

Jan. 2, 1968

B. MILLER ETAL

3,361,674

COPPER ETCHANT

Filed June 5, 1964

3 Sheets-Sheet 1

FIG. 1

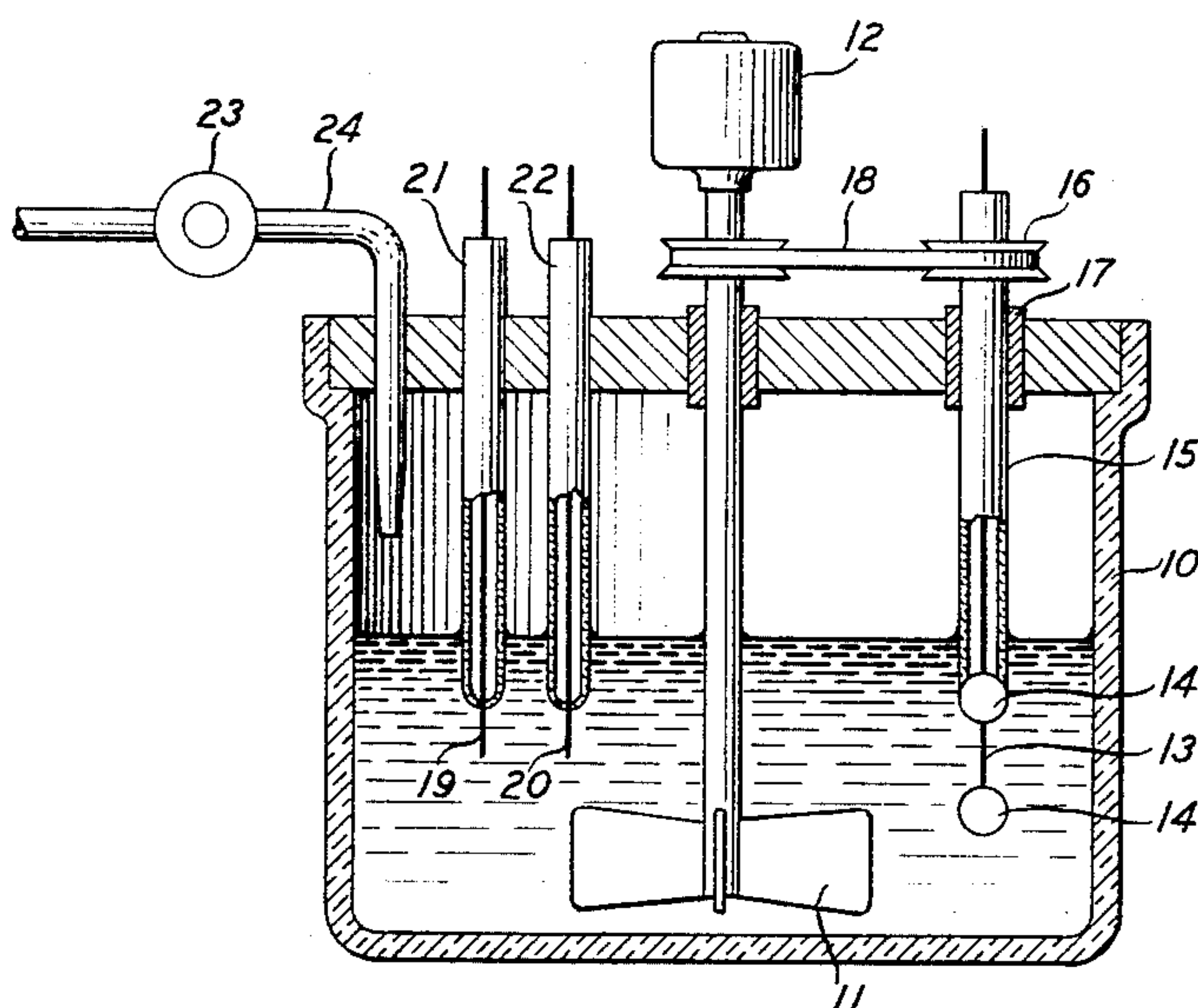
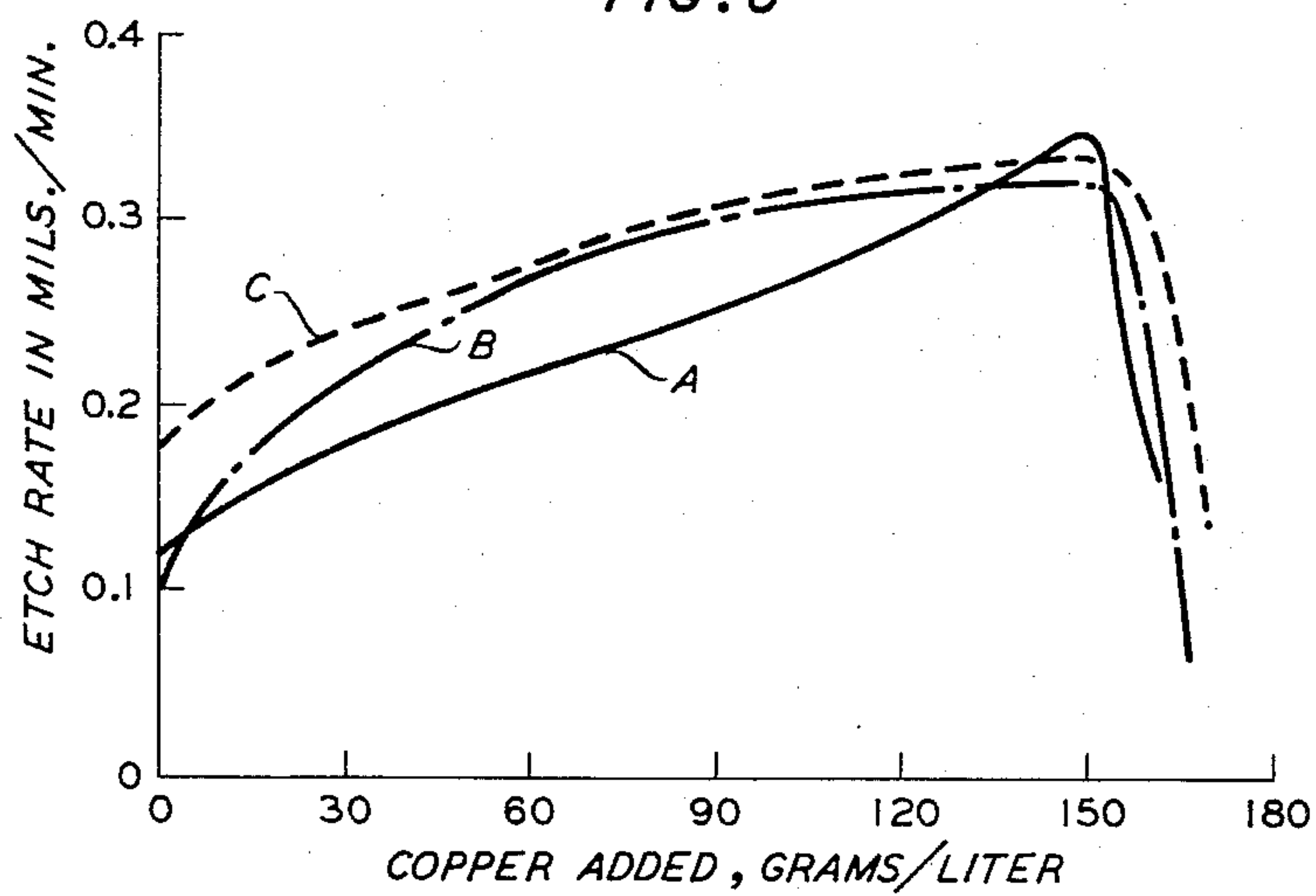


