Bulletin-No. 25*

INDIAN LAC RESEARCH INSTITUTE

NAMKUM, RANCHI, BIHAR & ORISSA,

INDIA.

Use of the Quinhydrone and Antimony Electrodes for Potentiometric Titrations of Resin Solutions. †

By

N. MARASIMHA MURTY and HAROLD WEINBERGER

with Wm. HOWLETT GARDNER

Potentiometric methods in general give more accurate values than other methods of titration in addition to revealing the nature of the acidity of a substance. They are indispensable for selecting the proper indicator when a non-aqueous solvent must be employed, or for titrating very dark colored solutions such as obtain with certain garnet lacs and seedlacs. Many of the advantages for the potentiometric method of titrating colored varnish solutions in the determination of acid and saponification numbers were discovered concurrently and independently at each of the above laboratories, but the junior authors and their colleagues published their results first, (1) (2) (3) (4).

It is not surprising, however, to find that the method developed by Gardner and Whitmore has not been widely used, since their procedure requires unusual care in the preparation of the hydrogen electrode and skill in manipulation, in addition to the complete exclusion of air from the titration vessel in order to obtain the proper equilibrium. With these disadvantages the average analyst would naturally choose one of the methods employing an organic indicator even if the end-point is not as sharp as that obtained with the potentiometric method.

---

* This bulletin is a joint contribution from the Indian Lac Research Institute and the Polytechnic Institute of Brooklyn, Brooklyn, New York, U. S. A. It is also Research Note *No. 2*, and contribution *No. 18* of the Shellac Research Bureau and contribution *No. 26* of the Department of Chemistry of the Polytechnic Institute of Brooklyn, co-operating with the United States Shellac Importers, Association.

† The note for the most part is based upon the investigations of the senior author, Mr. Murty. The data for the direct titration of the alkaline solution in the determination of saponification number is taken from a section of the thesis submitted by Mr. Weinberger, in partial fulfilment of the requirements for the degree of Bachelor of Science in Chemistry, at the Polytechnic Institute of Brooklyn, June 1931.

The Quinhydrone Electrode.

Since the quinhydrone electrode is obviously superior to the hydrogen electrode in this respect, (5), it seemed highly desirable to investigate the possibility of applying the method of Seltz and McKinney (6) to the determinations of both acid and saponification numbers. The reagents employed were 95% ethyl alcohol and 0. 1N alcoholic potash. A lithium chloride-agar bridge was used for establishing the liquid junction. The reference half-cell consisted of a gold electrode inserted into a solution of lithium chloride in 95% alcohol which contains a very small amount of quinhydrone.

The acid values obtained by this method, as also those determined by other methods, are given in Table I. It can be seen that the absence of inert atmosphere does not make any appreciable difference in the determination of the acid value. When the titration is carried out in a nitrogen atmosphere the curve can however be traced for a greater distance into the alkaline range as illustrated in figure 1. This procedure, nevertheless, is not suitable for titrating alkaline solutions obtained in determining saponification numbers.

For such determinations a known amount of standard acid can be added in excess to the saponified solution and this excess can then be titrated with alcoholic potash using the quinhydrone electrode. In Table II are given some saponification values obtained in this manner.

The Antimony Electrode.

Under certain circumstances, it may indeed be desirable to use an electrode which is even simpler in manipulation, and one which can also be used in the alkaline region. One such is the antimony electrode. This electrode has the further advantage in not being subject to poisoning by hydrogen sulfide.

Many commercial grades of shellac contain arsenious sulfide (orpiment) which unless previously removed by filtration produces soluble sulfides during the digestion with caustic in determining the saponification number (2). On titrating the saponified mixture, hydrogen sulfide is generated which may poison an hydrogen, or even a quinhydrone electrode and thus cause the voltage to fluctuate so widely that the titration cannot be accurately followed.

