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# A study of the electrolytic oxidation of antioxidants at a stationary platinum microelectrode

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A STUDY OF THE ELECTROLYTIC OXIDATION OF  
ANTIOXIDANTS AT A STATIONARY PLATINUM  
MICROELECTRODE

BY

MARK ANTHONY FORTE

A THESIS  
SUBMITTED TO THE GRADUATE FACULTY  
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FOR THE DEGREE OF  
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APPROVED:

AUGUST 1975

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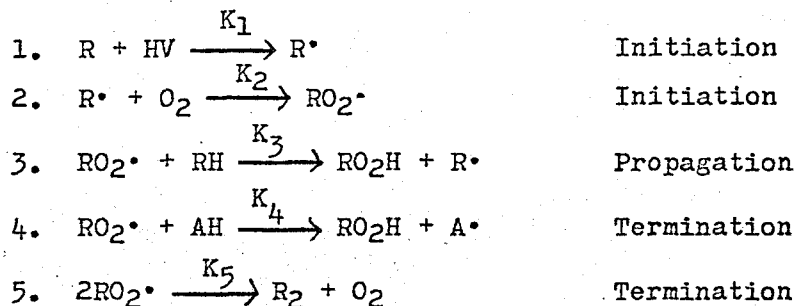
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## INTRODUCTION

Phenolic antioxidants have a wide variety of uses. They are employed to prevent oxidative and thermal degradation of everything from plastics to foodstuffs. They may even have potential as carcinostatic agents (12). In general, they act as chain terminators in free radical type reactions.

Although phenolic antioxidants occur naturally, e.g. Vitamin E (Tocopherols), they are generally tailored to their end use. For example, although the simple trisubstituted 2, 6-di-tert-butyl-4-methyl phenol would be suitable as a gasoline antioxidant, it would not be as good for use in polyethylene where exposure to the environment might cause leaching. In that end use a higher molecular weight compound such as 2, 4-bis (4' hydroxy-3', 5'-di-tert-butyl-phenoxy)-6n octylthio-1, 3, 5-triazine would be more satisfactory due to its low water solubility. Conversely, the higher molecular weight antioxidant would not be as useful in gasoline due to its low volatility which would lead to gum formation in a carburetor.

No matter what the end use, some means for determining the relative potency of the antioxidant is needed. Workers have measured antioxidant activity in terms of  $K_4$  in the following sequence of reactions:



Typically an induction period for oxygen uptake or carbonyl formation is measured in an appropriate substrate. This method is difficult and time consuming.

From thermodynamics the potency of antioxidants can be measured by  $\Delta H^\circ$  for the reaction  $AH \xrightarrow{K_4} A^\bullet + H$ . In the case where similar molecules are examined in the same solvent  $\Delta H^\circ \approx \Delta G^\circ = -nFE^\circ$ . So oxidation reduction potentials can be employed as a measure of antioxidant activity. This is most conveniently done polarographically at a platinum micro electrode. The dropping mercury electrode has been employed for these measurements (33) but it is not useful at potentials  $> +0.41$  due to oxidation of mercury. Penketh (33) measured the oxidation potential (OP) of a number of monohydroxy, polyhydroxy and alkoxyphenols and related them to the induction period increase (33) in gasoline. The measurements were made in aqueous buffered methanol solution. Other workers have measured oxidation potentials of various phenolic antioxidants in

acetonitrile and pyridine. However, no one has offered a solvent system suitable for measurement of the oxidation potential of the higher molecular weight antioxidants typically employed in polyethylene and other polymers. The objective of this research was to develop a solvent system in which the higher molecular weight phenols would be soluble and to employ the solvent system in the measurement of oxidation potential. The oxidation potential would then be related to other measures of antioxidant activity such as increase of induction period. The systems N, N-dimethyl-acetamide (DMAC) /water and DMAC/water/methylene chloride were found to be suitable. Oxidation potentials of a number of commercially available higher molecular weight antioxidants were measured in them. Simpler phenolics were also measured for comparison.

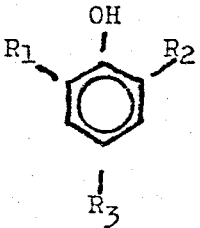
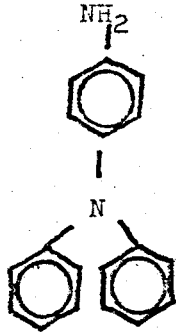
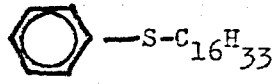
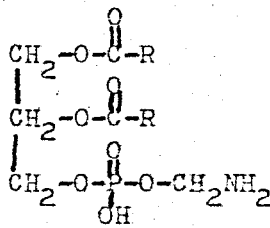


## HISTORICAL

## I. Types and Uses of Antioxidants

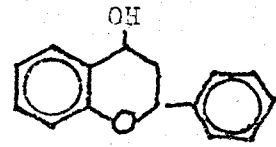
A variety of substances show antioxidant activity and a general statement on classification is difficult to make. However, antioxidants do fall into the broad classifications shown in Table I.

Table I  
Typical Antioxidants

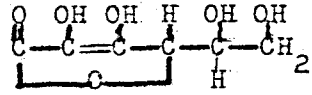
<u>Antioxidant type</u>	<u>Example</u>
Phenolic	 (often R <sub>1</sub> and R <sub>2</sub> are t-butyl)
Amino	
Disulfides, sulfides	$(C_4H_9S)_2$ , 
Phosphates	
Metal Organic or Complex	$M^{Z+} \left( H_2N-\overset{S}{\underset{M}{C}}-SH \right)_n$ ( $M^{Z+} = Co, Cu, Zn$ )

Naturally Occurring

Flavanols



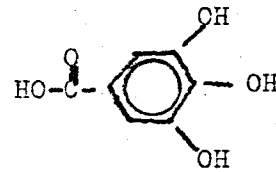
Ascorbic acid



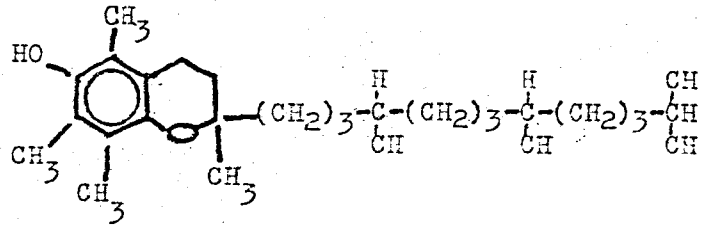
Oregano

fixture

Gallic acid



Vitamin E (Tocopherols)