FIG. 3



INVENTORS
B. MILLER
T. D. SCHLABACH, JR.
BY *John W. Wilde*
ATTORNEY

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FIG. 2

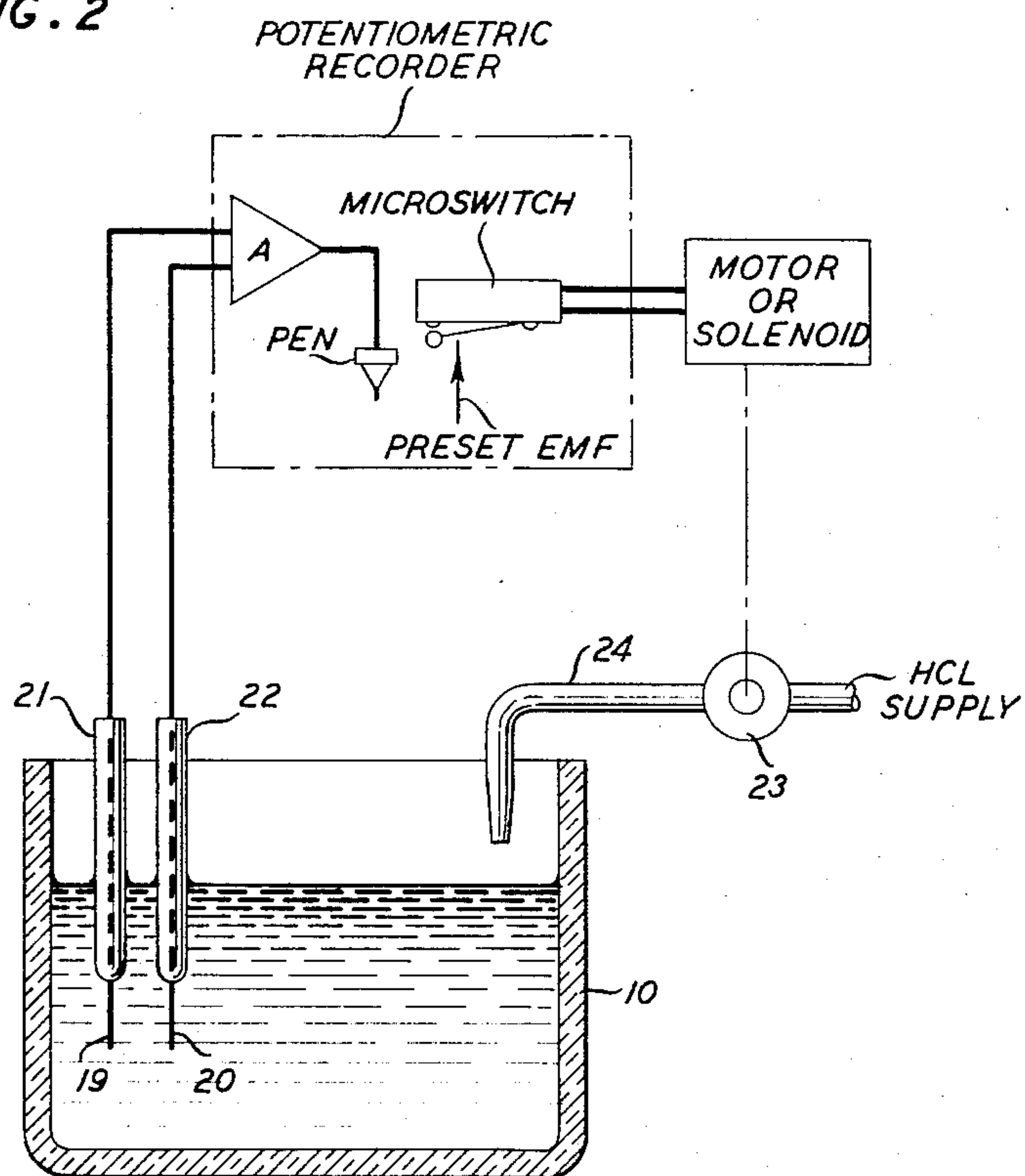
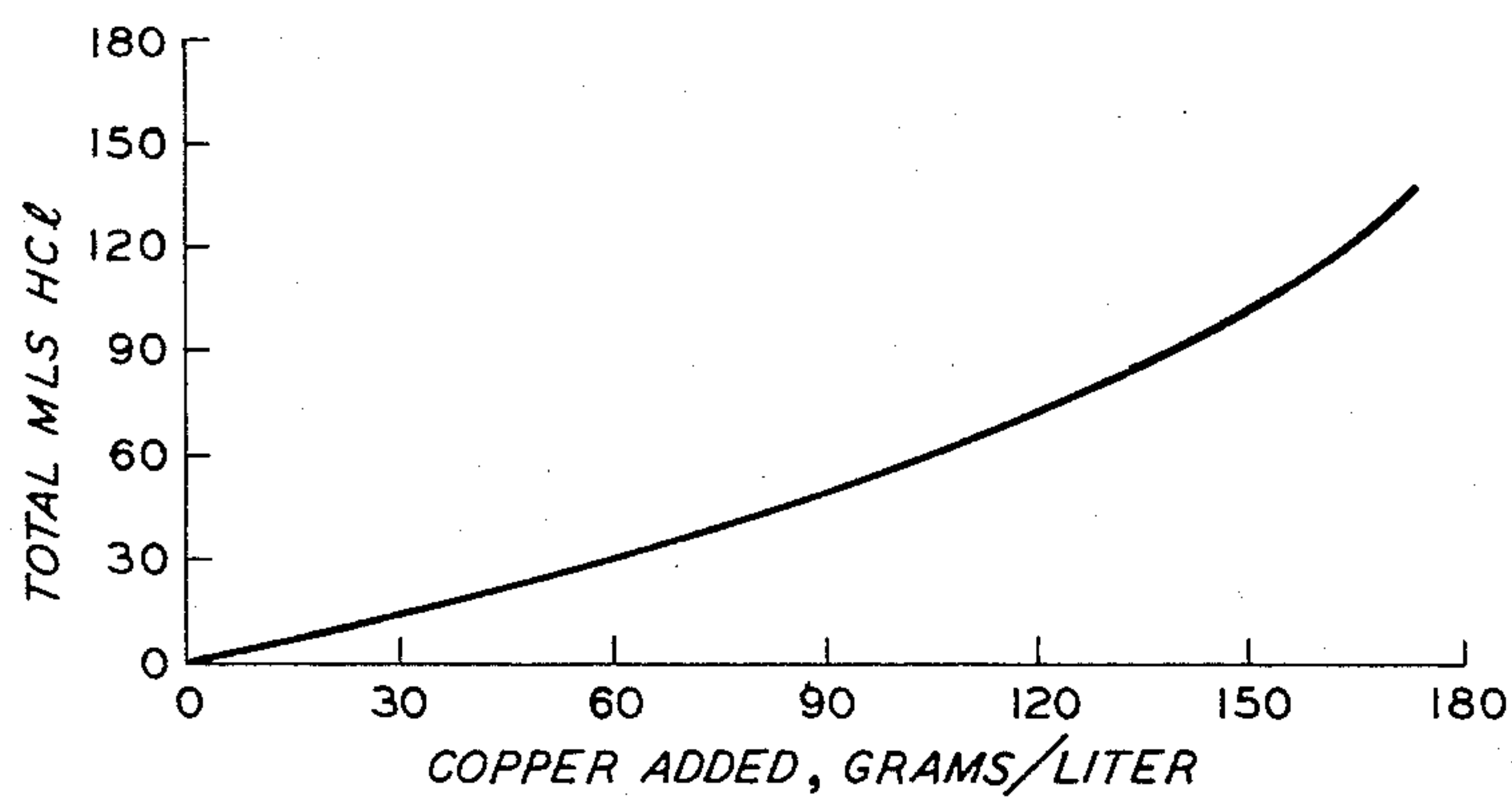