Since the antimony electrode is not subject to this disadvantage, it can be used with the calomel-lithium chloride reference electrode in 95% ethyl alcohol solutions and a complete titration curve (figure 4) can be obtained for the constituent acids liberated on saponification even if the arsenious sulfide has not been removed and the saponified solution has a strong odor of hydrogen sulfide.

The electrode is easily prepared by melting powdered antimony in a piece of glass tubing which has been sealed at one end. On cooling the antimony solidifies and the sealed end of the tube is then broken off giving an exposed metallic antimony tip. The top of the tube is filled with mercury to serve as a contact for the electrical connections.

The other details of the method, the potentiometer and reference electrode have been fully described in a previous contribution (1). In table I are given values for acid numbers determined by using this electrode, and it will be seen that they agree with the values obtained by other methods. The titration curves illustrated in figures 3 and 4 clearly show that steady potentials can be obtained with the antimony electrode for any region. The inflection end-point, however, is not as high as with the quinhydrone electrode and hence the precision is not quite as great, but still superior to that obtained with organic indicators.

Using either of the new electrodes, equilibrium is established much sooner than with the hydrogen electrode in non-aqueous solvents. The difficulty of continually cleaning and replating the indicating electrode has been eliminated and titration can now be carried out in an open vessel. The use of either of these electrodes places in the hands of the analyst and research worker a tool for acidemetry-alkalemetry in alcoholic media such as he has long needed.

In conclusion, the authors wish to thank Mrs. Norris, Dr. Aldis, and Mr. Gibson for their assistance in reviewing and publishing of this paper.

References Cited.

(1) Gardner, W. H. and Whitmore, W. F. Ind. Eng. Chem., Anal. Ed., *1, 205* (1929).
(2) Whitmore, W. F. and Weinberger, H., with Gardner, W. H., *ibid, 4,* 48 (1932).
(3) Weinberger, H., and Gardner, W. H., *ibid, 5,* 267 (1933).
(4) Caldwell, B. P., and Matiello, J., *ibid 4,* 52 (1932).
(5) Clark, M., The Determination of Hydrogen Ions, Williams and Wilkins Company, Baltimore, Md., 3rd Ed. (1928).
(6) Seltz, H., and McKinney, D.S., Ind. Eng. Chem., *20* 542 (1928).

TABLE I

Acid Value

Method.	Quinhydrone electrode.	Thyrmol blue.	Antimony electrode.	Albert stock.
Shellac	70.6	70.7	70.8	
,, ...	67.3	67.7	67.4	57.1
,, ...	67.7	68.0	67.7	56.9
Seed lac C154	81.7	81.5	81.9	...
Seed lac C59	41.5	41.8	41.6	...
Wax free lac	75.4	75.8	75.5	...
Bleached Lac	89.7	89.8	89.8	72.4
Indian Rosin	164	165.2	165.0	148
Pontinac	141	...	...	...
Sandarac	133	133.5	133.4	...
Shellac (in N. Atmosphere) ...	74.2	...	...	...
Shellac (in ordinary air) ...	74.23	...	...	...
Shellac	70.96	71.2	71.1	63.9
,, ...	70.96	71.2	70.9	63.9