They are used, as the name implies, to prevent oxidation and or degradation. The oxidation or degradation may occur as a result of exposure to high temperature, air, and or sunlight for long periods of time, or mechanical stress. One of the earliest applications of antioxidants was for the protection of rubber (43). Unprotected, rubber becomes embrittled from exposure to air and sunlight. Rubber is a difficult system to examine since the chemical nature of latex is changed by crosslinking with sulfur in vulcanization. However, it was realized quite early that the proper accelerator could add considerably to the life of the rubber. The residues of the accelerator as it was later found out are antioxidants. This is not now surprising since we now know that sulfur compounds such as  $(C_4H_9S)_2$  are good peroxide decomposers (43). This type of compound might easily form from a sulfur crosslink of low molecular weight isoprene units. A variety of antioxidants are presently employed to protect rubber in addition to sulfides. The two most important are phenolic and amino. In a novel use of amino antioxidants, M. E. Cain (10) has reacted the aromatic amine directly with the rubber substrate to prevent its removal in use.

With the advent of the automobile the increased use of rubber was accompanied by the growth in the use of petroleum, specifically gasoline. Unsaturated molecules in the mixture of hydrocarbons which make up gasoline are particularly vulnerable to oxidation (36). The end

products of the oxidation is a gum which is non-volatile at ordinary engine operating temperatures. Flood (15) and Brooks showed that addition of conjugated dienes had a large effect on the amount of gum formation. Table II shows the relative effect of unsaturates. Completely saturated molecules on the other hand are not prone to gum formation.

Table II  
Gum Formation in Gasoline

<u>Gasoline</u>	<u>Additive</u>	<u>%</u>	<u>Gum mg/100 ml</u>
Straight-run	Limonene	2	46
Refined cracked	none	-	7
Refined cracked	Limonene	2	634
Straight-run*	Isoprene	5	52
Refined cracked*	"	5	521

\*Exposed to light

The gum consists of polymeric peroxides such as  $\text{ROO}-\underset{\text{5}}{\text{CHCH}}=\underset{\text{5}}{\text{CHCHOOR}}$ . The most effective antioxidants are hindered phenols and amino compounds like the examples in Table I. The amino compounds are even effective in the presence of dissolved copper. Small traces (31) of copper increase the rate of gum formation. While the mechanism of gum acceleration is not known, the copper can be removed by chelation. The amino antioxidants tend to form complexes with copper.

Lubricating oil is a complex mixture of naphthalenic (25), aromatic and paraffinic hydrocarbons. The molecular weight ranges from ~ 300 to

800. Lubricating oils are oxidized to acids,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , carbonyls, alcohols and peroxides when exposed to air at high temperatures.

The oils contain natural inhibitors such as phenols and sulfur compounds. Almost all of the compound types listed in Table I have been used to prevent lubricating oil oxidation as well as (25) boron and silicon compounds, selenium and tellurium compounds.

The production of synthetic rubber during WWII paved the way for development of the great variety of high molecular weight polymers we use today. Polymeric materials present a special problem as anyone knows who has had a polyethylene trash can fall apart. The reaction rate of oxidation is slow when compared to gasoline because it involves a gas solid reaction. The properties of a polymer are due to the high molecular weight in addition to the chemical properties of the monomeric units. Therefore, even small amounts of oxidation can result in loss of physical properties due to chain rupture.

Bearing in mind the comparison which might be made between lubricating oil and gasoline, saturated polymers are oxidized at a slower rate than unsaturated polymers. Polyethylene is a typical example of a saturated polymer. To be put into a useful form it must be melted and extruded. It is thus submitted to thermal and oxidative degradation. In use it is exposed to sunlight (UV radiation) and the elements. These all lead to free radical chain rupture. A useful antioxidant

must act as a free radical chain stopper, peroxide decomposer, UV absorber and it must be water insoluble so it is not leached out by rainwater. Higher molecular weight substituted phenols are typically employed.

Antioxidants are also found in the foods we consume. They protect food from rancidification of fats. Ducloux in 1887 (25) and later Tsujimoto showed rancidification was due to oxidation of unsaturated fatty acids. Most antioxidants employed in foods are natural products since they must be edible. For example: C. W. Wright reported that American Indians of the Ohio Valley preserved bear fat by heating it with the bark of the slippery elm (25). Modern man has isolated the active ingredients, such as Vitamin E, ascorbic acid and gallic acid. The author has employed oregano (25) to prevent oxidation of unsaturated fatty acid triglycerides from pork chops in spaghetti sauce.

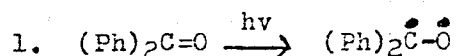
The list of uses of antioxidants is long and is growing. To cite an unusual use, Dadio (12) has shown that brewing antioxidants are potential carcinostatic agents.

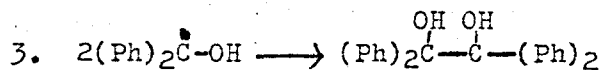
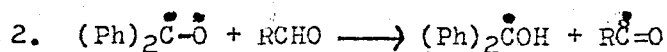
## II. Mechanism of Oxidation and Antioxidant Protection

Since the field of oxidation mechanism is large and since the research work was done on antioxidants for polymers, this survey will be confined to polymers and related hydrocarbons. A good review of ether peroxides is given by King (23).

