours Corroded	Total Chromium grm.	Chromium as Chromate grms.
8	0.001	Not measurable
	0.002	
16	0.002	" "
	0.001	" "
24	0.003	" "
	0.003	" "
32	0.003	" "
40	0.003	" "
48	0.006	0.0005
72	0.016	0.003
96	0.097	0.043

Comparing Figure 5 with Figure 4, and with the above analyses in mind, it can be seen that the potential due to chromate ions gradually takes charge. The process is self accelerating, and after about 40 hours (for the particular volume/surface area conditions used) corrosion increases rapidly.

It is concluded that the accelerating effect of chromium on the corrosion of stainless steels, in the standard apparatus, is associated with a raising of the Specimen Solution Potential in the presence of chromate ions.

6. Ultra-Violet Absorption of the Solution

A number of solutions was prepared as follows:-

- (1) 70% nitric acid freed from NO_2 by passing filtered argon through it for 15 minutes.
- (2) 350 ml of 70% nitric acid containing 0.9615 grm. chromic nitrate (\approx 0.125 grm. chromium) in solution, freed from NO_2 by argon as above.
- (3) 350 mls. of 70% nitric acid containing 0.2404 grm. chromic anhydride (\approx 0.125 grm. chromium) in solution, freed from NO_2 by argon as above.
- (4) 350 mls. of 70% nitric acid to which 0.9615 grm. chromic nitrate had been added, boiled for 72 hours under a reflux condenser, cooled (See under 7 below), purged with argon, and made up to the original volume with solution (1).

These solutions were analysed chemically by plotting Ultra Violet Absorption Curves (2), (3) and (4) after dilution from 50 mls. to 200 mls.; solution (1) was used as a base.

Density/wavelength curves are shown in Figure 6. The difference in characteristic between both the curves for the chromate and for the boiled solution of the nitrate and that of the nitrate without boiling is striking, and is a further indication of the nature of the changes taking place in boiled chromic nitrate solution.

7. The Effect of the Condenser on Corrosion

All the tests so far described were carried out under reflux condensers. An internal type of condenser, referred to as a "Cold Finger" was tried, and showed a marked effect on corrosion. The apparatus is illustrated in Diagram 1(b). Nitric acid boiled under "Cold Finger" condensers appeared quite brown in colour, and the free space above the solution was filled with brown fumes, especially in strong sunlight. The presence of so much NO_2 would be expected to interfere with the oxidation of chromium nitrate, and careful analysis of a number of solutions has failed to show the presence of any measurable quantity of chromate. A solution of chromic nitrate in 70% nitric acid, boiled under a "Cold Finger" condenser for 4 days, showed no change in colour, and contained no chromate at the end of that time.

A series of tests was carried out in which the two types of condenser were directly compared. The standard specimens of 18/13/1 were used, in 350 mls. of acid. For the first 552 hours, acid changes were carried out every 48 hours, but thereafter at 72 hour intervals, in order to accentuate the difference in the results.

/The results

The results are shown in Table V, and plotted in Figure 7. It will be seen that the steady corrosion rate under reflux condensers, was more than twice that under "Cold Fingers".

The upper half of Table VI shows some results extracted from Table III, illustrating the effect of added chromium on corrosion, under reflux condensers. The lower half of Table VI shows the results when the same experiments were repeated under "Cold Finger" condensers. It will be seen that under "Cold Fingers" the effect of chromium on corrosion was negligible.

These tests amply confirm the view that chromium only accelerates corrosion when present in the hexavalent form.

The different action of the two types of condenser probably arises as follows:-

In the flask with reflux condenser (Diagram 1a), immediately over the solution and up to the neck, the enclosed gas, mist or vapour, is clear and colourless, as is the condensate falling into the flask. Immediately above this, the condenser space holds brown NO_2 fume. This fume is present whether there is a specimen in the solution or not, it is not affected by closing the outlet of the condenser with a liquid trap, and it appears to depend to some extent on the quality of the light falling on the flask. Attempts to find which part of the spectrum is responsible have not been successful, except that sunlight was found to cause more NO_2 than any artificial light, and some NO_2 was present even in complete darkness. However, whether the reason be difference in density, temperature gradients, or the effect of convection currents, it seems that the concentration of NO_2 in the interior of the flask is quite low. These conditions only obtain during actual boiling. As soon as boiling stops, the column of NO_2 drops into the flask, colours the solution, and begins to reduce any chromate present. Therefore, when analysing these solutions for chromate, it is essential to remove the condenser, and with it the column of NO_2 , before removing the flask from the hot plate. The flask should then be quenched in a water bath, whilst a current of air is blown over the surface of the liquid.

With a "Cold Finger" condenser, the whole interior of the flask is generally filled with brown fume, the condensate forming on the Finger and falling into the solution is coloured, and the solution itself is also brown. The amount of fume varies considerably from flask to flask, and from hour to hour, but the amount of NO_2 which seems necessary to prevent the formation of chromate must be quite small, as no measurable quantity of hexavalent chromium has yet been found in any flask fitted with this type of condenser, even when the presence of fume has been hardly noticeable.

Conclusions

The experiments reported above were undertaken with a view to exploring the mechanism by which accelerated corrosion can occur in exposing 18/13/1 and 18/8/1 austenitic steels to boiling nitric acid. The following conclusions have been drawn from the results obtained.

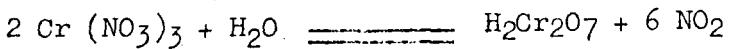
1. The solution of iron and nickel from the steel has little effect on the corrosion rate. Ferric nitrate slightly raises the electrode potential in boiling nitric acid, nickel nitrate decreases the potential.
2. The solution of chromium as nitrate has no effect unless the nitric acid is boiling. At the boiling point, chromic nitrate is slowly oxidised to the hexavalent form, the electrode potential of the steel is raised, and the rate of corrosion increased in some relation to the

/concentration

concentration of hexavalent chromium. Further work in this field is necessary.

3. The addition of certain reducing agents to the boiling solution leads to reduction of the hexavalent chromium to chromic nitrate, and the corrosion rate falls to a steady value unless oxidation is allowed to resume.

4. The oxidation of chromic nitrate to the hexavalent form may occur according to the simplified equation.



The reaction would then be controlled by the rate of removal of nitrogen peroxide from the boiling solution.

5. A closed system, in which nitrogen peroxide is not allowed to escape (internal condenser type) does not give rise to the oxidation of chromium, as suggested in 4 above. A system open to the atmosphere, however, will allow the escape of nitrogen peroxide, and hence the formation of hexavalent chromium. The rate of dissolution of 18/13/1 and 18/8/1 steels is thus affected by the atmosphere immediately above the boiling nitric acid.

6. A high ratio of surface area of metal to volume of corroding solution will accentuate the rate of corrosion by reason of the building up of high concentrations of hexavalent chromium.

Acknowledgment

The authors wish to acknowledge suggestions and the assistance of Mr. F. Jones in the analytical work recorded in this paper, and advice and discussion on the electro-chemical measurements by Dr. J.S. Broadley.

APPENDIX

The progressive penetration rate at any time is given by the expression $\frac{W_0 - W_t}{\frac{A_0 + A_t}{2}} \times 8760 \times C$ $\times t$ (in hours)

The penetration rate for any period will be given by

$$\frac{W_{t_1} - W_{t_2}}{\frac{A_{t_1} + A_{t_2}}{2}} \times 8760 \times C \times (t_2 - t_1)$$

The period penetration rate does not reach its average steady value for about 800 hours and thereafter becomes fairly constant. The adjusted progressive penetration rate is calculated by substituting the values at 800 hours or a similar period for W_0 and A_0 in the first expression and ignoring any previous readings. It is in fact the average of all the period penetration rates after that point and gives a more accurate estimate of the rates at which a steel will corrode over very long periods.

W_0 = original weight.
 W_t = weight at time t .
 A_0 = original area.
 A_t = area at time t .
 C = a constant depending on the density and the units used
 t = time in hours.