TABLE II

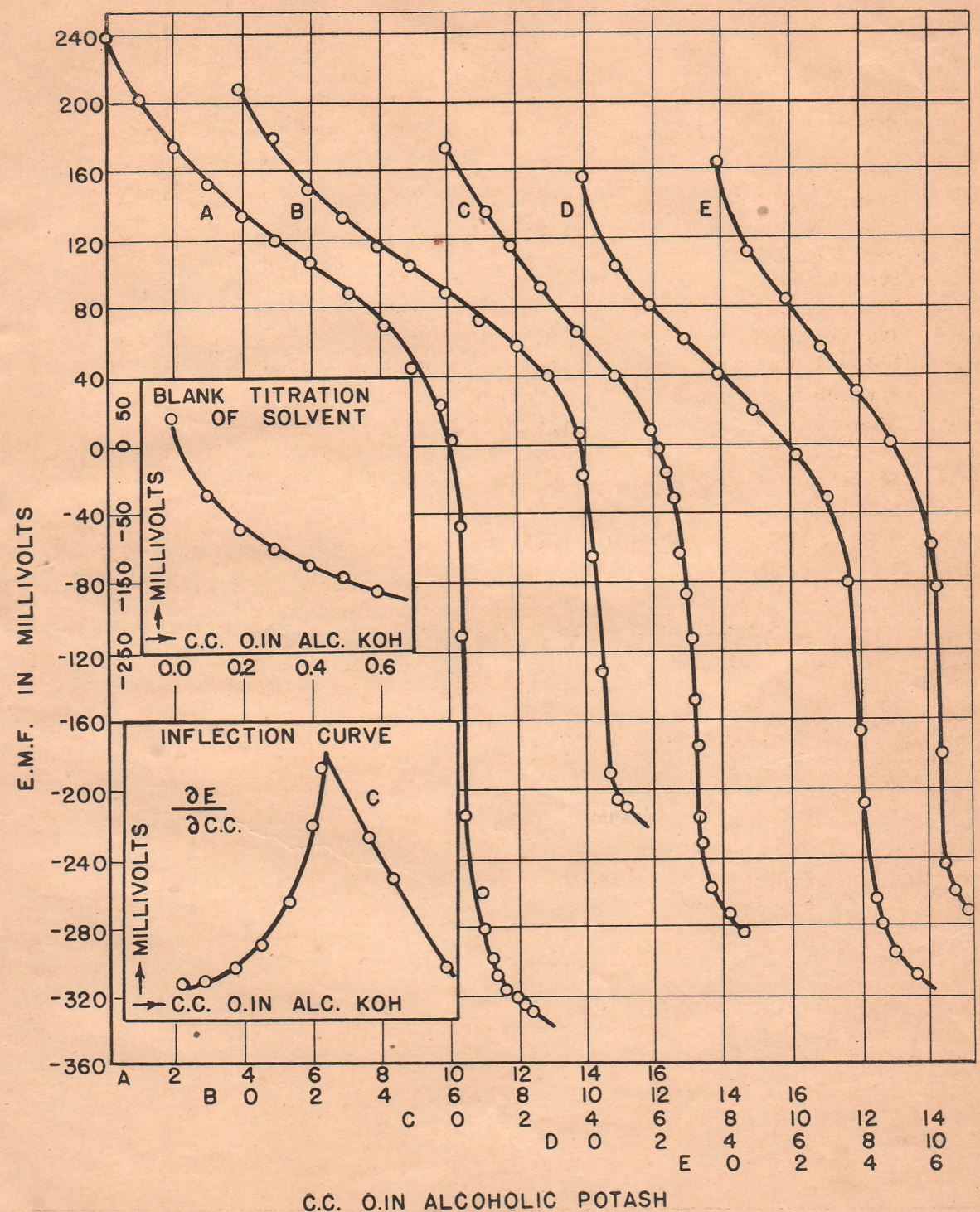
Saponification Value with Quinhydrone Electrode

No.	Sample.	Saponification Value.
1	Shellac	221
2	,, ...	214
3	,, ...	203
4	,, ...	208
5	Seed-lac (Kusum)	210
6	Wax-free lac	223
7	Pontinac	186
8	Sandarac	176
9	Rosin	182

Printed by P. C. Ray at Sri Gouranga Press, 5 & 6, Chintamani Das Lane, Calcutta and Published by Dr. H. K. Sen, Director, Indian Lac Research Institute, Namkum, Ranchi.

FIG. 1.

