

INVESTIGATION
on the
POSSIBILITY OF DIFFERENTIAL REDUCTION
from the
STANDPOINT OF OXIDATION-REDUCTION POTENTIALS.

Thesis

by

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The object of this work was the investigation of the possibility of differential reduction by maintaining a known reduction potential in the solution of reductants. The compounds investigated belonged to the irreversible systems which have been investigated by J. B. Conant and co-workers, and whose apparent reduction potentials have been tabulated.

In previous work of Conant and others, the reduction of this class of compounds had been studied by following the reaction with a bare platinum electrode, whose potential against a calomel half cell would vary as to the relative amounts of the reduced and oxidized reagent changed in the solution surrounding the electrode. It was thus possible to determine the rate of reduction by various reagents of known reduction potential, and to stipulate as the Apparent Reduction Potential of a compound the reduction potential of that reagent which would give appreciable reduction in a given length of time.

With the data thus obtained it seemed possible to devise a mechanism for the accurately controlled differential reduction of a mixture of these

compounds, since each compound would remain unreduced until the reduction potential of the solution became less than the A. R. P. of the compound.

Various methods were tried for the study and application of this principle. They were essentially the same in that the reduction-oxidation potential of the solution was always followed by a bare platinum electrode and calomel half cell with a saturated KCl bridge. Variations consisted in the different ways of mixing the reducing agent and the solution of the compounds, and consisted of (1) the use of a buffer or catalytic agent in the form of a reversibly oxidized and reduced organic compound, (2) the absence of a buffer, (3) the alternate and suitably regulated inflow of both solutions into the cell, (4) the very slow continuous addition of the reducing agent, and (5) the rapid mixing of both reductant and reducing agent. From the E. M. F. curves thus obtained it was possible to draw certain conclusions and recommendations concerning the optimum conditions.

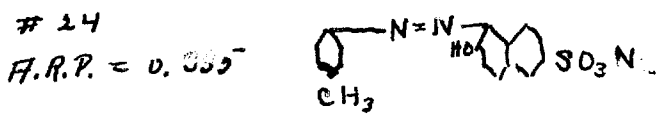
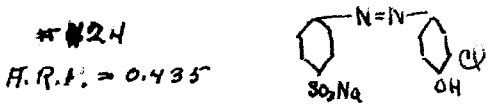
The cell employed was a two liter bottle with a mechanical stirrer and mercury seal, and provided with an inlet and exit for nitrogen, inlets for two burettes, a platinum wire electrode and a KCl bridge

to a calomel half cell. A potentiometer was used to measure the electromotive force developed.

The nitrogen was bubbled through several bottles containing pyragallol and brought into the cell through glass tubing. The exit was closed by a water seal. The cell was always swept with nitrogen for fifteen minutes before any reducing agents were introduced, and an appreciable flow continued throughout the entire experiment.

The reducing agent was a 0.1N solution of $TiCl_3$ in 0.2NHCl.

The first compounds to be investigated were the azo dyes:



(The values for the A. R. P. given here are against the hydrogen electrode, and hence do not check the potential ranges given later).

Dye No. 24 was yellow, while the other two were red, so that the color changes gave a check on the electrometric titrations. Dye No. 5 was found to give a colloidal gel at a concentration of .0002 molal in 0.2NHCl, and was soon discarded in favor of No. 6. The solution finally adopted was a mixture of .001molal No. 24 and .001 molal No. 6 in 0.2 NHCl. Each dye was standardized separately against $TiCl_3$.

Chloran^{anilic}~~itic~~ic acid was used in a buffer, the plan being to reduce the chloran^{ilic}~~itic~~ic acid until it had reached the proper potential, (see Fig. I), and then to add such an increment of dye that the chloran~~itic~~^{ilic}ic acid would reduce the more easily reducible of the dyes, then to reduce the rapidly reacting chloran^{ilic}~~itic~~ic acid which was again in the oxidized form by more $TiCl_3$. The presence of the reversible system formed by the oxidized and reduced portions of the chloran^{ilic}~~itic~~ic acid would thus keep the potential controlled, and prevent the titanium from arriving at such a potential as would reduce the red dye.

The results, using a solution .0006M in dye No. 24, and .0002 molal in dye No. 5, are in Table I.