FIG. 1

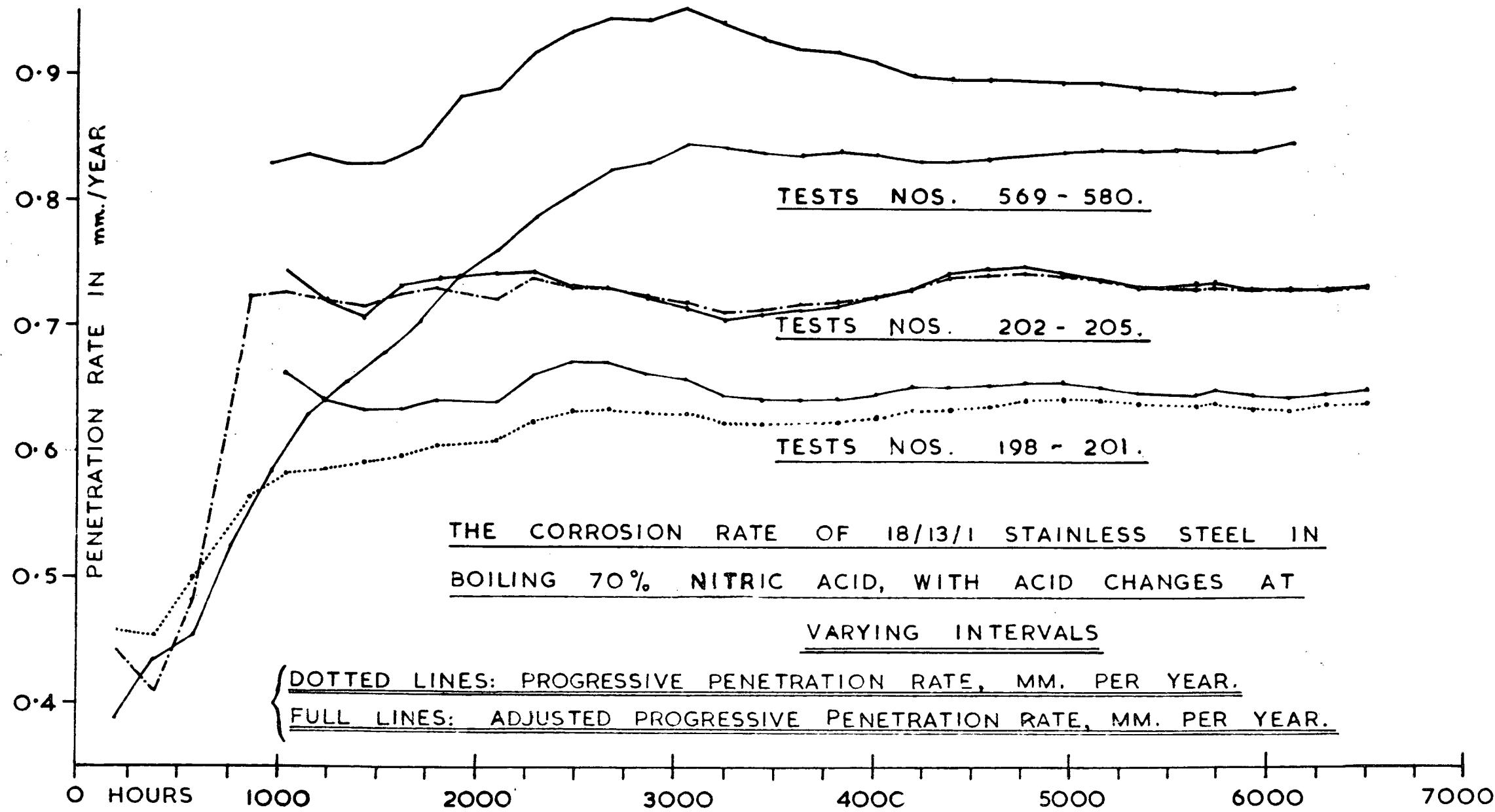


FIG. 2

POTENTIAL - TIME CURVE OF PLATINISED PLATINUM
ELECTRODE IN 400 ML. 70% HNO₃ SOLUTION
CONTAINING 1.35 GM. Cr(NO₃)₃.9 H₂O PER 400 ML.,
SOLUTION BOILING UNDER REFLUX CONDENSER.