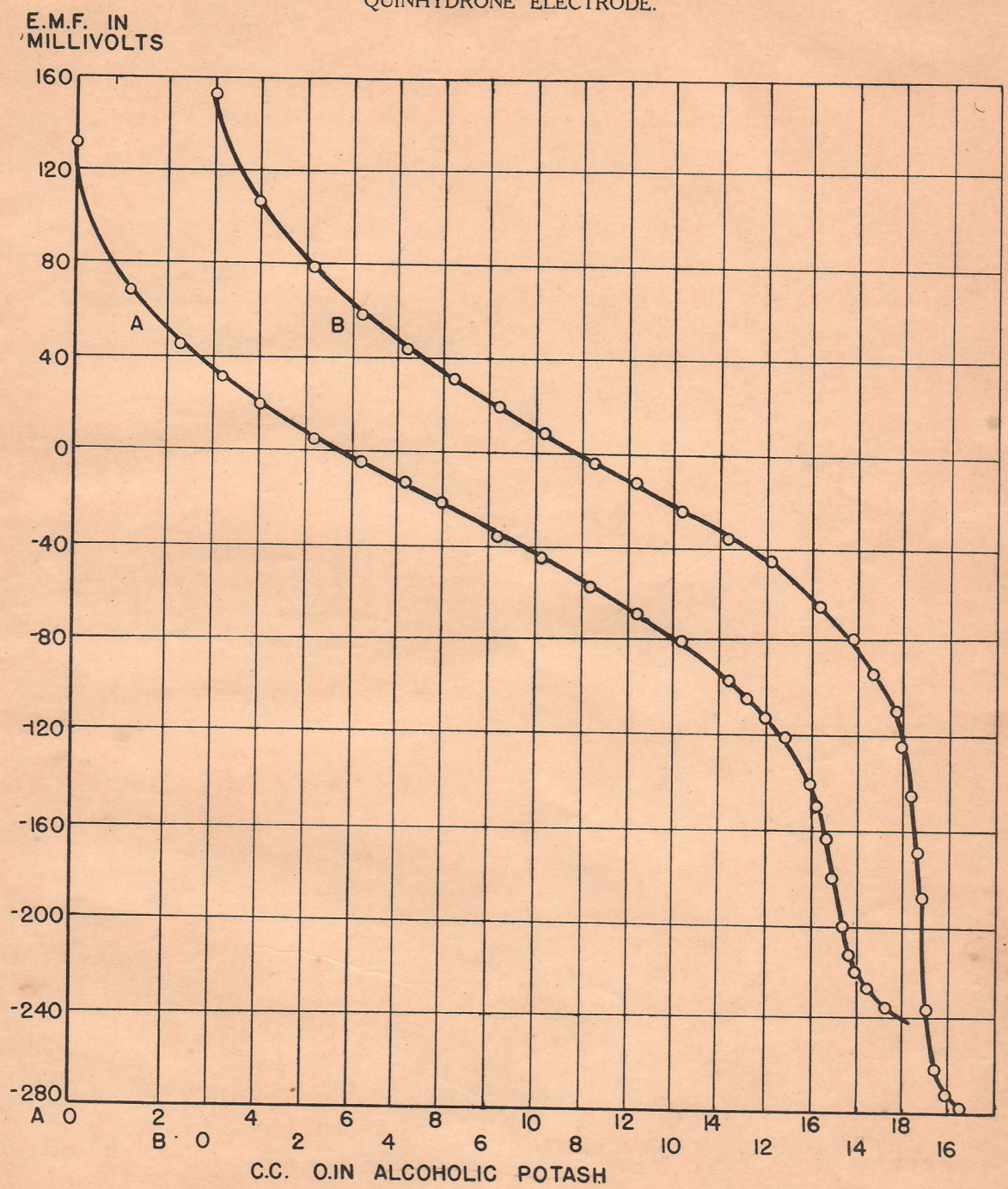
QUINHYDRONE ELECTRODE.



Titration curves.—(A) Shellac in nitrogen atmos., (B) Shellac in air, (C) Dark shellac, (D) Kusum seed lac, (E) wax-free lac.

FIG. 2.