FIG. 4



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FIG. 5

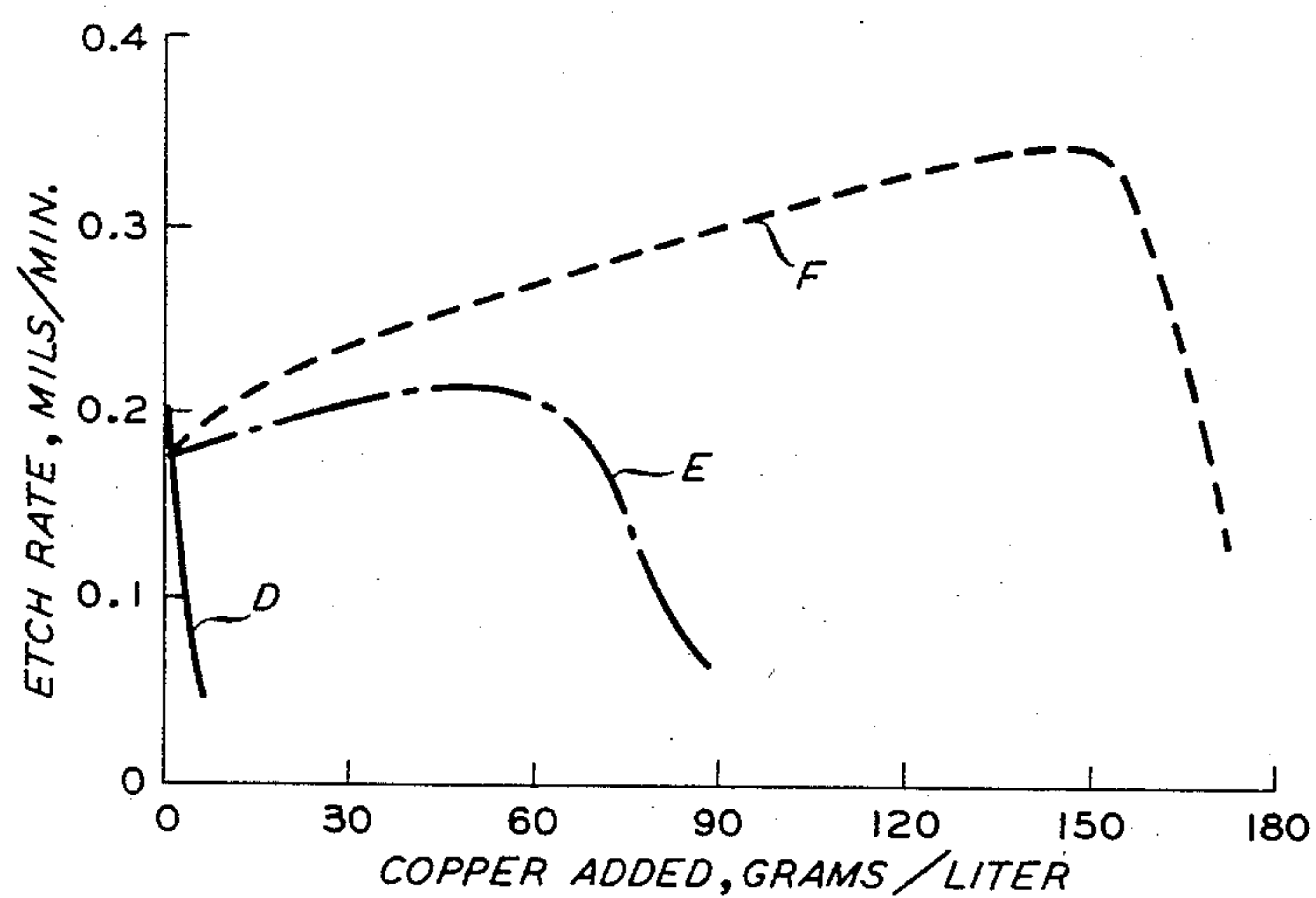
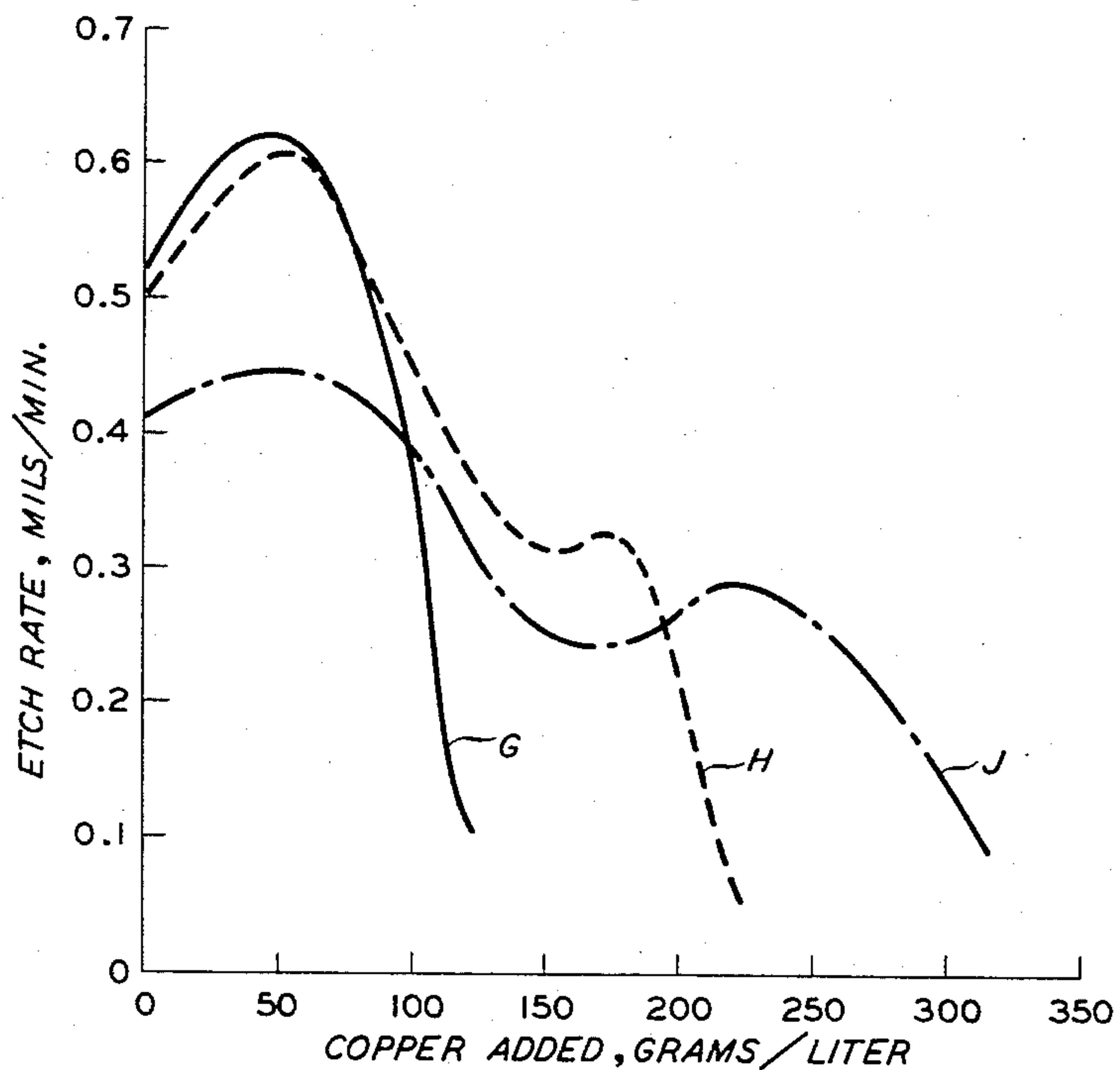