TABLE I

Increments cc. $TiCl_3$	Increments cc. Dye	Range of Voltage	Time of Cycle
3.1	100 cc. of .001 molal chloranitic acid	.244, .116	
1.5	50.0	.128, .056	43 min.
0.9	50.0	.105, .055	20
1.0	50.0	.108, .055	15
1.5	100.0	.121, .064	
2.0	100.0	.113, .057	10
1.8	100.0	.118, .069	20
1.8	100.0	.118, .070	16
<u>2.0</u>	<u>100.0</u>	.119, .051	10
12.5	650.0		
8.7		.065, .004	

Thus we had established an E. M. F. curve with the chloranitic acid, and by alternate additions of dye and $TiCl_3$ had slid up and down on it from 120 to 60 millivolts, reducing dye No. 24 as it was added to the solution.

The potential fell very rapidly when $TiCl_3$ was introduced, but it took about fifteen minutes for the dye to oxidize the chloranitic

acid back up on each cycle. When these cycles were finished, the red colored residue of dye No. 5 was titrated till colorless, the potential range dropping to 65 - 4 millivolts. The ratio of the volumes of $TiCl_3$ in these two titrations was 1.35, while the ratio of the two concentrations was 3.0. Apparently the chloranitic acid did not completely reduce the dye No. 24, so that there was a cumulative residue from each cycle.

The next step was to conduct a sufficiently slow reduction to be able to perceive precisely what happened throughout the entire titration. Solutions .001 molal in dye No. 24 and dye No. 6 were prepared. Chloranitic acid was reduced, 420 cc. of dyestuff introduced, and $TiCl_3$ allowed to slowly flow in until the potential dropped rapidly. The $TiCl_3$ was then added in 0.1 cc. increments at 5 minute intervals to allow the system to come to equilibrium. When the potential no longer fell rapidly, the rate of the inflow of $TiCl_3$ was increased, with occasional five minute stops to ascertain what the equilibrium potential was.

The curve thus developed (Fig. II) had several significant features. The inflection point on the curve corresponded to roughly half the total

volume of $TiCl_3$ required to decolorize the solution, the ratio being 0.525, while the ratio of each dye to the total amount of dye present was 0.500. Hence there is a very sharp and definite separation in the reduction of these two dyes, whose A. R. P. differ by only 100 millivolts. Furthermore, the curve drawn through the equilibrium peaks is approximately parallel to the curve of the potentials that have been depressed by a rapid inflow of $TiCl_3$, so that the character of the reduction can be studied even though the potentials of the true equilibrium are not attained.

It was next interesting to investigate whether or not the reversible part of the irreversible system which was postulated by J. B. Conant would be sufficiently influential in stabilizing potentials to do away with the necessity of the presence of chloran^litic acid. According to this hypothesis the irreversible cleavage of the ~~azo~~ dye is preceded by a reversible reduction, and the latter might well assume all the functions of the reversible system hitherto furnished by chloran^litic acid. The experiment was carried out as above except for the absence of chloran^litic acid, with the discovery of a curve (Fig. III)

similar in all respects to that of Fig. II.

In order finally to acquire a completely uniform curve that would be unbroken by equilibrium intervals, a titration extending over six hours was undertaken, in which 0.1 cc. increments of $TiCl_3$ were added every minute to a solution similar to that of Fig. III, and the potentials read 45 seconds after their addition. This curve (Fig. IV) shows without any ambiguity the sharpness of the change from one potential level to the other as one and then the other dye is reduced. The rise and subsequent constancy of potential at the end of the titration is unexplained.

A short investigation of the differential reduction of the nitro groups in 3 - 5 dinitro benzoic acid was undertaken. A solution containing 1.0 grams of the acid was heated to 90 degrees to speed up the reactions and 6 equivalents of $TiCl_3$ were added, over a time of 3 hours, at which time the potential began to drop noticeably. To a similar solution 6 equivalents were added in about 20 minutes, the potential curve being about 50 millivolts lower.

Both solutions were evaporated to dryness and the residue extracted with 200 cc. of boiling water. The solution was brought to an acid concentration of

10^{-2} , and extracted with 50 cc. of ether. The ether upon evaporation gave 0.50 grams of 3 amino 5 nitro benzoic acid for the carefully reduced solution and 0.34 grams for the rapidly reduced, which ratio is assumed comparable to the relative concentrations of the mono-amino acids, since at that acid concentration the diamino compound is very soluble in water. There was no evidence of the dinitro compound since there was no product insoluble in strong acid, but the presence of the diamino benzoic acid was evinced by the development of a green decomposition product in both water phases.