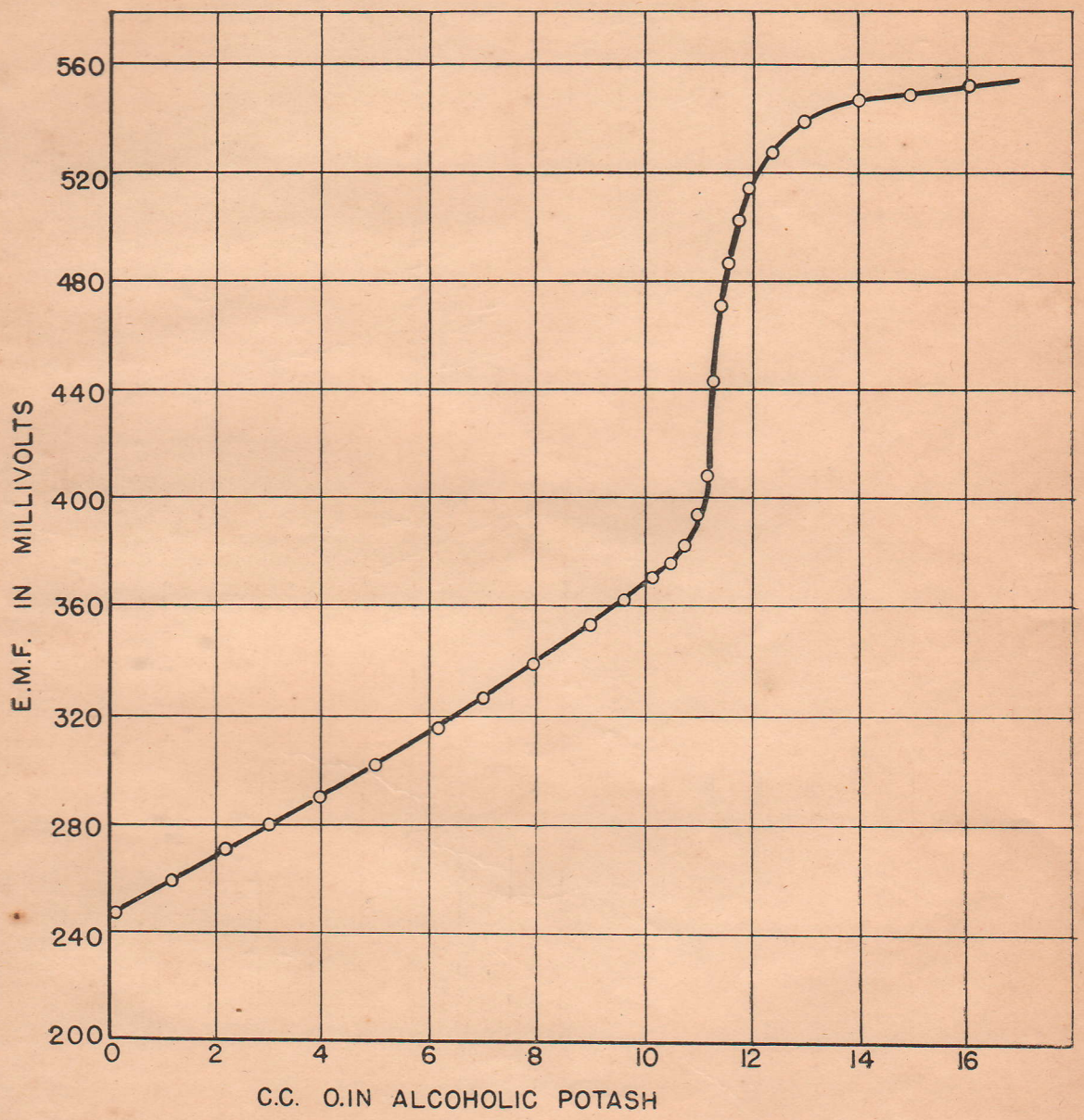
QUINHYDRONE ELECTRODE.



Titration curves.—(A) Pontinac, (B) Rosin.

FIG. 3.