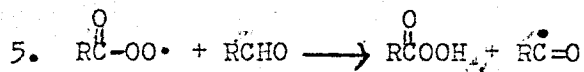
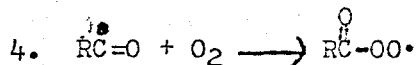
Quite early it was observed by Genthe (36) that linseed oil absorbs oxygen slowly during the initial period, but the rate at some point accelerates. He also found that addition of ethyl or benzoyl peroxide decreased this initial induction period. The concept of auto acceleration arose from these observations. By 1928 Stephens (36) had isolated a peroxide of cyclohexene obtained from reaction of cyclohexene with oxygen in daylight. The compound proved to be a hydroperoxide. Farmer and Sutton developed the hydroperoxide theory of auto-oxidation whereby unconjugated olefinic compounds add an oxygen molecule in a chain reaction. The oxygen molecule attaches itself to the carbon atom adjacent to the double bond to form the hydroperoxide  $R-CH=CH_2-CH_2OOH$ . Backstrom (36) suggested that photochemical autoxidation of acetaldehyde in the presence of benzophenone occurs by a free radical chain reaction. The following sequence of steps were proposed:

Oxygen excluded





Oxygen present



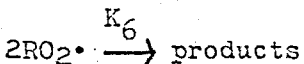
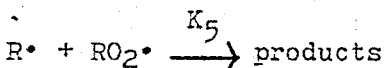
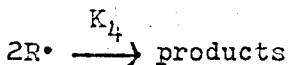
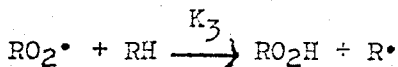
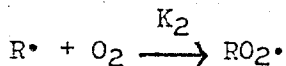
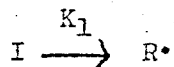
Formation of benzpinicol lends support to the free radical chain reaction theory.

Peroxides are the main source of chain initiating radicals by their decomposition. Dialkyl peroxides are more stable than hydroperoxides, but it is the O-O bond which breaks in both. A number of workers have shown that transition metal ions induce decomposition of hydroperoxide. This is probably the reason for the activating effect of metals on autoxidation.

The chemical reactions of high polymers are similar to those shown above. Polyolefins, polyvinyl chloride, polyamides and carbohydrates all are attacked by oxygen to give hydroperoxides. Oxidation in polymers leads to chain rupture due to decomposition of alkyl peroxides; carbonyl and olefin formation, and crosslinking by addition reactions of alkoxy radicals. All of these change the physical properties of the polymer. Chain rupture reduces molecular weight and tensile strength is reduced. Crosslinks cause embrittlement so stress causes cracks to form. From the kinetic viewpoint, the basic autoxidation scheme shown



below is a good generalization for hydrocarbons and polymers (41).



(I-initiator; RH-hydrocarbon  
or polymer)

The steady-state approach allows one to put the rate equations into a mathematically tractable form.

$$R_i \text{ the rate of initiation} = K_4 [R\cdot]^2 + 2K_5 [R\cdot] [RO_2\cdot] + K_6 [RO_2\cdot]^2$$

$$\text{To simplify assume } K_5 = (K_4 K_6)^{\frac{1}{2}}$$

$$\text{So } R_i = (K_4^{\frac{1}{2}} [R\cdot] + K_6^{\frac{1}{2}} [RO_2\cdot])^2$$

The rate of oxygen absorption;

$$\frac{-d [O_2]}{dt} = K_2 [R\cdot] [O_2]$$

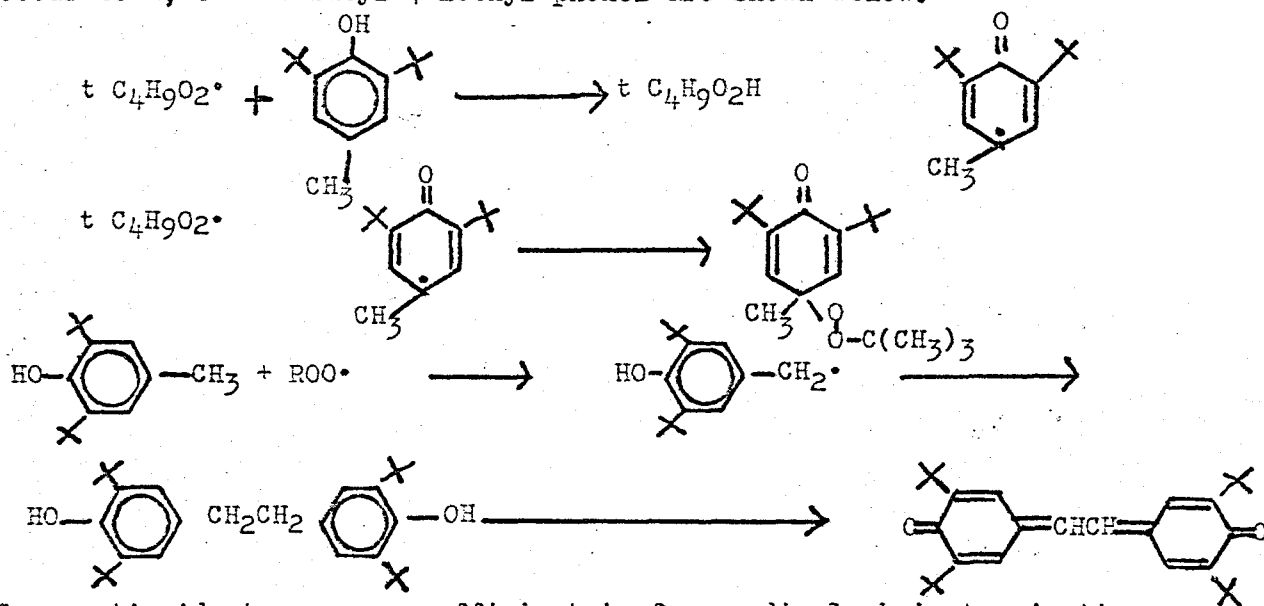
and when appropriate substitutions are made

$$\frac{-d [O_2]}{dt} = \frac{K_2 K_3 [O_2] [RH] R_i^{\frac{1}{2}}}{K_3 K_4^{\frac{1}{2}} [RH] + K_2 K_6^{\frac{1}{2}} [O_2]}$$

By making appropriate changes in oxygen pressure or by adding diluents to a system the various rate constants can be evaluated.