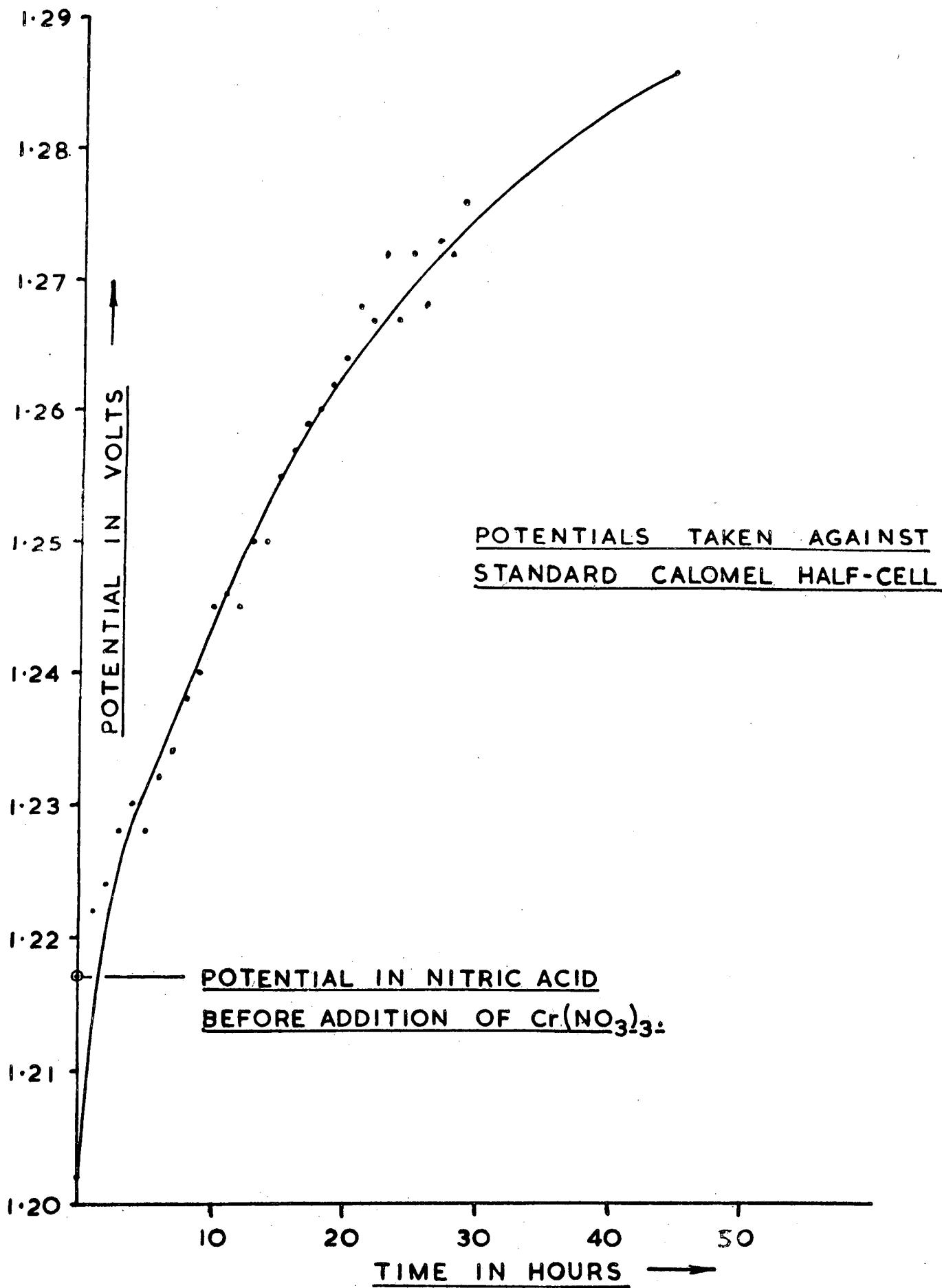


FIG. 3

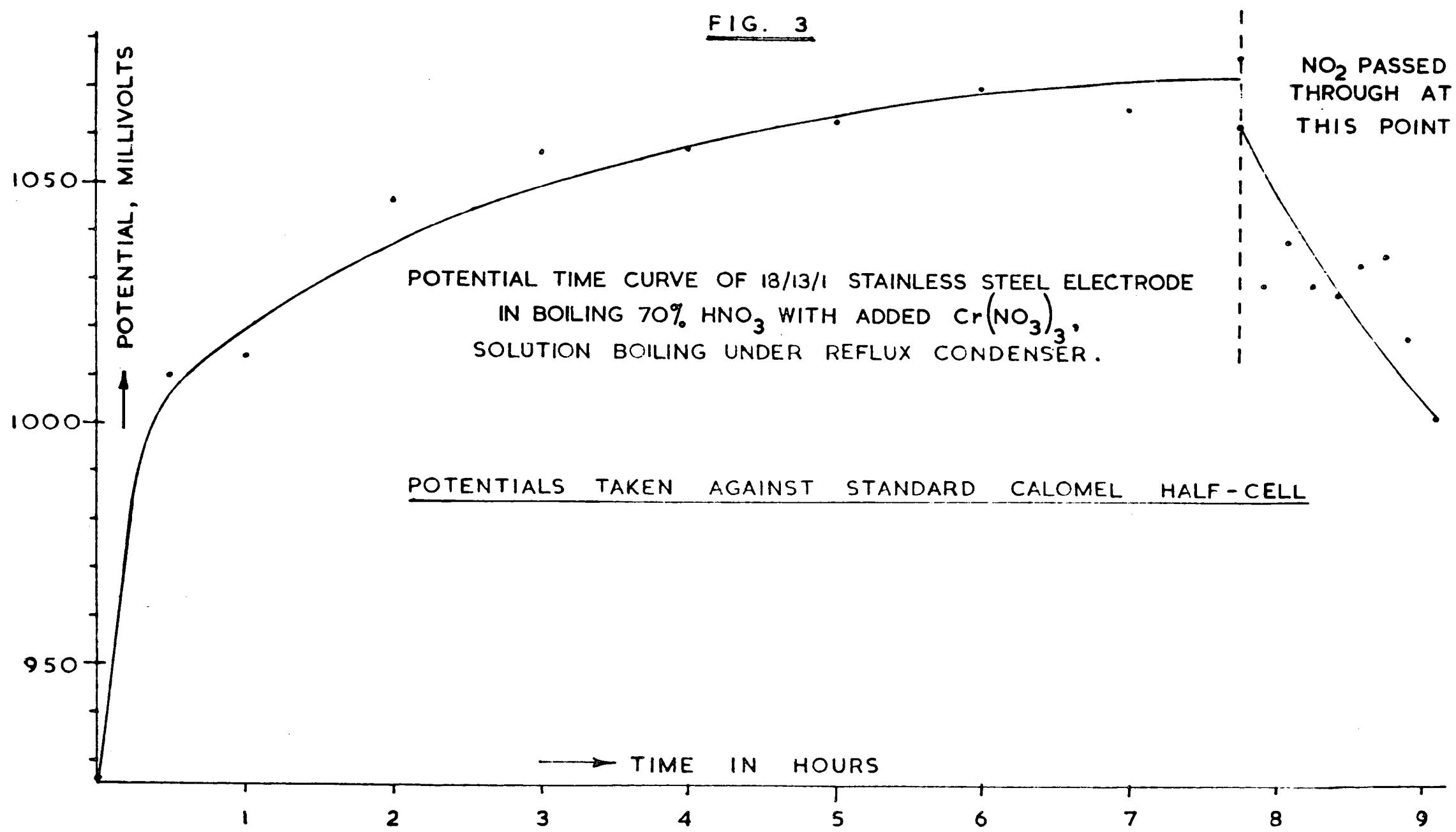


FIG. 4

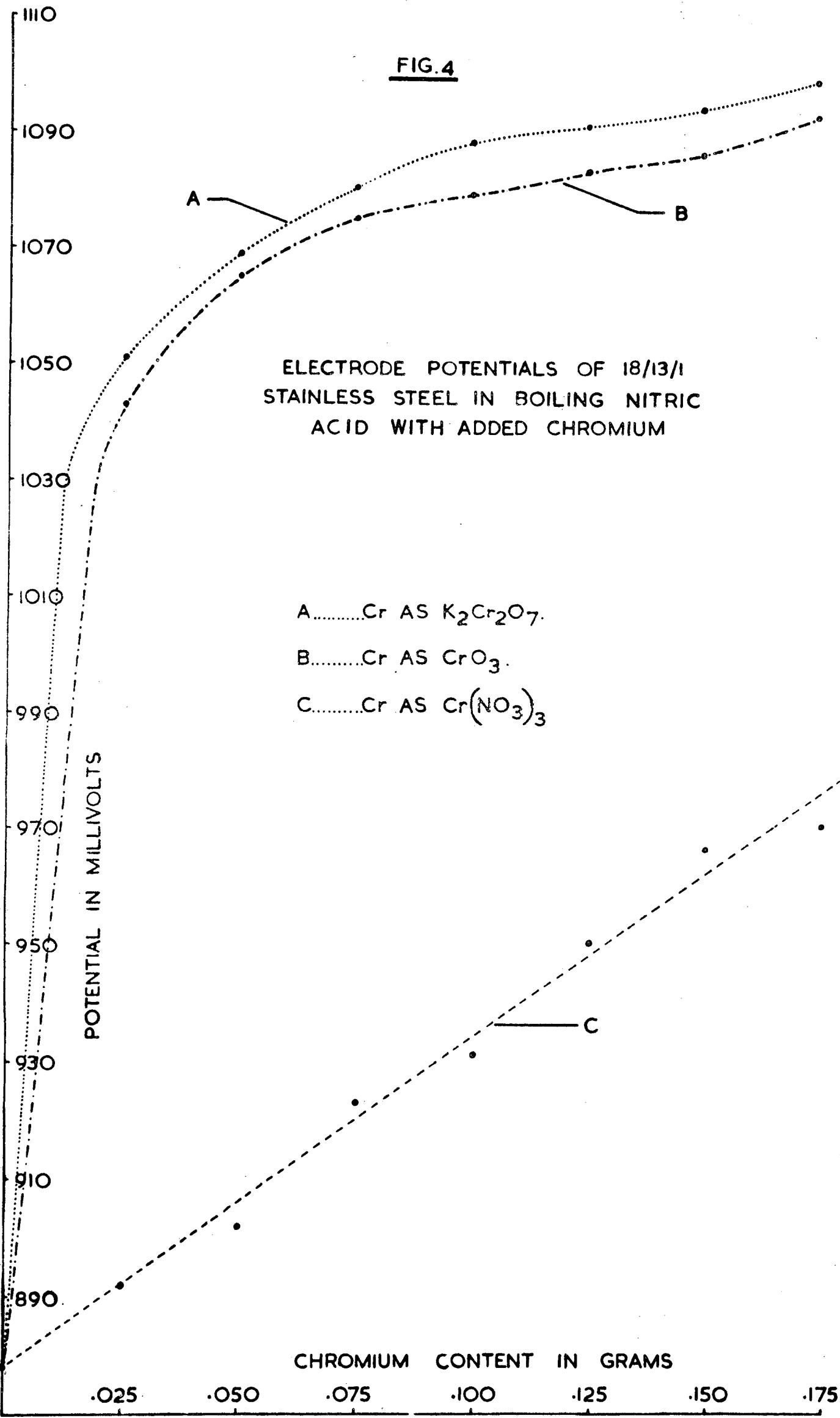


FIG. 4A