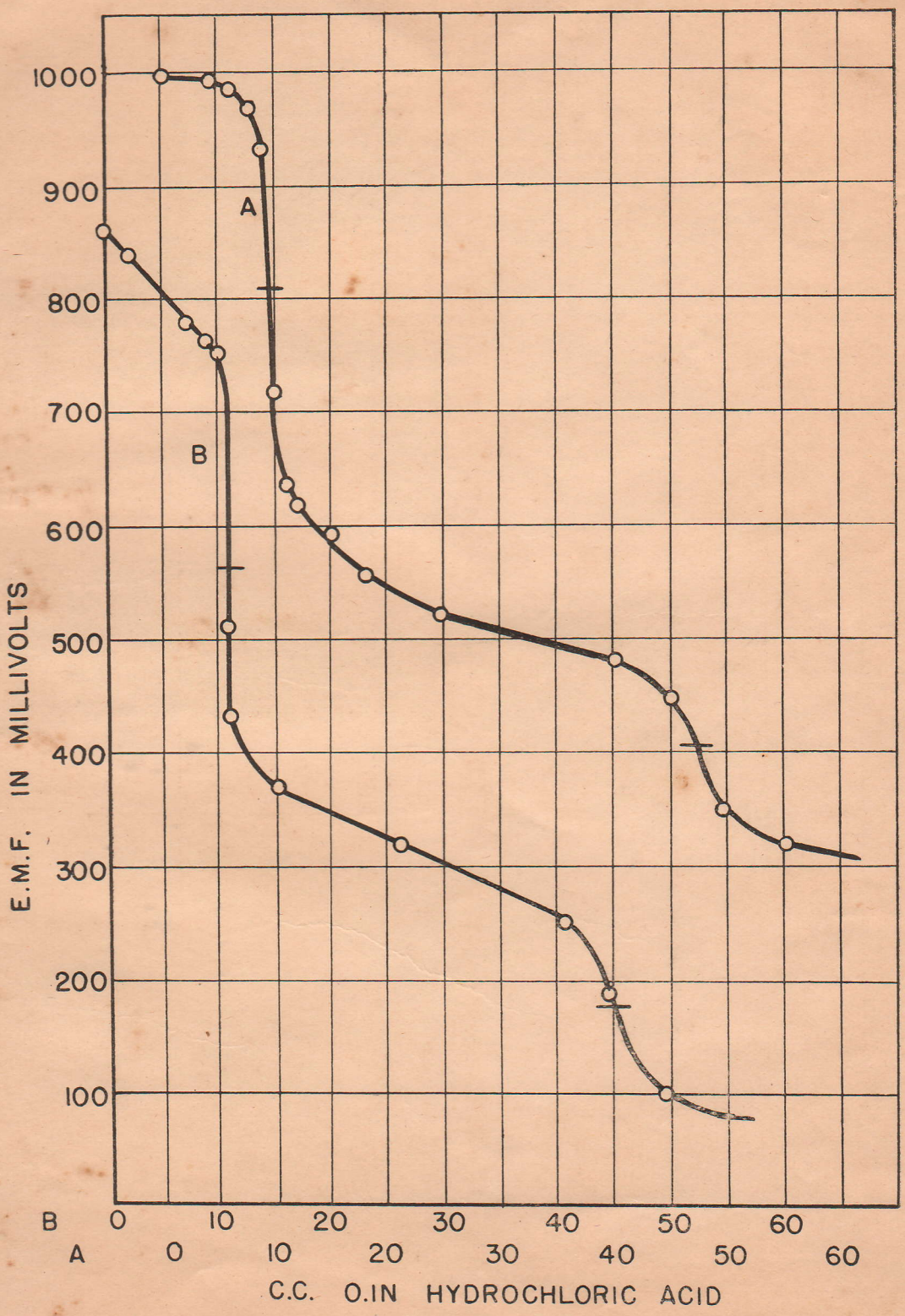
ANTIMONY ELECTRODE.



Titration of Shellac Solution.

FIG. 4.

ANTIMONY ELECTRODE.



Titration curves for Saponified Shellac Solution.