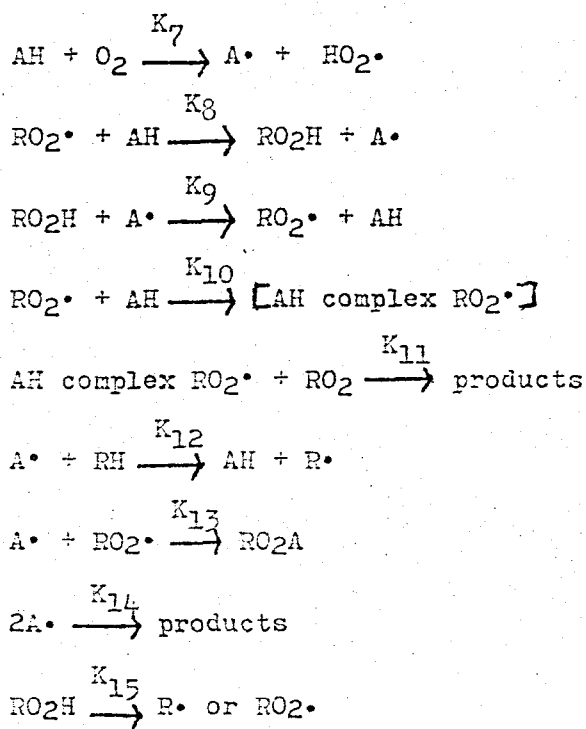
Antioxidants act by decomposing peroxides and trapping free radicals during the critical initiation period. The chain is therefore shortened or eliminated. Two of the typical reactions which can

occur to 2, 6-di-*t*-butyl-4-methyl phenol are shown below.



Some antioxidants are more efficient in free radical chain termination and others are more effective at decomposing peroxide. When the two types are combined we obtain an effect known as synergism. The sum total of the protection is greater than the sum of the individual contributions.

From the kinetic viewpoint the following steps can be added:



### III. Measurements of Antioxidant Effectiveness

Relative measurements of antioxidant effectiveness can be obtained from kinetic studies. The ratio of reaction rates of any two antioxidants in a particular system is a measure of their relative effectiveness. Hammond and coworkers (19) studied the autoxidation of tetralin in chlorobenzene in the presence of N-methyl-aniline and azobisisobutyronitrile initiator. If steady-state conditions are assumed for the set of equations for oxidation in the presence of an inhibitor in section II then this leads to a comparison of antioxidants if initiator and substrate are held constant. The relative efficiency

$$k_{11}/k_{11\text{ref}} = \frac{[AH]}{[AH]_{\text{ref}}} \left( \frac{R_{\text{ref}}}{R} \right)^2$$

where ref refers to a reference compound.

This seems to make evaluation of antioxidants very simple until we remember that in another system the results may be different due to a change in mechanism of oxidation. A good free radical chain stopper may not be as good for decomposing peroxides. Furthermore, the initial rates of inhibited oxygen absorption are altered by a powerful antioxidant and the approximations become less accurate. The induction period is proportional to the efficiency and concentration of the antioxidant. A number of tests for systems such as oils, petroleum and polymers have been developed to measure the induction period.

Phenolic antioxidant effectiveness is, of course, related to the position of substituents on the aromatic ring (45). (Table III shows the relationship between various measurements of effectiveness and

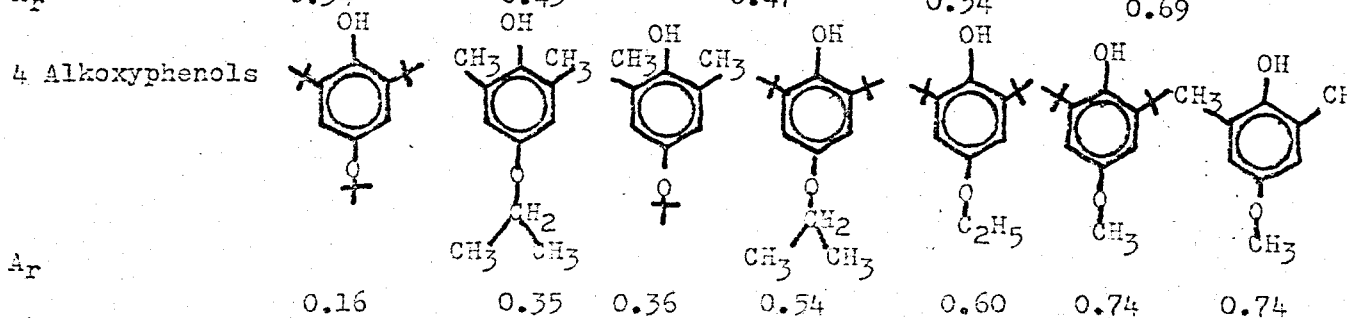
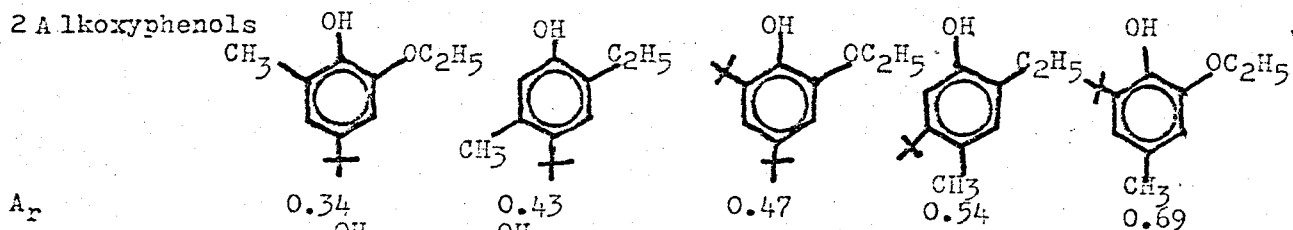
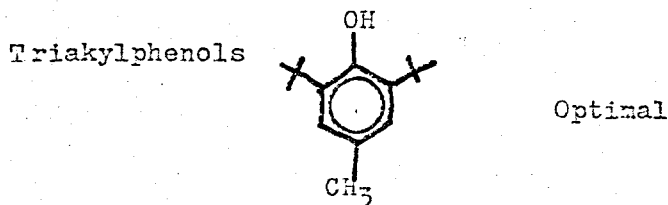
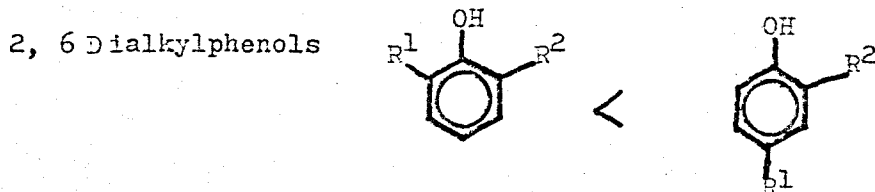
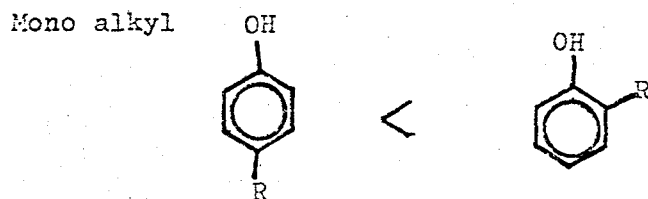
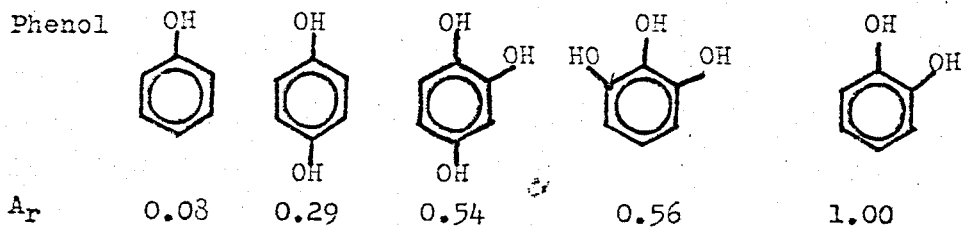
structure). The information may be generalized as follows:

- Electron releasing groups increase activity in ortho and para positions and to a degree in the meta position
- Electron withdrawing groups (nitro, carboxy, halogen) decrease activity
- Branched alkyl groups considerably increase activity in ortho and decrease in para position

Pospisil (35) performed an extensive study of the relationship between the composition of phenols and the effectiveness at 130°C in isotactic polypropylene. The values of relative activity,  $A_r$ , were calculated from values of induction periods. Of the phenols pyrocatechol is most effective as can be seen from the data in Table III.

Table III

## Phenol Effectiveness From Induction Period

Phenol effectiveness increasing  $\longrightarrow$ 

## Methylene bisphenols

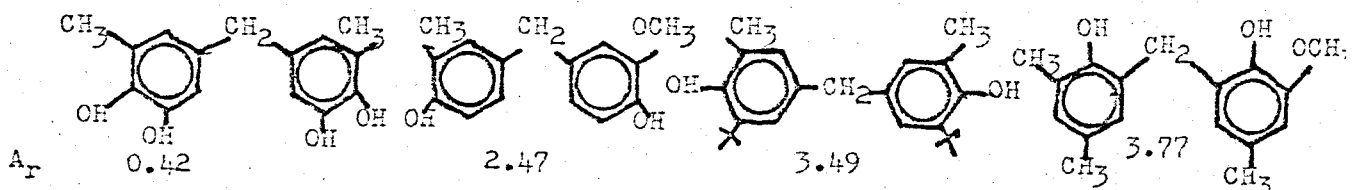
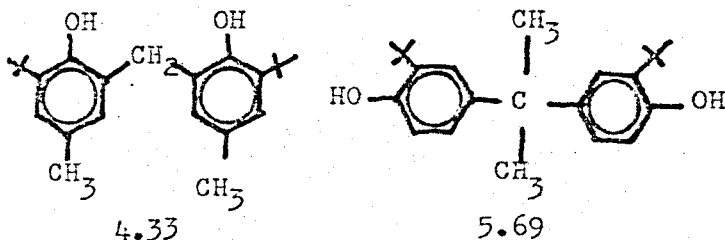


Table III cont.



Ar

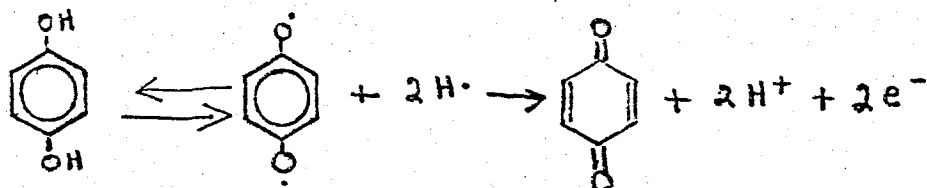
4.33

5.69

To be effective, polyphenols must be capable of quinone formation. However, hydroquinone is not as effective as pyrocatechol since it reacts directly with oxygen. This uses it up inefficiently compared to free radical chain termination.

The methylene bisphenols are surprisingly much more effective than their alkyl and alkoxy phenol counterparts. The substituent effects of monophenols are to a certain extent applicable to the bisphenols. This is especially true of the symmetrical compounds. However, the situation becomes complicated when an antioxidant free radical is formed. In the case of the bisphenol, the effect of the unpaired electron can be delocalized over the other ring. This contributes to the stability of the free radical. Consequently, the activity of the antioxidant is greater than what would be predicted from addition of twice the amount of monophenol.

As was mentioned in the introduction, the oxidation potential is a measure of the effectiveness to be expected of a phenolic antioxidant. It has been shown (36) that  $E^\circ$  is a measure of  $\Delta H^\circ$  for the reversible reaction of hydroquinone.



$E^{\circ}$  can be measured quite easily polarographically. The problem arises that  $E^{\circ}$  cannot be directly determined from  $E_{\frac{1}{2}}$  because most phenolic antioxidants are irreversibly oxidized. Conant (11) introduced the quantity called the "apparent oxidation potential." He used reversible oxidation reduction couples to determine the oxidation or reduction potentials of irreversible reactions of phenols. Fieser (4) improved on this with his "critical" oxidation potential. He also added the phenol to an oxidation reduction system of measured potential. When the potential was sufficiently low, the phenol was not oxidized. This was termed the "critical" oxidation potential. Needless to say, this kind of approach is tedious and suitable reference systems do not abound. So, although measurements of  $E_{\frac{1}{2}}$  do not strictly lead to  $E^{\circ}$  values, workers have used these measurements as measures of antioxidant effectiveness.