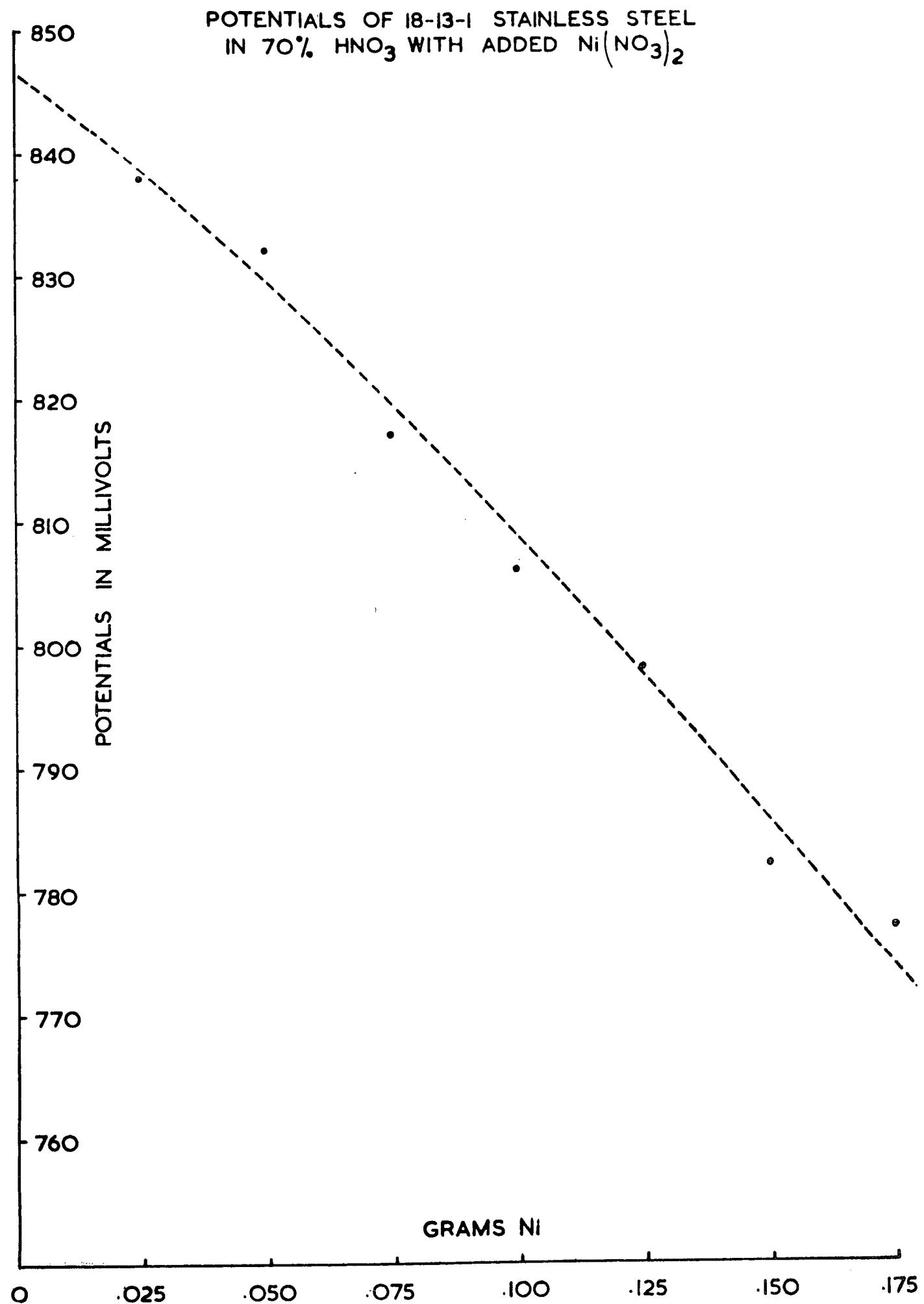


FIG. 4B

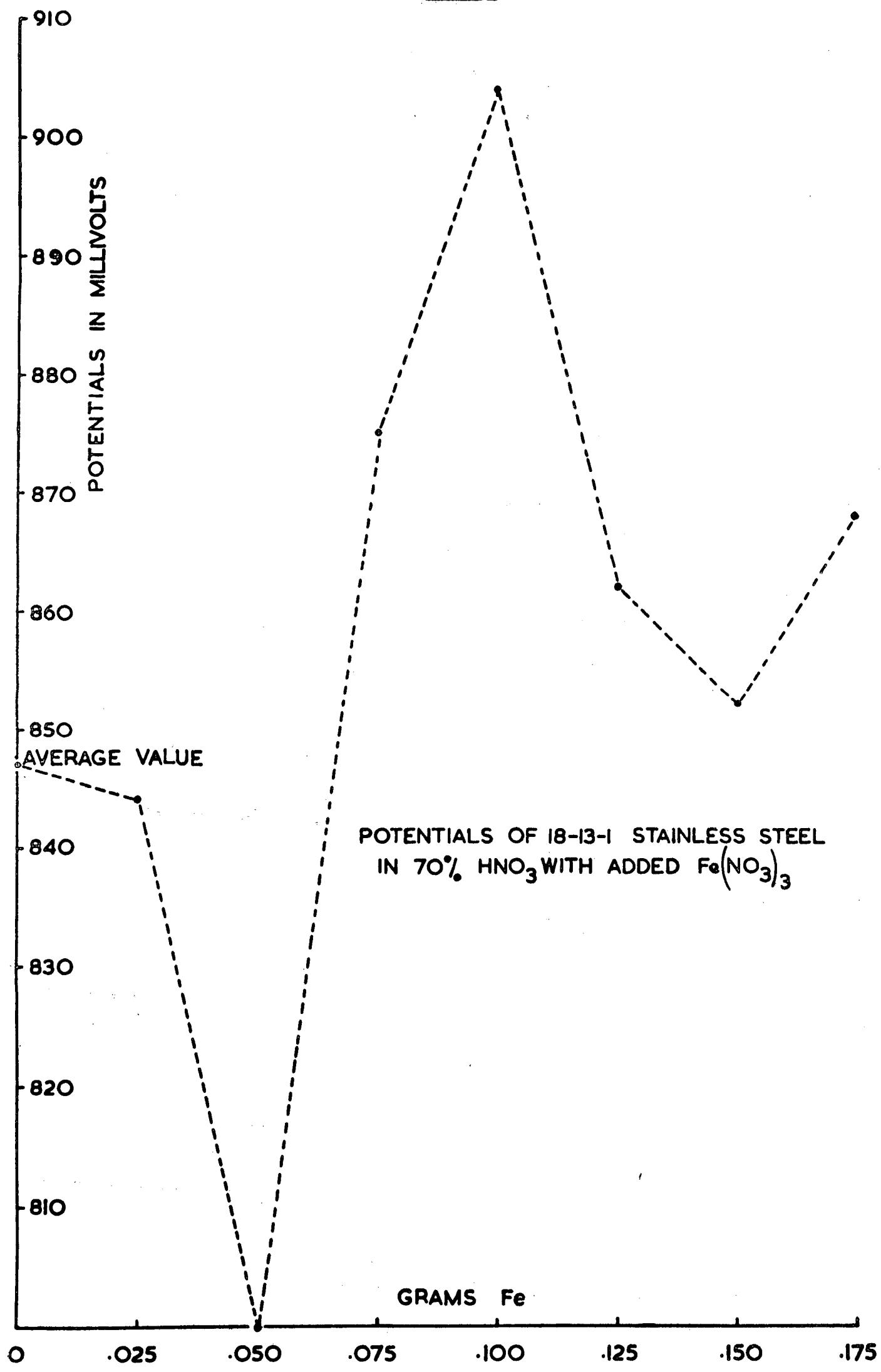


FIG. 5

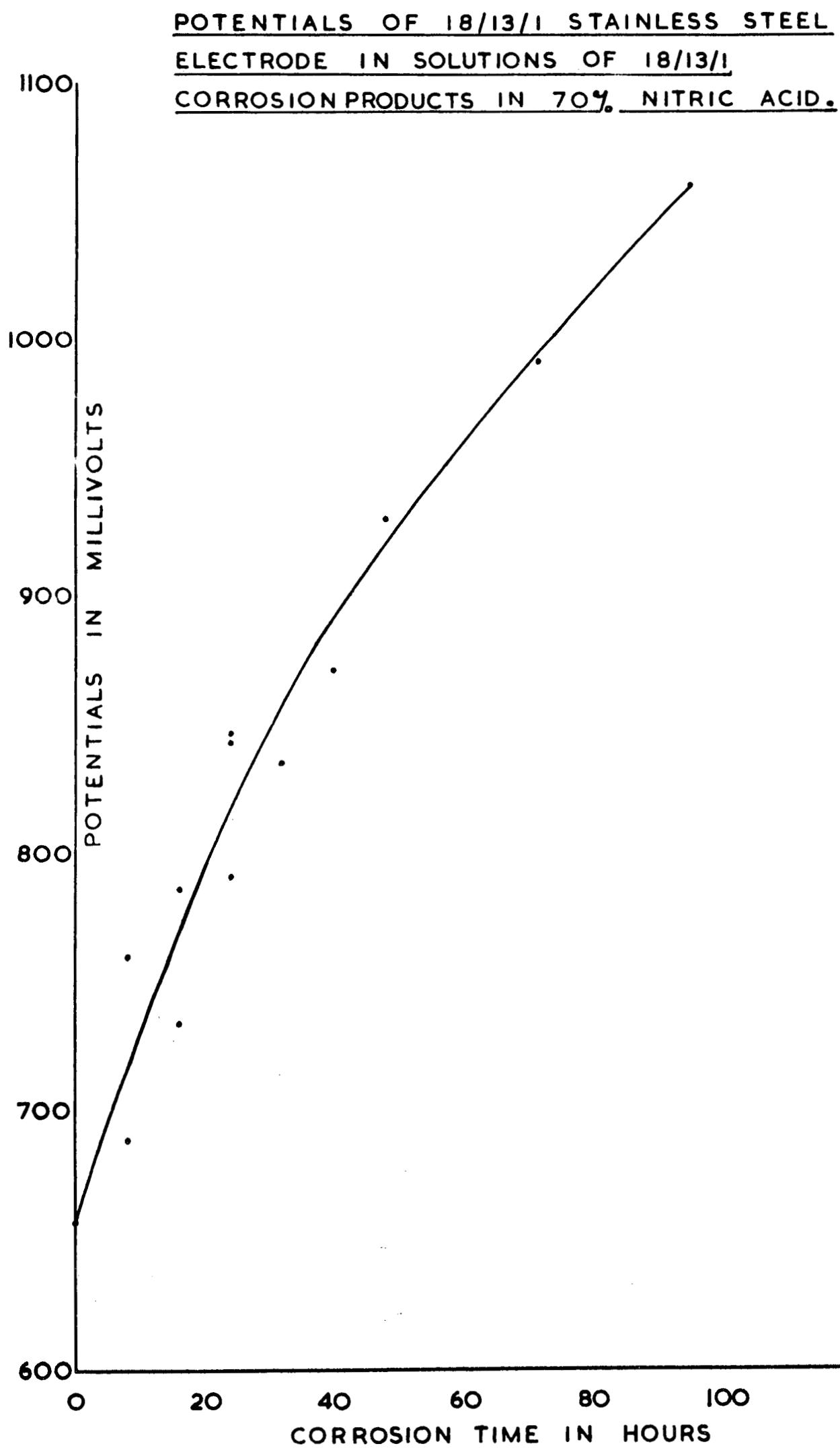


FIG. 6.