In conclusion, it has in certain cases been shown to be eminently possible to effect differential reduction merely by a careful watch of the oxidation reduction potential as reported by a bare platinum electrode, and also that the potential may be controlled by varying the rate of addition of the reducing agent. Furthermore, it has been shown possible to electrometrically titrate a mixture of azo dyes having sufficiently different "apparent reduction potentials".

The time necessary to effect a sharp differential reduction of course depends on the rapidity

of the reaction. With these types of compounds the time required is in general from 1 to 3 hours at 20 degrees Centigrade, which time may be considerably shortened at higher temperatures, since the ordinary titration of an azo dye by reduction takes but a few minutes. If the reducing agent is introduced too rapidly it appreciably attacks the compounds which are desired unreduced, as occurred in the second reduction of the dinitro benzoic acid.

SUMMARY

A mixture of two azo dyes was subjected to successful differential reduction by following the reduction potential of the solution with a bare platinum electrode.

A partial study of the differential reduction of 3,5 dinitro benzoic acid was made.

In conclusion I wish to thank Professor James B. Conant, who, in his visit to the California Institute of Technology, introduced me to that field of organic electro-chemistry in which he stands unique, and to whom the essence of this paper is due in its entirety.

Electrometric Titration
of
Chloranilic Acid with
 $TiCl_3$

Fig. I

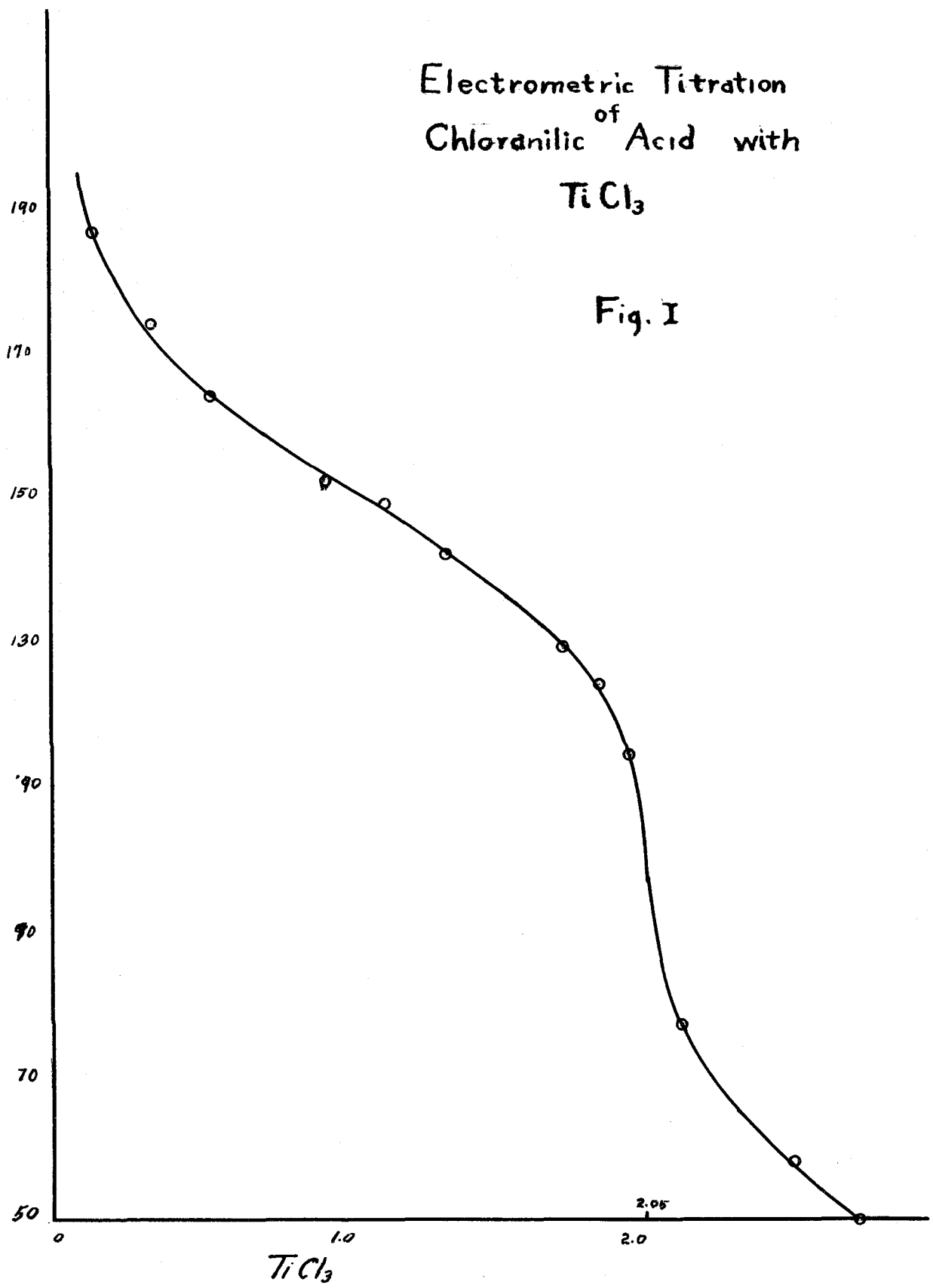


Fig. II

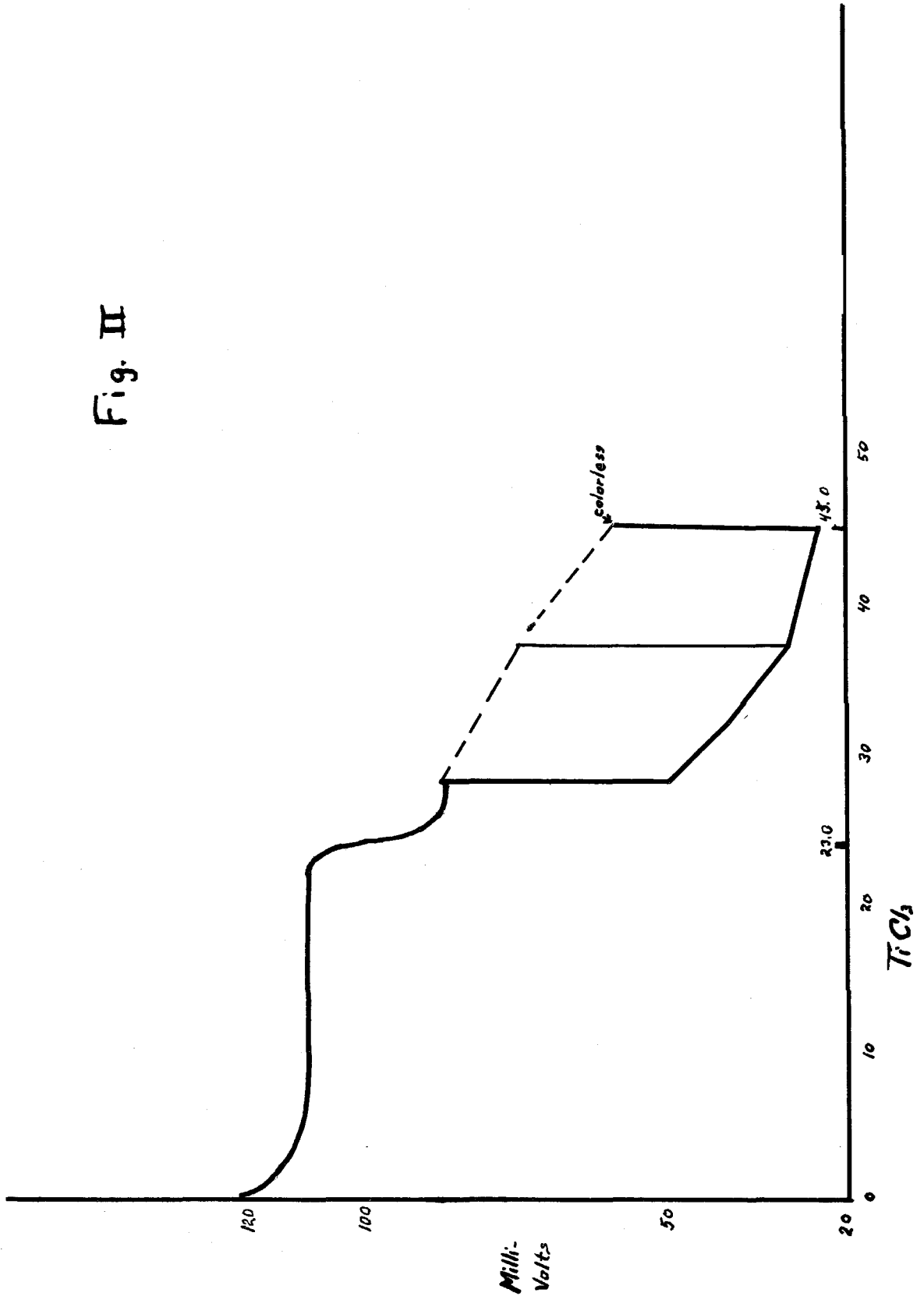


Fig. III

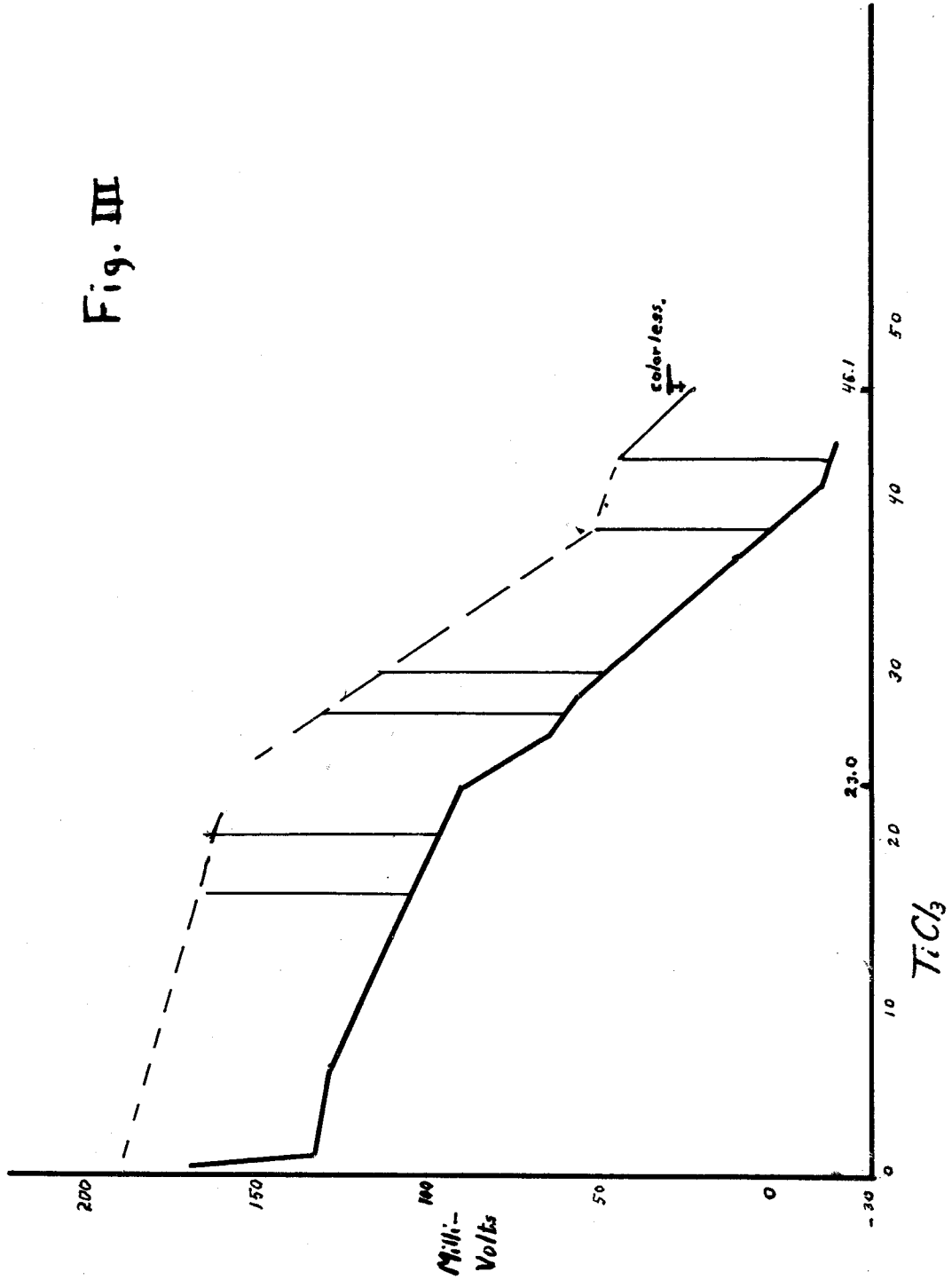


Fig IV