#### IV. Polarographic Oxidation of Antioxidants

##### A. Electrodes

In one form or another, the SCE is used as a reference electrode (2) and most tabulations are referred to it. On the other hand, a great variety of materials have been used as working electrodes. The working electrode is defined as the electrode where the primary polarographic reaction occurs. In the case of oxidation of a phenol it is the anode. The voltage is applied across the working electrode and a larger auxiliary electrode which does not become polarized. Potential of the working electrode is measured vs SCE. The potential of the auxiliary electrode is usually not measured. The working electrode can be held stationary in an unstirred solution or it can be rotated or vibrated. Concentration polarization occurs at all small electrodes and is the basis for voltammetry. In the case of dropping mercury or moving solid electrodes, the solution is renewed around the electrode. This affects the shape of the wave. Since mercury becomes oxidized at about 0.4 v, other materials have been used as working electrodes in the oxidation of phenolic antioxidants.



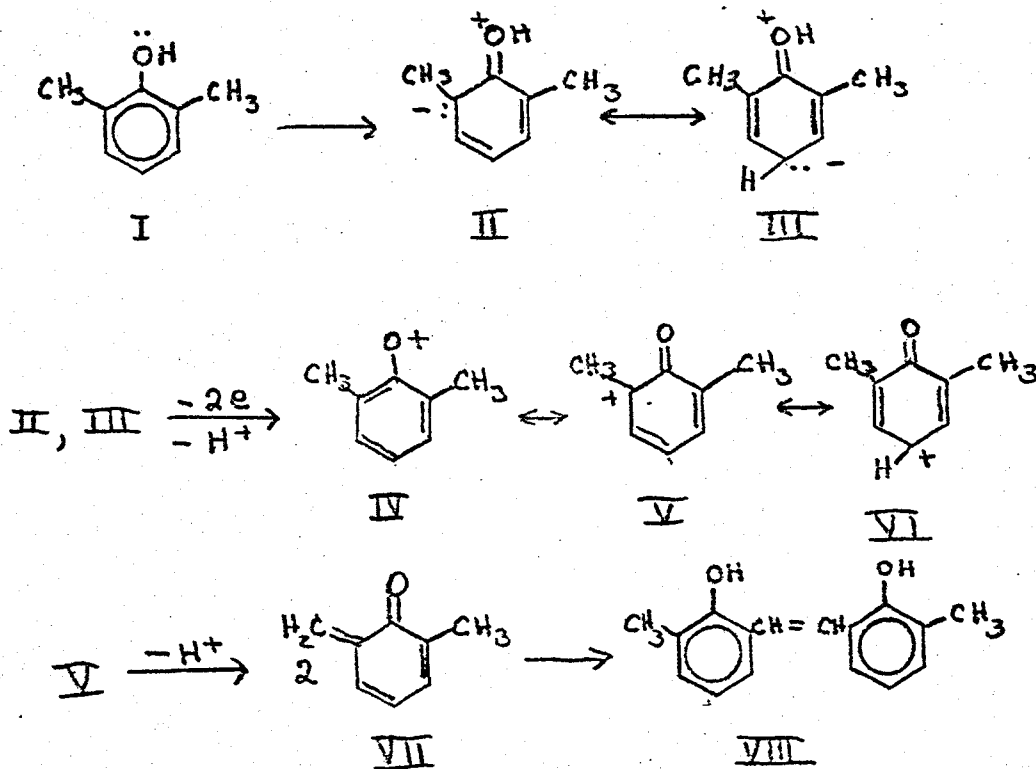
They include: platinum; wax coated carbon; carbon paste and pyrolytic graphite. There seems to be no general agreement on which material is best. Penketh (33) attempted to use a wax coated graphite electrode like that of Gaylor (17), but had difficulty obtaining reproducible oxidation waves. He found platinum was better. On the other hand, Gorokhovskii (18) oxidized 28 phenols with a graphite electrode rotated at 1900 rpm. The graphite rod employed was spectroscopically pure and was vacuum impregnated with paraffin with an addition of polyethylene. Arzamanova (5) also used a graphite electrode, but he stirred the solution. There seems to be general agreement that a fresh electrode surface should be employed between scans. This is obtained by breaking the tip of the graphite electrode off and exposing a fresh layer by removing wax. Penketh simply wiped his platinum electrode off with a tissue.

#### B. Solvent Systems

Studies of anodic oxidation of phenols have generally been done in buffered aqueous alcohol mixtures. The alcohol is introduced to help dissolve phenols which for the most part are water insoluble. The buffer serves as electrolyte. Turner and Elving (47) demonstrated that pyridine containing 0.1 M lithium perchlorate as electrolyte could be used in the oxidation of phenol, hydroquinone, catechol and resorcinol. From the positive potential limit of  $\sim 1.4$  vs silver-silver nitrate,

it could probably be employed to study numerous other phenolic antioxidants. The nitrogen base would also probably assist in dissociation of the proton in the first step of oxidation.

Iwakura, (21) studied the anodic oxidation of 2, 6-xyleneol in acetonitrile. Conductivity measurements indicated the phenol was not dissociated in this solvent. They therefore proposed that the oxidation proceeded via the following mechanism:



Acetonitrile was also used by Lutskii (30) in a study of the relationship between  $E_1^2$  and the energy of the  $\pi$  electrons of the phenol ring as a variety of substituents were added.