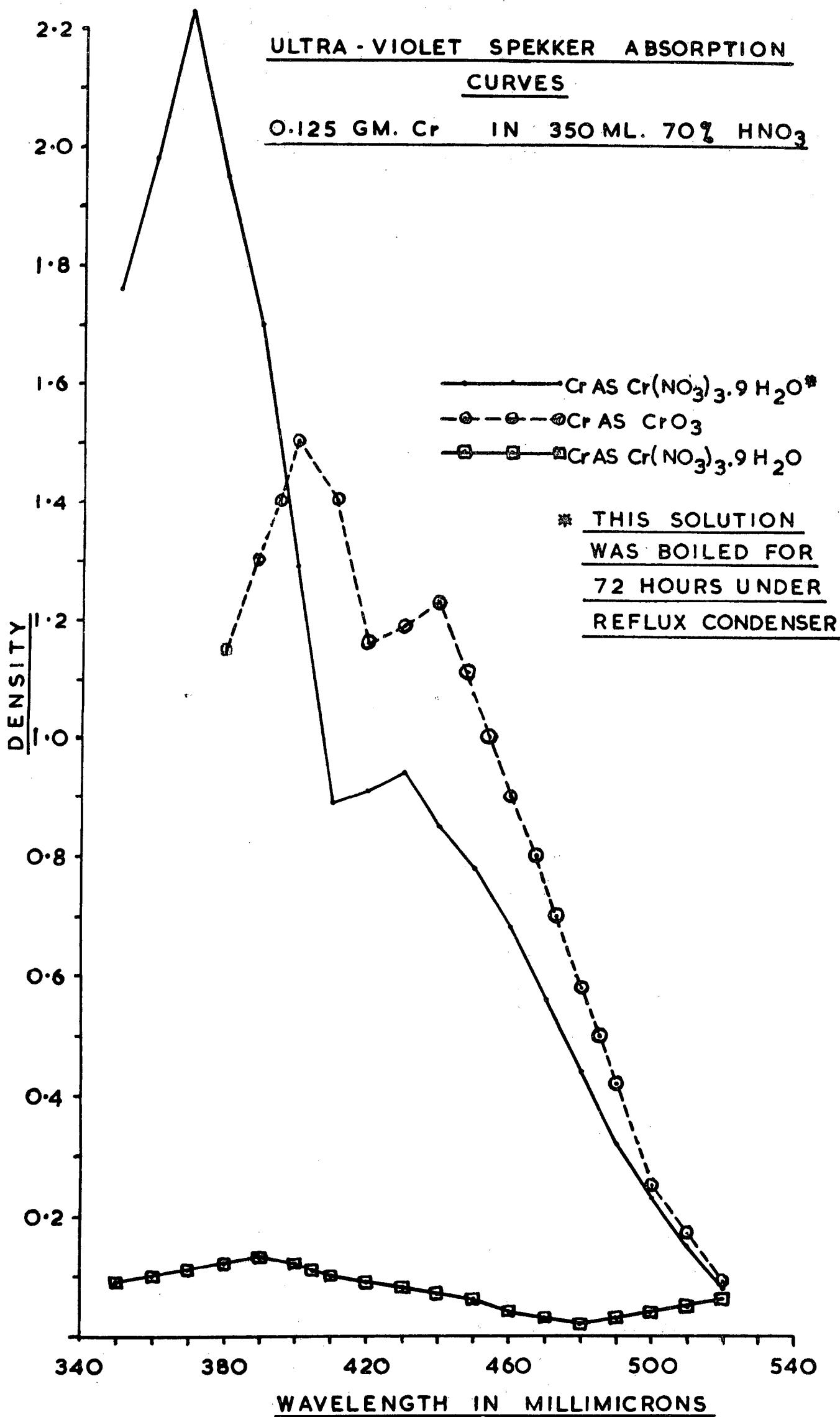


FIG. 7.

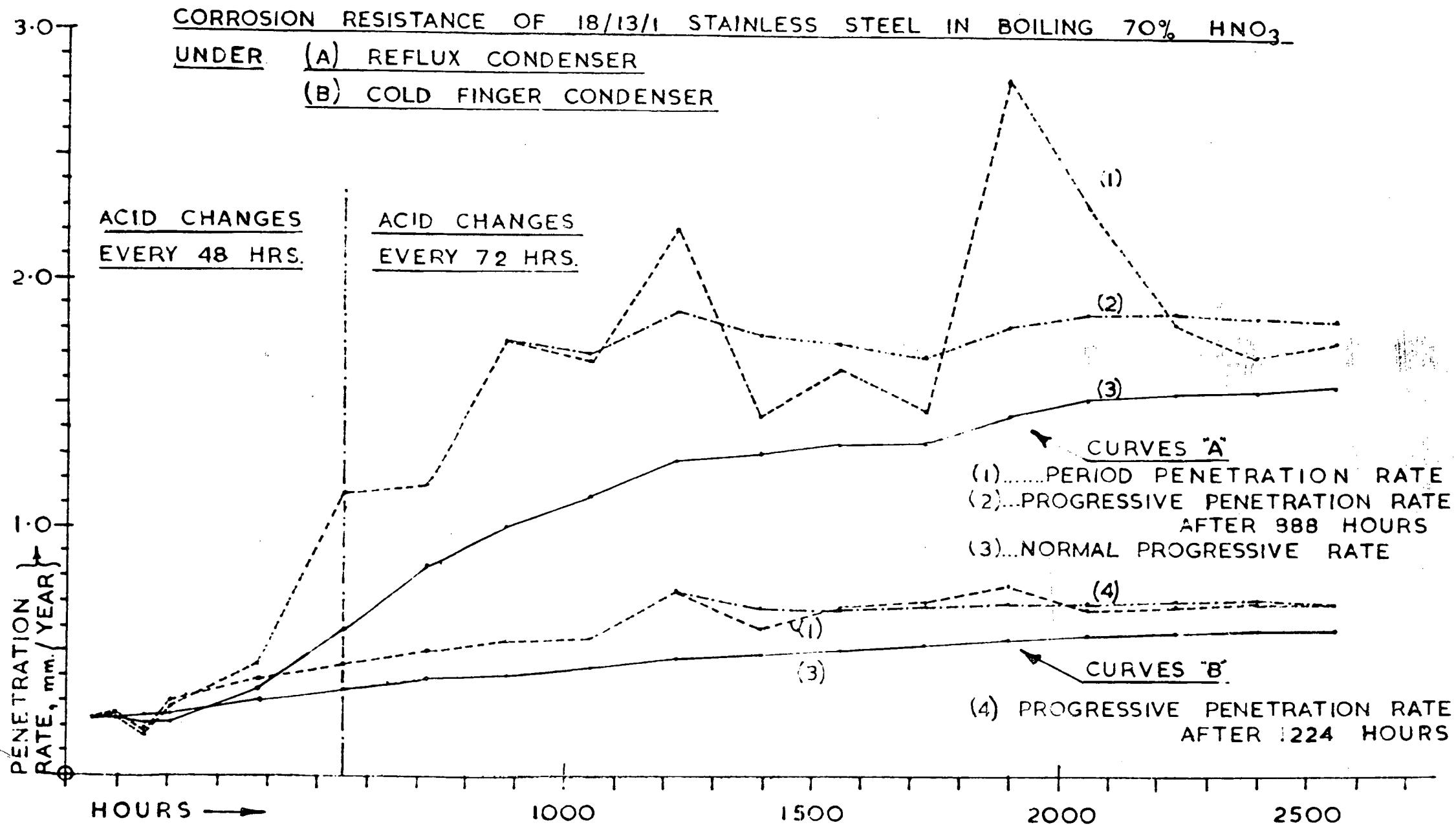
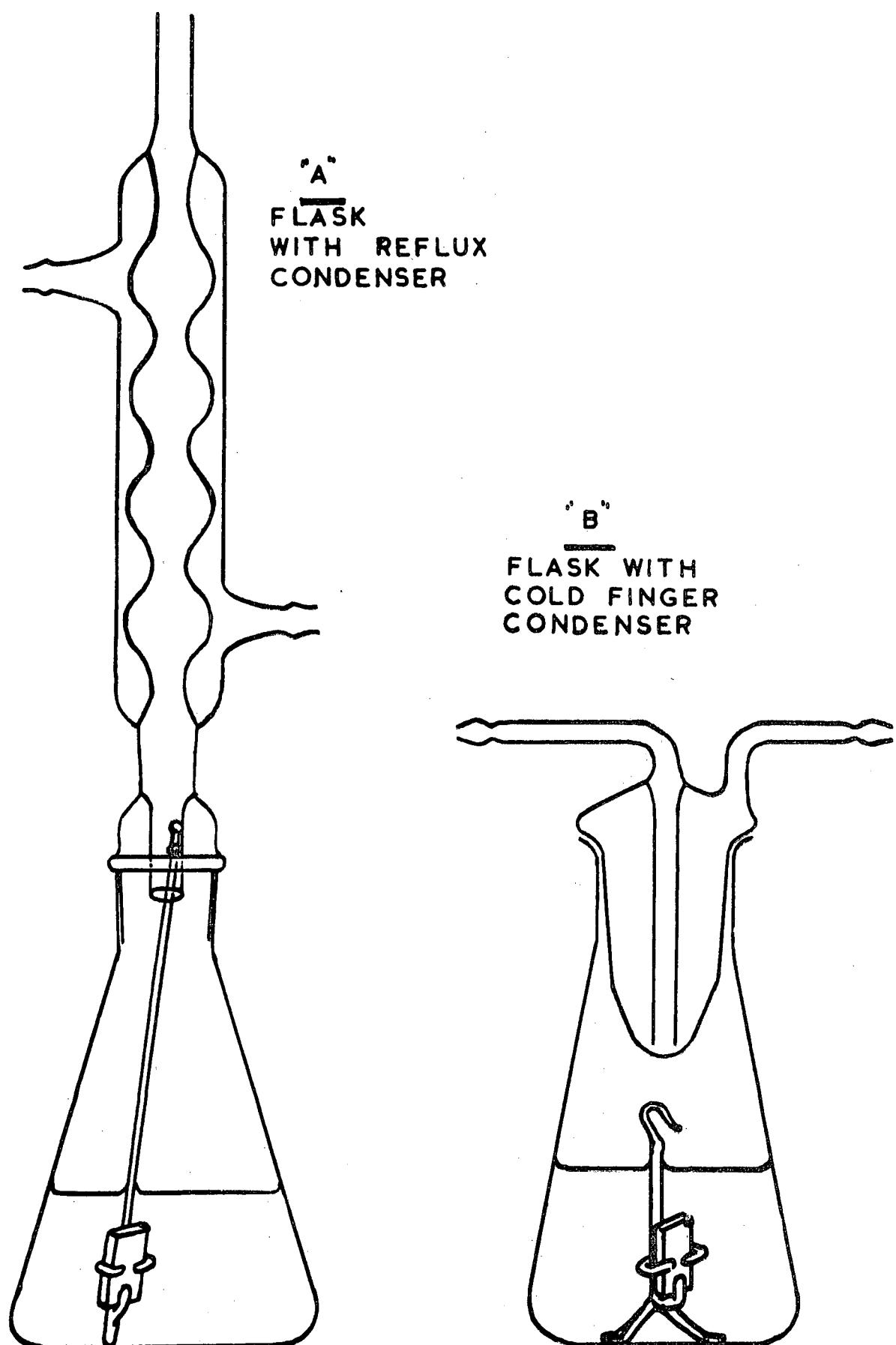