FIG. 6



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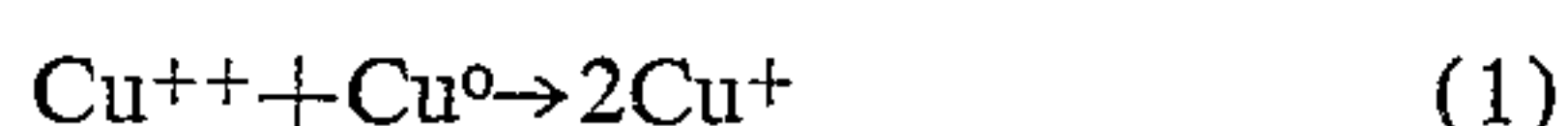
Barry Miller, Plainfield, and Thomas D. Schlabach, Jr.,
Whippany, N.J., assignors to Bell Telephone Labora-
tories, Incorporated, New York, N.Y., a corporation of
New York

Filed June 5, 1964, Ser. No. 372,959
1 Claim. (Cl. 252—79.1)

This invention relates to solutions for chemically etch-
ing copper.

Etching copper is of considerable technological im-
portance particularly in the fabrication of electrical de-
vices and elements such as printed wiring boards. The
photoengraving art also has a significant interest in etch-
ing copper.

One of the most successful of the existing chemical etch
solutions for copper relies on cupric chloride in chloride
solution via the reaction:

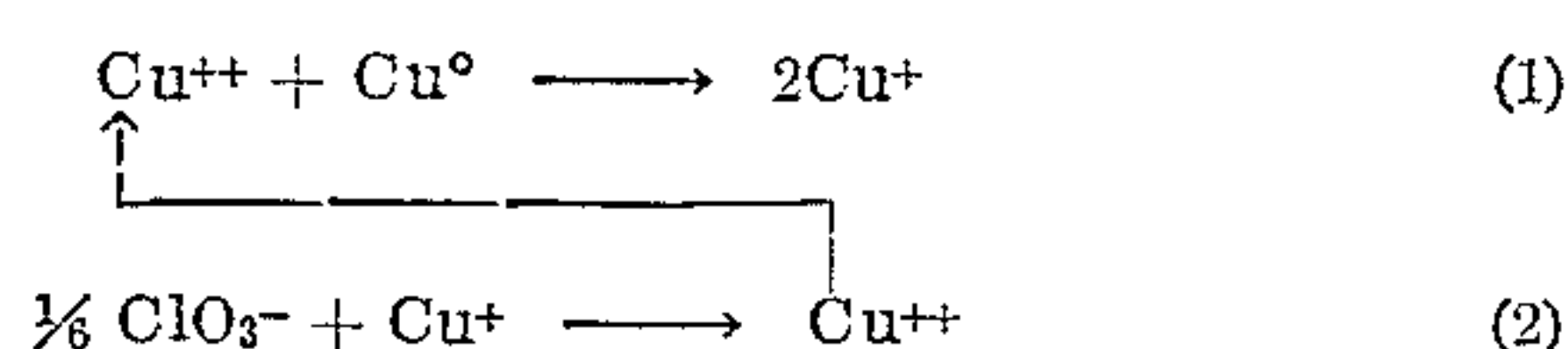


The equilibrium constant is very favorable in sufficient
chloride but the rate of etching falls off quite rapidly
in this medium and imposes a practical limit, usually on
the order of half of theory. Electrolytic regeneration via
anodic reaction to yield Cu^{++} with plating of copper at a
relatively small and polarized cathode has been suggested
as a means of extending the effective life of the etching
solution. However, this technique, on a large scale, re-
quires a sizable initial investment in equipment and high
power consumption.

In principle, the continuous electrolytic technique
offers significant advantages over the chemical methods
of regeneration which have been proposed. Agents such as
oxygen and hydrogen peroxide have been used in conjunc-
tion with necessary additions of acid to reoxidize Cu^+ ,
but these reagents are relatively active and unstable and
necessitate batch processing. Air oxidation has been sug-
gested and tried; however, it is inherently slow and is
limited to spray work.

These and other difficulties are in whole or part over-
come by the use of a soluble chlorate ClO_3^- to oxidize
the cuprous ion formed as a result of reaction (1). This
presents a continuous regeneration process for the de-
sired cupric ion and the effective life of the solution is
considerably lengthened.