Reid (21) has prepared an extensive review of the simple amides: formamide; N-methyl-formamide; N, N dimethylformamide; acetamide; N-Methylacetamide and N, N dimethylacetamide. He indicates the amides are good solvents for salts and organic solutes alike. All of the amides have dielectric constants  $>74$  except DMF and DMAC which have dielectric constants of 36.7 and 37.8 respectively. They tend to be viscous except for DMF and DMAC. Therefore, all things considered, DMF and DMAC are the best of the amides for polarography. Both of these solvents are available in high purity from Dupont. The applications brochure (1) from Dupont indicates the polarographic behavior of quinones and hydroquinones has been studied in DMF. No doubt the pair of electrons on oxygen in DMF and DMAC assist in removal of the hydrogen from phenolic compounds upon anodic oxidation. Both solvents are known to form hydrochlorides when mixed with HCl. A significant amount of work has been done with DMF as a solvent. For this reason DMAC was chosen as the solvent for analysis of phenolic antioxidants in this work.

### C. Anodic Oxidation of Phenolic Antioxidants

The statement has been made: "An art may become a science if it is concerned with less than about seven variables." (15) This statement, when applied to organic electrochemistry, shows it to be a borderline case. Although hydroquinone has had practical application as a redox system for aqueous pH measurement, a controversy exists over the number of electrons transferred in the oxidation in acetonitrile. Parker (52) states that the anodic oxidation in acetonitrile proceeds via a two electron intermediate. Eggin (15), on the other hand, has

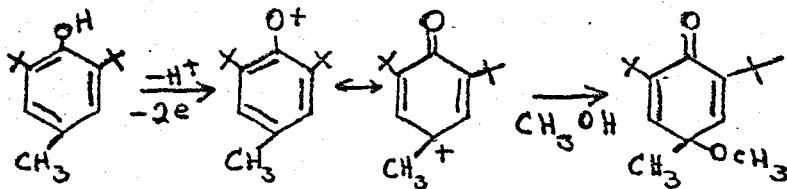
reinterpreted Parker's data and proposes a one electron intermediate based on a different value for the diffusion coefficient. As pointed out by Adams (2) the value of  $ua/mM/cm^2$  may vary for an organic reaction on different electrodes even though it remains essentially constant for an inorganic compound. He cites as an example the comparison of ferrocyanide (one electron transfer and N, N-dimethyl aniline) oxidation at several electrodes. The results shown in Table IV point out the risk in making judgments about the number of electrons transferred in the oxidation of an organic material on the basis of current measurements.

Table IV

Current/Electrode Area Relationship  
For Organic and Inorganic Molecules

Electrode	$ua/mM/cm^2$	
	Ferrocyanide	Dimethylaniline
Pt foil circle	43.5	109
12 gauge Pt wire	44.3	129
Rectangular Pt foil	39.7	61.8
Carbon paste	42.6	86

Severe film formation hinders mechanism studies of phenol oxidations. However, Vermillion and Pearl (43) studied the oxidation of 2, 6-di-tert-butyl-4-methyl phenol in acetonitrile. These workers performed a controlled potential electrolysis of 2, 6-di-tert-butyl phenol in acetonitrile buffered by an addition of tetraethylammonium hydroxide in methanol. The principal product was 2, 6-di-tert-butyl-4-methyl-4-methoxy cyclohexadienone. They proposed that it formed through methanol addition to a mesomeric structure of the phenoxonium ion.



They also showed that in the presence of excess strong base the phenoxide anion would be produced. The electrode reaction then shifted to one electron. From these results they suggested that the aqueous solution behavior at low pH should correspond to a two electron process and a one electron at high pH. Additional work in 50% water/isopropanol buffers appears to confirm this. A technique which should elucidate the structures of free radical intermediates in electrode processes has been pioneered by Maki and Geske (2). They have performed voltametric studies inside the microwave cavity of an E.P.R. spectrometer. Preliminary work shows that a variety of radical ions can be produced in non-aqueous media. Adams (2) has extended this work to aqueous media.

#### D. Treatment of Data

Since the oxidation of phenolic antioxidants involves electrons and hydrogen ions,

$$E = E^{\circ} - \frac{0.059}{n} \text{ pH at } 25^{\circ}\text{C.}$$

To determine  $E^{\circ}$  or  $E_{1/2}^{\circ}$ , the authors who have worked in aqueous buffered media plot  $E_2$  vs pH and extrapolate to zero pH. At this point  $E_2$  presumably equals  $E_{1/2}^{\circ}$ . In some cases  $\Delta E_2 / \Delta \text{pH}$  is reported to indicate the number of electron change which has occurred. Gorokhovskii (18) has reported  $\Delta E_2 / \Delta \text{pH}$ ,  $\tan \theta$ , for the 23 phenols shown in Table V.

Table V

Polarographic Characteristics of Phenols in the Oxidation of Their  $4 \cdot 10^{-4}$  M Solutions in Buffer Media at a Rotating Graphite Electrode

No.	Compound	$E_{1/2}^0$ , V	$E_{max}^0$ , V	$E_{1/2}$ at pH 7, V	$\tan \alpha$
1	Phenol	1.13	1.24	0.59	0.077
2	Hydroquinone	0.62	—	0.27	0.050
3	Resorcinol	1.0	0.69	0.68	0.046
4	2,4-Dinitroresorcinol	0.69	—	0.49	0.023
5	2,6-Di-tert-butylphenol	1.09	1.25	0.28	0.11
6	2,6-Xylenol	0.95	0.96	0.44	0.074
7	2-Benzyl-4-chlorophenol	0.83	1.05	0.45	0.061
8	Mesitol	0.91	—	0.36	0.074
9	m-(2,6-Dimethylbenzyl)phenol	0.94	—	0.40	0.078
10	2,4,6-Tri-tert-butylphenol	0.87	0.39	0.40	0.068
11	o-tert-Butylphenol	1.0	1.16	0.53	0.069
12	2-tert-Butyl-4-chlorophenol	0.96	1.19	0.51	0.065
13	o-Cresol	1.08	1.12	0.53	0.079
14	p-Cresol	0.99	1.13	0.49	0.073
15	2-(2,6-Dimethylbenzyl)-p-cresol	0.92	1.09	0.45	0.067
16	2-tert-Hexyl-p-cresol	0.98	—	0.47	0.073
17	2,6-Bis(2-methylbenzyl)-p-cresol	0.77	0.76	0.31	0.066
18	2-(2-Methylbenzyl)-p-cresol	0.93	1.1	0.45	0.067
19	2-Propyl-p-cresol	0.85	—	0.56	0.041
20	2-Nonyl-p-cresol	0.80	0.98	0.41	0.057
21	2-tert-Butyl-p-cresol	0.93	1.2	0.50	0.068
22	2-Benzyl-p-cresol	0.87	1.12	0.39	0.068
23	2-tert-Octyl-p-cresol	0.86	0.96	0.37	0.07
24	o-tert-Hexylphenol	0.70	0.97	0.50	0.02
25	p-Nitrophenol	0.90	—	0.49	0.06
26	2,4-Bis(2,6-dimethylbenzyl)phenol	0.93	1.05	0.46	0.067
27	4-Chloro-2-(2-methylbenzyl)phenol	0.90	1.08	0.49	0.059
28	2,6-Dibenzyl-4-chlorophenol	0.81	—	0.41	0.068