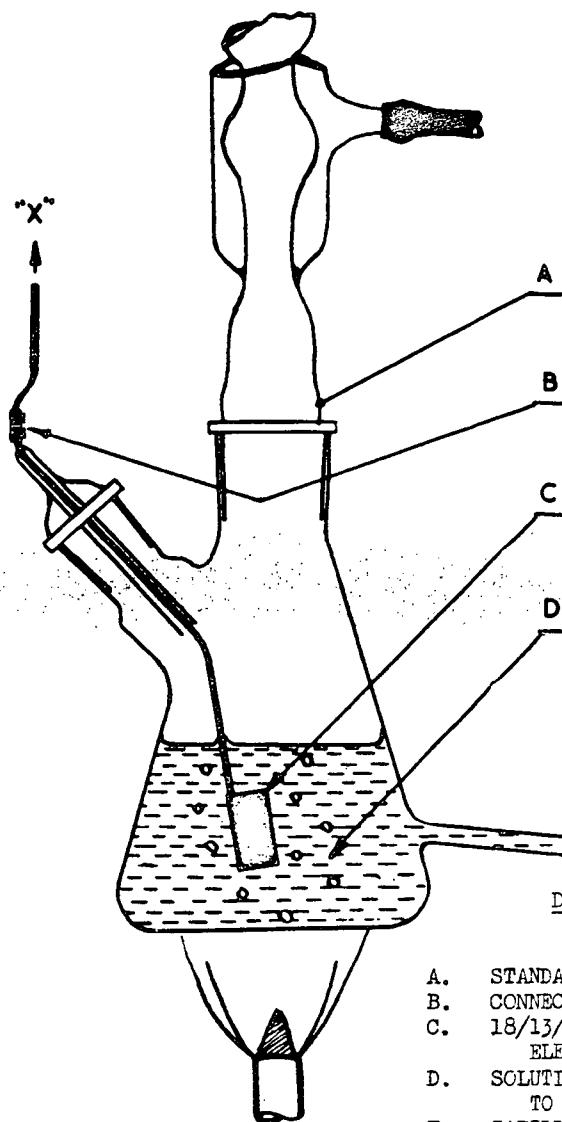
DIAGRAM NO. 1



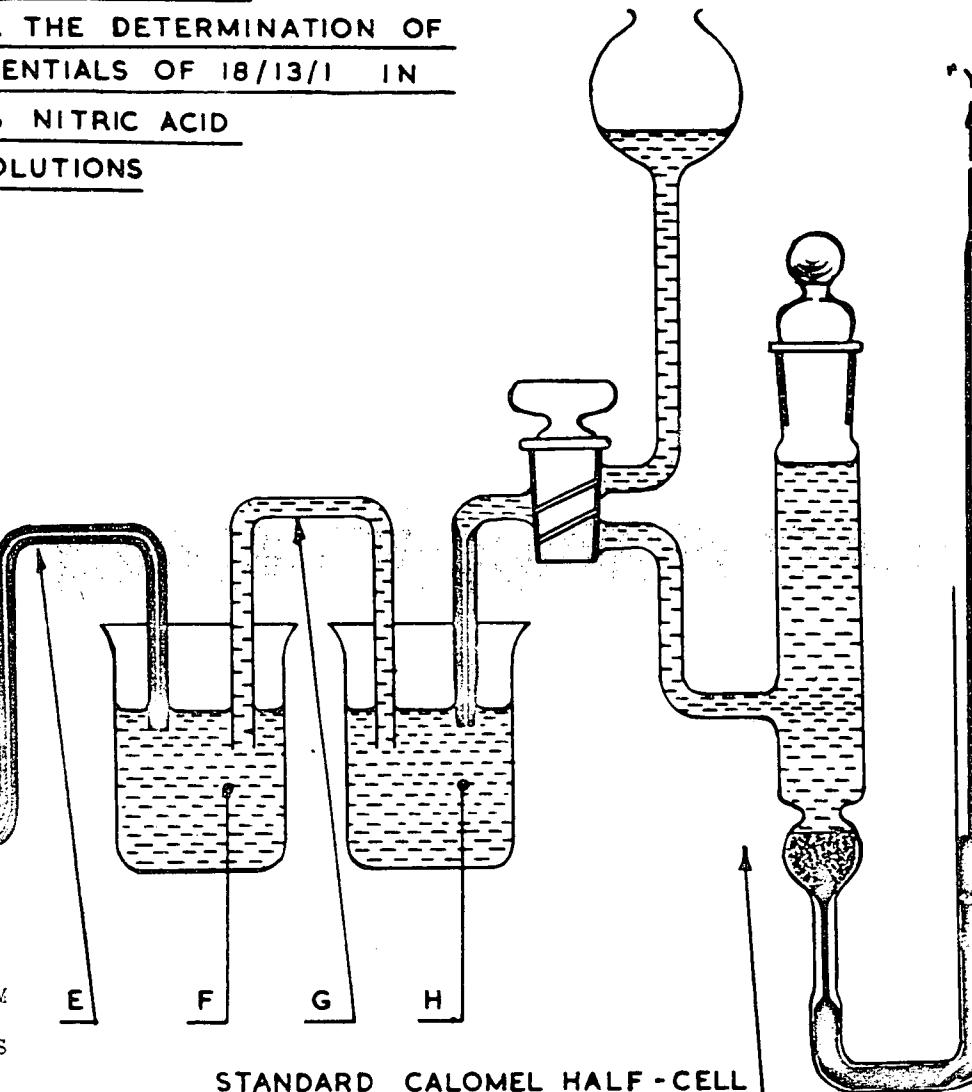
HALF FULL SIZE.
LIQUID LEVELS CORRESPOND TO SOLUTION
VOLUME OF 350 MLS.

DIAGRAM NO. 2.

APPARATUS FOR THE DETERMINATION OF
ELECTRODE POTENTIALS OF 18/13/1 IN
VARIOUS NITRIC ACID
SOLUTIONS



- A. STANDARD REFLUX CONDENSER.
- B. CONNECTION TO ELECTRODE "C".
- C. 18/13/1 OR PLATINISED PLATINUM ELECTRODE.
- D. SOLUTION IN WHICH POTENTIAL IS TO BE MEASURED.
- E. CAPILLARY BRIDGE
- F. 70% COLD NITRIC ACID.
- G. POTASSIUM CHLORIDE BRIDGE.
- H. SATURATED POTASSIUM CHLORIDE SOLUTION.



The diagram is one-half full size.

TABLE I
EFFECT OF SPECIMEN SURFACE AREA SOLUTION VOLUME RATIO ON CORROSION OF 18/13/1 STAINLESS STEEL IN BOILING CONCENTRATED NITRIC ACID

TEST NO.	Solution Volume ml.	SPECIMEN SURF. AREA SOLUTION VOLUME RATIO in sq.in/ml	PROGRESSIVE RATE OF PENETRATION, MILLIMETRES PER YEAR, AFTER FOLLOWING TOTAL HOURS																								
			6	24	47	94	192	384	672	847	1037	1228	1420	1612	1804	1996	2188	2572	2764	2956	3148	3340	3532	3724	3916	4108	4300
186)			.20370	.41203	.55084	.75884	.94793	.38443	.69891	.63182	.59010	.66290															
187)	100	0.01396	.33333	.49537	.58393	.66901	1.0301	.41713	.59770	.60121	.54219	.62148															
188)			.31481	.45833	.61703	.81558	.86111	.32769	.53838	.54471	.53685	.59064															
189)	125	0.011168	.24074	.32870	.43027	.52481	.78011	.63504	.57280	.55442	.49249	.53309															
190)			.31481	.45370	.51301	.55790	.74885	.21421	.34097	.30855	.27575	.26387															
191)	150	0.009306	.31481	.38889	.48937	.69147	.1939	.29948	.38504	.35647	.31231	.28254															
192)	200	0.00698	.29639	.47222	.73251	.56736	.62848	.16282	.21592	.20295	.2057	.24052	.24788	.28462	.27192	.26055	.24563	.23392	.24143	.22123							
193)			.20370	.42129	.53665	.56500	1.0301	.15198	.14947	.16158	.15072	.14460	.16120	.24076	.25303	.24488	.23179	.22815	.21791	.20641							
194)			.20370	.37057	.43027	.46807	.49943	.74189	.80787	.84486	.82027	.84645	.82856	.90495	.98004	.96441	.96405	1.0194	1.0465	1.0554	1.0539	1.1084	1.2320	1.2713	1.2492	1.2152	
195)	300	0.004653	.24074	.37500	.41845	.49999	.58623	.75405	.77397	.77186	.75688	.76837	.76604	.34822	.87201	.88633	.88604	.88707	.91550	.92666	.92799	.98040	1.0549	1.1566	1.1723	1.1710	1.1776
196)			.22222	.40278	.45627	.53308	.57119	.66261	.70106	.70572	.69356	.68811	.68388	.70320	.71908	.72400	.73075	.73730	.74218	.74502	.74537	.75057	.76399	.76949	.76149	.76087	
197)	450	0.003102	.20370	.37963	.46100	.51772	.58276	.65451	.67361	.68455	.70674	.70557	.69413	.69369	.70216	.70641	.72721	.73094	.73810	.74025	.74720	.76277	.76926	.76054	.75819		
			4700	4892	5084	5276	5468	5660	5852	6044	6236	6428	6620	6812	7004												
210)																											
211)		Continued from above																									
212)																											
213)	330	0.0042303																									
214)																											
215)	360	0.00387																									
216)																											
217)	390	0.0035769																									
218)																											
219)	420	0.0033238																									
220)																											
221)	450	0.003102																									
			4700	4892	5084	5276	5468	5660	5852	6044	6236	6428	6620	6812	7004												
210)		Continued from above																									
211)																											
220)		Continued from above																									

SPECIMEN SIZE: 1" x 1/2" x 1/16"
SOLUTION CHANGE: MONDAYS, WEDNESDAYS AND FRIDAYS.