According to the invention the etching proceeds prin-
cipally through the continuous sequence:



Reaction (2) is aided by the presence of acid as is
evident from the equation prescribing the over-all
reaction:



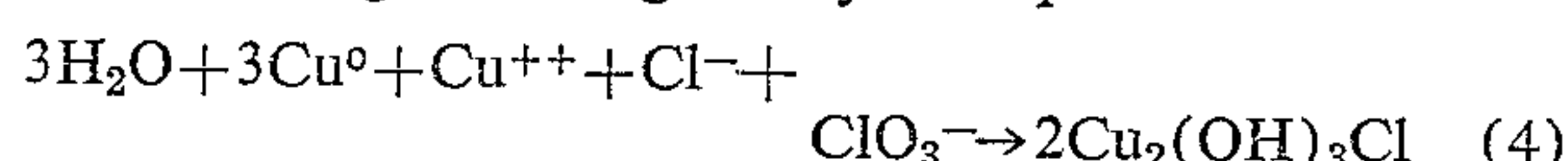
Since the chlorate provides six electrons per mole and
has a very low equivalent weight it is practical to provide
a considerable reservoir of chlorate in the initial solution.
Theoretically, one mole of chlorate is sufficient to dis-
solve three moles of copper metal before the etch rate
falls off and the solution becomes exhausted.

If the total stoichiometric amount of acid (H^+), con-
veniently added as HCl , is added to the initial solution,
 Cl_2 and/or ClO_2 gases may be liberated by side reaction.

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While these reactions tend to be slow the products are
noxious and may detrimentally attack parts of the work-
piece such as the organic resins of wiring boards. Accord-
ingly, it is expedient to add the acid approximately as it is
consumed. This can be done conveniently by monitoring
the electrode potential of the solution and adding acid to
maintain the value within an indicated range.

Where it is found to be inconvenient to make periodic
acid additions the etchant solution of this invention will
provide an unexpectedly long effective life without acid
additions. The novel mechanism responsible for this alter-
native etching mode is given by the equation:



The etching capacity of this solution is again limited by
the equivalence of 3 mols Cu^0 /mol ClO_3^- and also by
the cupric ion: 3 mol Cu^0 /mol Cu^{++} in the original solu-
tion. This is distinguished from the conventional use of
cupric ion etches which have one-third of this capacity
since there is, in that case, a one-to-one stoichiometry
 $\text{Cu}^0/\text{Cu}^{++}$. Furthermore, the equilibrium of reaction (4)
is especially advantageous due to the formation of insol-
uble $\text{Cu}_2(\text{OH})_3\text{Cl}$.

Reaction (4) also requires the initial presence of excess
chloride which is conventional and typically added as
 NaCl . The addition of NaCl as a complexing agent is also
helpful in the previous case even though chloride is ob-
tained from the HCl additions.

The understanding of these and other aspects of the
invention will perhaps be aided by the following detailed
description. In the drawing:

FIG. 1 is a schematic representation of an etching ap-
paratus used to demonstrate the principles of this inven-
tion;

FIG. 2 is a schematic representation of an etching cell
with an associated servo mechanism for automatically
controlling the acid additions to the cell in accordance
with the novel regenerative mechanism represented by
reaction (3) of this invention;

FIG. 3 is a plot of the etch rate vs. time (expressed as
copper etched, gms./liter) for three characteristic solu-
tions formulated according to this invention;

FIG. 4 is a plot of HCl additions vs. time (copper
etched) for the three etch solutions of FIG. 3 illustrating
the stoichiometric behavior of the reaction expressed by
equation (3);

FIG. 5 is a plot of etch rate vs. time (copper etched)
for a solution operated according to reaction (3), a solu-
tion operating according to reaction (4), and a typical
prior art etchant solution; and

FIG. 6 is a plot of etch rate vs. time (copper etched)
for three solutions of this invention having different ini-
tial ClO_3^- content showing the direct dependence of effec-
tive life on the concentration of this constituent.

Etch solutions were tested using the apparatus of FIG.
1. The solution being tested was placed in a trimmed 400-
ml. beaker 10, provided with a 4-blade paddle stirrer 11
driven by motor 12. Etch time measurements were made
on a copper plated wire 13. The wire was a 1 cm. section
of 64-mil platinum wire having a copper plate 0.96 mil in
thickness. The terminals of the wire section were provided
with polyethylene seals 14 to define a constant exposed
area. The plated wire 13 was suspended in a glass rod 15
which is supported in the solution by a collar 16 and
bearing 17. The support rod 15 is rotated with a belt 18
attached around the collar 16 and driven by the stirrer

shaft so that the etching action on the plated section is uniform.