TABLE 2
EFFECT OF FREQUENCY OF SOLUTION REPLACEMENT ON CORROSION OF 18/13/1 STAINLESS STEEL IN BOILING 70% NITRIC ACID

TEST NO.	TEST DETAILS	PERIOD CHANGE	AVERAGE RATE OF PENETRATION mm/yr. after :																								
			6	24	47	94	192	384	568	867	1049	1241	1433	1625	1817	2105	2297	2489	2681	2873	3065	3257	3449	3641	3833	4025	4217
			HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	HRS	
198)			.51852	.28704	.22695	.39362	.42955	.43610	.47926	.55491	.57992	.58286	.58293	.58810	.59329	.59673	.61031	.62247	.								

TABLE III
EFFECT OF CORROSION PRODUCTS IN KNOWN CONCENTRATIONS ON CORROSION OF 18/13/1 STAINLESS
STEEL IN CONCENTRATED NITRIC ACID

Test No.	Solution Details &c.	Progressive Penetration Rate in mm./year after Total Corrosion Hours as Below											
		48	96	168	216	357	504	672	840	1008	1152	1344	1536
698	} 70% HNO ₃ + 7.2 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre {	.258333	.302662	.612103	.741667	1.498101	1.990366	2.483614	2.494312	2.782264			
699		.279167	.301389	.527116	.610597	1.001681	1.606658	2.366369	2.397368	2.799537			
614	} 70% HNO ₃ + 3 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre { } 70% HNO ₃ + 2 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre { } 70% HNO ₃ + 1 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre { } 70% HNO ₃ + .5 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre { } 70% HNO ₃ + .05 gm. } Fe(NO ₃) ₃ 6H ₂ O per litre { } 70% HNO ₃	6	24	47	94	192	394	575	768	960			
613		.40741	.15278	.20331	.23641	.37905	.64844	.79053	.88744	1.05324			
612		.55556	.17130	.21040	.23641	.34144	.58854	.89098	.92506	1.08796			
611		.51852	.19444	.21277	.25414	.37037	.70978	.89063	1.05411	1.21354			
610		.48143	.16667	.21513	.22577	.37731	.60706	.77990	.82784	.91898			
609		.40741	.11111	.19858	.22813	.28356	.51215	.59536	.68258	.74606			
608		.31481	.12963	.16785	.18913	.29109	.50579	.59034	.64511	.71759			
607		.53704	.17130	.20331	.21513	.28069	.42853	.52271	.57624	.62118			
606		.53704	.18519	.19385	.24941	.31529	.43432	.51072	.55961	.61204			
605		.48148	.15741	.20804	.21158	.25521	.35648	.42957	.48119	.54664			
604		.33333	.12963	.15839	.19149	.24769	.34983	.41121	.45110	.48380			
603		.38889	.17130	.18913	.18676	23206	.31800	.36367	.44488	.44317			
		48	96	168	216								
702	} 70% HNO ₃ + 5.828 gms. } Cr(NO ₃) ₃ 9H ₂ O per litre {	18.5189	24.4371	28.9294	30.0576								
703		15.5337	16.4993	20.1029	28.1712								
		48	96	168	216	384	552	720	800				
810	} 70% HNO ₃ + .476 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre { } 70% HNO ₃ + .238 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre { } 70% HNO ₃ + .0476 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre { } 70% HNO ₃ + .0238 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre { } 70% HNO ₃ + .0119 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre { } 70% HNO ₃ + .0024 gm. } Cr(NO ₃) ₃ 9H ₂ O per litre {	1.0069	2.1285	7.3982	6.9342	5.7069	4.8281	4.7347	5.0614				
811		1.2421	1.1769	3.7262	3.9918	3.1642	3.6221	3.5831	3.7591				
812		3.063	2.472	5.027	4.624	4.332	3.811	3.691	3.813				
813		4.227	4.312	4.884	6.046	5.826	4.997	4.704	4.747				
814		.2896	.1566	.4406	.5428	1.0725	1.160	1.194	1.155				
815		.2505	.2492	.45	.4517	.06377	.7172	.8054	.8468				
816		1.090	.7188	.8505	.8688	.9876	1.025	1.072	1.099				
817		.3218	.3982	.7890	.8565	1.020	1.158	1.199	1.239				
818		.2176	.2037	.2176	.2325	.3215	.4147	.4546	.5729				
819		.1620	.1736	.1839	.1903	.2465	.3213	.4028	.4301				
820		.1898	.1875	.1978	.2011	.2836	.3466	.4178	.4432				
821		.2384	.1956	.2163	.2289	.2884	.3321	.3753	.3892				
		48	96	168	216	357	504	672	840	1008			
700	} 70% HNO ₃ + 3.2571 gm. } Ni(NO ₃) ₂ 6H ₂ O per litre {	.21388	.21134	.22367	.26558	.31048	.32753	.37556	.41915	.46062			
701		.24537	.22696	.23631	.25339	.32346	.36108	.40892	.44300	.48174			

Spec. Size: 1" x $\frac{1}{2}$ " x $\frac{1}{8}$
 Sol. Vol. 350 ml.
 Sol. Change: Mondays,
 Wednesdays & Fridays.

Spec. Size: 1" x $\frac{1}{2}$ " x 0.131"
 Sol. Vol. 350 ml.
 Solution Change: Mondays,
 Wednesdays and Fridays.

Spec. Size: 1" x $\frac{1}{2}$ " x $\frac{1}{8}$
 Sol. Vol. 350 ml.
 Sol. Change: Mondays,
 Wednesdays & Fridays.

Spec. Size: 1" x $\frac{1}{2}$ " x $\frac{1}{8}$
 Sol. Vol. 350 ml.
 Sol. Change: Mondays,
 Wednesdays & Fridays.

TABLE IV

EFFECT OF CORROSION PRODUCTS IN KNOWN CONCENTRATIONS ON CORROSION OF 18/8/1 STAINLESS STEEL
IN CONCENTRATED NITRIC
ACID.