The acidity of the solution was continuously monitored by a pair of wire electrodes 19 and 20 supported in glass sleeves 21 and 22. Electrode 19 is a silver wire and monitors a silver-silver chloride couple. This effectively serves as a reference electrode since the total shift due to molality and activity coefficient from "fresh" to "exhausted" etchant states is less than 75 millivolts for the silver potential in the solutions considered. Acid additions are automatically controlled by a solenoid controlled stopcock 23 on burette 24.

The details of the monitor and servo assembly are shown in FIG. 2. Voltages are measured directly on a potentiometric recorder (Varian G-10 or Mosely 3S) equipped with a microswitch activated by the recorder pen assembly when the potential exceeded a preselected voltage value. The switch in turn controls the motor- or solenoid-operated burette stopcock 23 to add concentrated (12 M) hydrochloric acid in an amount necessary to bring the platinum electrode potential up to the value where the switch would be reversed and the stopcock closed.

As is evident from the following data the solutions forming the basis for this invention were used successfully both with and without acid additions.

In FIG. 3 the etch rate in mils/minute is plotted vs. the amount of copper dissolved in grams/liter. The abscissa reflects the effective life of the solution. Data is given for three different etch solutions with compositions indicated by the following:

	Curve A	Curve B	Curve C
M CuCl ₂ -----	1.0	0.5	0.6
M NaClO ₃ -----	1.5	1.5	1.5
M NaCl-----	0	0.5	1.2

These data suggest the dependence of the capacity or effective life of the etching solution on the original concentration of NaClO₃ since each solution exhibits approximately the same copper capacity.

FIG. 4 plots the optimum schedule of acid additions for the same three solutions used to obtain the data of FIG. 3.

The addition of acid as required by the schedule up to the stoichiometric maximum (indicated by the line) provides for the maximum life of the solution as measured by the NaClO₃ content.

FIG. 5 is a plot of etch rate over the effective life of three etch solutions. Curve D is a solution formulated according to the prior art relying simply on the capacity of cupric chloride to oxidize the copper. The effective life is considerably limited. Curves E and F give results for an etch solution formulated according to this invention and based upon the capacity of NaClO₃ as an oxidant to extend the effective operating life of the solution. The composition of the etchant used for the data of curves E and F corresponds to that of curve C in FIG. 3 (0.6 M CuCl₂, 1.2 M NaCl, 1.5 M NaClO₃). The etch mode of curve E did not include acid additions. The data for curve F was obtained using periodic additions up to the stoichiometric amount of HCl. The etch procedures used to obtain the data for both curves E and F are clearly more effective both in terms of the effective life of the solution and the over-all uniformity of the etch rate.

FIG. 6 is a plot showing data similar to that given in the preceding figures. This figure illustrates the effective life of three different etch solutions and the dependence of the capacity of the solution on the concentration of NaClO₃. Curves G, H and J were obtained using differing

concentrations of NaClO₃ according to the following schedule:

	Curve G	Curve H	Curve J
M CuCl ₂ -----	2.0	2.0	2.0
M NaCO ₃ -----	0.5	1.0	2.0
M NaCl-----	2.0	2.0	2.0

The concentration of chlorate useful to obtain the results of this invention ranges from a significant amount, 0.1 M, to the solubility limit. A useful range is 0.1 M to 3 M. The chlorate can be added initially or as the etching progresses. Spent solutions can be rejuvenated by adding chlorate and sufficient acid to solubilize enough cupric chloride for the requirements of reaction (4). Whereas the chlorate is conventionally added as sodium chlorate, any soluble chlorate is effective within the concentration limits prescribed. All the solutions mentioned herein are understood to be aqueous solutions.

The CuCl₂ may likewise be included in widely varying concentrations from 0.1 M to the solubility limit which is approximately 4 M. The concentration of CuCl₂ determines the maximum etch rate assuming a favorable equilibrium and the etch rate may vary significantly depending upon the application for which the etch process is intended.

The foregoing constituents, CuCl₂ and NaClO₃, are the essential ingredients according to this invention. However it is often found desirable initially to include an excess chloride concentration to provide a more favorable equilibrium by complexing the cuprous product intermittently formed from dissolved copper. Again, the amount of chloride included for this purpose is largely a matter of choice in the specific behaviour of the solution. Consequently this constituent is generally prescribed in an amount of zero to saturation. The chloride is conveniently added as NaCl, however, other soluble chlorides may be used as well. A useful concentration range is 0.1 M. to 5 M.

Various other modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. An etch solution consisting essentially of water having the following essential ingredients in the approximate quantities indicated:

sodium chlorate—0.1 molar to 3 molar
cupric chloride—0.1 molar to 4 molar
sodium chloride—0.1 molar to 5 molar.

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LEON D. ROSDOL, *Primary Examiner*.

JULIUS GREENWALD, SAMUEL H. BLECH,
Examiners.

S. D. SCHNEIDER, *Assistant Examiner*.