Test No.	Solution Details &c.	Penetration Rate in mm/year after total corrosion hours as below																
		48	96	168	216	384	552	720	888	1056	1224	1392	1560	1728				
990	70% HNO ₃ + 2.857 gm.	0.5265	0.5372	0.6345	0.7277	0.9337	1.0930	1.1643	1.2160	1.2616	1.3092	1.3511	1.3010	1.4000		Specimen size 1" x ₂ ¹ Nominal Sol. Vol. 350 ml. Temp. Boiling Point Sol. Change: Mondays, Wednesdays & Fridays		
991	Fe(NO ₃) ₃ 6H ₂ O per litre	0.5247	0.5529	0.6554	0.7407	0.9157	1.0453	1.1232	1.2263	1.3892	1.3250	1.3823	1.3354	1.5013				
992	70% HNO ₃ + 1.4285 gm	0.2540	0.3852	0.5914	0.6485	0.9144	1.0824	1.2056	1.2480	1.2852	1.3447	1.3805	1.4531	1.4834				
993	Fe(NO ₃) ₃ 6H ₂ O per litre	0.5643	0.5358	0.6655	0.7642	0.9802	0.9677	1.0701	1.1419	1.2466	1.4000	1.3376	1.3908	1.4224				
994	70% HNO ₃ + 0.4762 gm.	0.5309	0.5078	0.6521	0.7688	0.9120	1.0692	1.1381	1.1869	1.2408	1.2771	1.3197	1.3671	1.3935				
995	Fe(NO ₃) ₃ 6H ₂ O per litre	0.5311	0.4901	0.5833	0.6649	0.8359	0.9812	1.0488	1.0851	1.1262	1.1575	1.1978	1.2133	1.2340				
996	70% HNO ₃ + 1.9047 gm.	0.2649	0.3818	0.5294	0.6811	0.8504	1.0158	1.0788	1.1060	1.1744	1.2119	1.2533	1.2884	1.3047				
997	Ni(NO ₃) ₂ 6H ₂ O per litre	0.5055	0.4779	0.5531	0.6331	0.7899	0.9366	0.9901	1.0410	1.0839	1.1178	1.1629	1.2084	1.2319				
998	70% HNO ₃ + 0.9524 gm.	0.5230	0.5048	0.5999	0.6966	0.8457	0.9944	1.0762	1.1179	1.1549	1.2916	1.2265	1.2738	1.2997				
999	Ni(NO ₃) ₂ 6H ₂ O per litre	0.4861	0.4695	0.5724	0.6487	0.8806	1.0309	1.1130	1.1673	1.2269	1.2544	1.2839	1.3173	1.3335				
1000	70% HNO ₃ + 0.4762 gm.	0.4993	0.5022	0.6237	0.7436	0.8598	0.9850	1.0402	1.0899	1.1300	1.1576	1.1870	1.2150	1.2374				
1001	Ni(NO ₃) ₂ 6H ₂ O per litre	0.5242	0.5242	0.6293	0.7122	0.8811	1.0199	1.0708	1.1189	1.1634	1.2051	1.2493	1.2788	1.3017				
		48	96	168	216	384	552	787	955	1123								
891	70% HNO ₃ + 2.9 gm.	6.119	5.678	4.398	4.881	8.425	6.945	7.286	7.325	7.040						Specimen size 1" x ₂ ¹ x ₃ ¹ Nominal Sol. Vol. 350 ml. Temp. Boiling Point Sol. Change: Mondays, Wednesdays & Fridays		
892	Cr(NO ₃) ₃ 9H ₂ O per litre	3.192	4.100	3.268	3.900	4.946	5.453	5.297	5.579	6.035								
893	70% HNO ₃ + 1.43 gm.	4.860	5.436	5.354	4.825	4.642	4.958	4.670	4.794	4.755								
894	Cr(NO ₃) ₃ 9H ₂ O per litre	0.768	2.345	3.582	4.220	5.509	6.047	5.530	5.324	5.435								
895	70% HNO ₃ + 0.95 gm.	1.278	1.946	3.021	2.902	2.875	2.868	2.819	2.516	2.438								
896	Cr(NO ₃) ₃ 9H ₂ O per litre	1.789	2.683	2.649	2.987	2.633	3.892	3.662	3.556	3.583								
897	70% HNO ₃ + 0.143 gm.	1.306	1.661	1.756	1.766	2.396	2.206	2.138	2.110	2.030								
901	Cr(NO ₃) ₃ 9H ₂ O per litre	1.243	1.829	2.171	2.807	1.972	1.922	1.934	1.892	2.030								
899	70% HNO ₃ + 0.095 gm.	0.389	0.430	0.536	0.655	0.778	1.250	1.230	1.296	1.540								
900	Cr(NO ₃) ₃ 9H ₂ O per litre	0.406	0.476	0.538	0.657	1.047	1.275	1.244	1.889	1.402								
		48	96	168	216	384	552	720	888	1056	1392	1560	1728	1896	2064	2232	2400	
902	70% HNO ₃	0.618	0.580	0.655	0.730	0.932	1.057	1.166	1.215	1.245	1.3155	1.3345	1.3520	1.3638	1.3700	1.3805	1.3969	Completed
903		0.567	0.573	0.623	0.724	1.082	1.162	1.229	1.286	1.325	1.3843	1.4043	1.4142	1.4151	1.4275	1.4182	1.4433	
904		0.567	0.553	0.623	0.728	0.917	1.048	1.133	1.172	1.203	1.2737	1.2969	1.3105	1.3217	1.3644	1.3760	1.3918	
905		0.538	0.536	0.604	0.711	0.985	1.012	1.153	1.217	1.256	1.3137	1.3548	1.3686	1.3938	1.3999	1.4088	1.4314	

TABLE V
JOB NO. 317

CORROSION RESISTANCE OF 18/13/1 STAINLESS STEEL IN BOILING SOLUTIONS OF 70% NITRIC ACID
CONTAINING KNOWN AMOUNTS OF CHROMIC NITRATE UNDER REFLUX AND COLD FINGER CONDENSERS.

	Test Nos.	Solution and other Details	Total Penetration Rate, mm/Year, after Following Hours								
			48	96	168	216	384	552	720	800	
TESTS UNDER REFLUX CONDENSERS	810)	1 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	1.007	2.129	7.398	6.934	5.707	4.828	4.735	5.061	
	811)		1.242	1.177	3.726	3.992	3.164	3.622	3.583	3.759	
	812)	.5 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	3.063	2.472	5.027	4.624	4.332	3.811	3.691	3.813	
	813)		4.227	4.312	6.884	6.046	5.826	4.997	4.704	4.747	
	814)	.1 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2896	.1566	.4406	.5248	1.073	1.160	1.194	1.155	
	815)		.2505	.2492	.3847	.4517	.6377	.7172	.8054	.8468	
	816)	.05 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	1.090	.7188	.8505	.8688	.9876	1.025	1.072	1.099	
	817)		.3218	.3982	.7890	.8565	1.020	1.158	1.199	1.239	
	818)	.025 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2176	.2037	.2176	.2325	.3215	.4147	.4546	.5729	
	819)		.1620	.1736	.1839	.1903	.2465	.3213	.4028	.4301	
	820)	.005 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.1898	.1875	.1978	.2011	.2836	.3466	.4178	.4432	
	821)		.2384	.1956	.2163	.2289	.2884	.3321	.3753	.3892	
Weights of Specimens for above Tests corrected to Standard Hours by Graphs.											
TESTS UNDER COLD FINGER CONDENSERS	1031)	1 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2060	.2720	.3300	.3606	.5486	.6085	.6312	.6343	
	1032)		.1667	.2083	.2527	.2572	.2967	.3897	.5127	.5224	
	1033)	.5 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.1806	.3495	.3314	.2845	.3504	.3927	.4201	.4313	
	1034)		.1991	.2581	.3214	.3503	.4288	.4783	.5165	.5219	
	1035)	.1 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2245	.2211	.2341	.2433	.3006	.3623	.4046	.4171	
	1036)		.1944	.2083	.2163	.2274	.3307	.3827	.4514	.4753	
	1037)	.05 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2153	.2407	.2646	.2804	.3649	.4453	.5100	.5308	
	1038)		.2269	.2569	.2553	.2685	.3478	.4130	.4553	.4835	
	1039)	.025 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2153	.2107	.2269	.2289	.3122	.3345	.3818	.3957	
	1040)		.2060	.1956	.2050	.2176	.2951	.3430	.4338	.4560	
	1041)	.005 gm. Cr ₂ (NO ₃) ₃ 9H ₂ O per 2100 ml. 70% HNO ₃	.2361	.2396	.2573	.2505	.3336	.3583	.4068	.4244	
	1042)		.1667	.1944	.2295	.2248	.2627	.3213	.3710	.3881	
	1043)	70% HNO ₃		.1968	.1887	.2017	.2155	.3102	.3750	.4185	.4381
	1044)			.1065	.1482	.1687	.1939	.2682	.3410	.3975	.4210

Specimen size: 1" x 1/2" x 1/8" Approx.

Solution Volume: 350 ml.

Solution Change: Mondays, Wednesday and Fridays.

TABLE 6

CORROSION RESISTANCE 18/13/1 STAINLESS STEEL IN 70% HNO₃ AT BOILING
POINT 1 UNDER

(a) REFLUX CONDENSER

(b) COLD FINGER CONDENSER

TEST NO.	SOLUTION DETAILS ETC.	PERIOD PENETRATION RATE MM/YR AFTER FOLLOWING <u>PERIOD HOURS</u> :											
		48	48	72	48	168	168	168	168	168	168	168	168
887	350 cc 70% HNO ₃ at 123.5°C	0.233	0.230	0.169	0.293	0.502	1.726	2.590	2.646	2.136	2.173	1.397	1.564
888	with <u>Reflux</u> condenser	0.235	0.254	0.154	0.254	0.414	0.559	0.840	0.8780	1.201	2.262	1.522	1.724
889	350 cc 70% HNO ₃ at 123.5°C	0.213	0.244	0.217	0.282	0.365	0.419	0.504	0.518	0.534	0.677	0.586	0.668
890	with <u>Cold Finger</u> Condenser	0.237	0.258	0.179	0.322	0.413	0.475	0.520	0.567	0.588	0.818	0.619	0.703
		PERIOD PENETRATION RATE MM/YEAR CONTINUED FROM ABOVE											
887	As Above	3.095	2.602	1.766	1.7161	1.5595							
888		2.109	2.022	1.892	1.6818	1.9762							
889	Cold Finger	.812	.636	.691	.6842	.6941							
890		.746	.735	.694	.7249	.7335							
		PROGRESSIVE PENETRATION RATE MM/YR AFTER FOLLOWING HOURS :											
		48	96	168	216	384	552	720	888	1056	1224	1392	1560
887	350 cc 70% HNO ₃ at 123.5°C	0.233	0.232	0.205	0.199	0.385	0.791	1.213	1.486	1.593	1.674	1.662	1.6442
888	with <u>Reflux</u> condenser	0.235	0.245	0.226	0.239	0.315	0.389	0.494	0.567	0.669	0.887	0.961	1.0464
889	350 cc 70% HNO ₃ at 123.5°C	0.213	0.228	0.233	0.236	0.293	0.331	0.372	0.399	0.421	0.456	0.472	.4932
890	with <u>Cold Finger</u> Condenser	0.237	0.247	0.251	0.267	0.341	0.374	0.408	0.438	0.462	0.511	0.524	.5437
887	As Above	1896	2064	2232	2400	2568							
888		1.7426	1.8082	1.8130	1.8076	1.7912							
889	Cold Finger	1.1788	1.2481	1.2966	1.3254	1.3692							
890		.5397	.5478	.5585	.5673	.5756							

48 Hr Solution change up to 552 Hrs then 72 Hour
solution change. Specimen size 1" x 1/2" Softened
and pickled polished No.1 emery.