$\tan \alpha$  of 0.06 - 0.07 corresponds to a one electron change. The authors also found that at  $\text{pH} > \text{pK}_a$   $E_{1/2}^0$  assumes a constant value which does not change with further increase in pH.

In the cases where authors have studied the antioxidants in a non-aqueous media,  $E_{1/2}^0$  is reported without additional treatment.

## EXPERIMENTAL

## I. Reagents

N, N dimethyl acetamide (DMAC)- $(\text{CH}_3)_2\text{N}^{\text{O}}\text{CCH}_3$ , molecular weight 87.12, 99+% pure obtained from Dupont.

Methylene chloride ( $\text{MeCl}_2$ )- $\text{CH}_2\text{Cl}_2$ , molecular weight 84.93 reagent grade was obtained from Fisher Scientific.

Ethylene Glycol ( $\text{Et}(\text{OH})_2$ )- $\text{CH}_2\text{OHCH}_2\text{OH}$ , molecular weight 62.07 reagent grade was obtained from Fisher Scientific.

Water was deionized by passage through a mixed bed ion exchange resin.

Lithium chloride  $\text{LiCl}$ , molecular weight 42.39 reagent grade was obtained from Baker Chemical.

Magnesium perchlorate  $\text{Mg}(\text{ClO}_4)_2$  molecular weight 223.21, reagent grade was obtained from Merck.

Phenols investigated are shown in Table VI in the Appendix with their source. They were analyzed as received.

## II. Apparatus

Polarographic scans were made with a Princeton Applied Research Model 174 polarographic analyzer.

The cell employed was obtained from Metrohm and electrodes were:

Anode-one cm x 0.1 cm platinum wire sealed in glass; cathode-platinum wire coil; reference-saturated calomel with asbestos wick.

Current vs potential scans were recorded on a Houston Omnigraphic Model 2200-3-3, 11" x 17" x-y recorder.

Samples were weighed on a Mettler Type H or a Sartorius analytical balance.

In addition the usual miscellaneous laboratory apparatus was used.

This included a magnetic stirrer, volumetric glassware and a torch for sealing platinum wire into glass tubing.



### III. Procedure

Potential scans were made at room temperature which varied from 21 to 26°C. Solvent mixtures were prepared in volumes of 500 to 2000 ml and stored in ground glass stoppered flasks. Solutions of antioxidants were prepared by dissolving 100 mg in 25.0 ml of DMAC. The solutions were used within two hours of preparation. Some of the antioxidant solutions in DMAC turned color after a few days. This was assumed to be caused by quinone formation through reaction with a hydroperoxide which can form in DMAC. Five ml of the antioxidant solution was pipetted into approximately 75 ml of solvent mixture in the polarographic cell as had been done by Penketh (33). The solution was then stirred by a magnetic stirrer or a stream of nitrogen. No effort was made to remove oxygen since it does not interfere in the anodic reaction.

In the check out of the instrument and technique, antioxidants were dissolved in 25 ml of methanol. Five ml of methanol solution was added to 75 ml of a buffered solution of methanol/water. The buffers were prepared as described by Penketh (33).

The unstirred solutions were anodically scanned from 0 volts to the solvent decomposition point, usually at a rate of 5 mv/sec. The full scale current range was usually set at 0.05 ma.

The values obtained are vs saturated calomel electrode as reference.

No correction was made for the IR drop across the cell because it was felt to be small due to the large excess of supporting electrolyte.

The electrode was conditioned for about 5 minutes before each scan or until the current became essentially constant at the initial potential of zero vs SCE. This was indicated by no pen deflection in the "y" direction on a setting of 0.05 ma. The anode and cathode were rinsed with acetone between runs. The anode was dried by wiping with a tissue to remove any possible accumulation of insoluble oxidation products. Newly prepared electrodes were conditioned by running 4-5 scans of  $1.1 \times 10^{-3}$  M solutions of 2, 6-di-tert-butyl-4-methyl phenol. When not in use the electrodes were stored in deionized water.

## IV. Data and Results

A. Preliminary Development of Technique of Anodic Oxidation-  
Comparison of Results with Those Obtained by Penketh

A one cm platinum electrode as described by Penketh was prepared and employed to oxidize  $1.1 \times 10^{-3}$  M, 2, 6-di-tert-butyl-4-methyl phenol in pH 2 buffer. The sample was initially scanned in the DC mode at 5 mv/sec. Two break points were found for this compound as Penketh had indicated (Fig. 1). He reported 0.570 and  $0.680 \pm 0.030$  v for  $(OP)_0$ . The  $(OP)_0$  value was obtained by extrapolating the voltage at initial current rise (OP) from background to zero pH. For most antioxidants a plot of (OP) vs pH resulted in the following relationship:  $OP = (OP)_0 - 0.058pH$ . The 2, 6-di-tert-butyl-4-methyl phenol had a break point at pH 6 above which the slope was 0.099 and 0.047 below. At pH 2 Penketh's OP values are calculated to be 0.48 and 0.59 while 0.54 and 0.72 were found in this work. The differences observed are greater than 2 sigma and may be due to different methods of determining  $(OP)_0$  from the curves. The break observed for the second wave was so weak that the voltage obtained is only an estimate. According to the Polarograph manufacturer, Princeton Applied Research, differences of 0.05 v are not uncommon when comparisons are attempted with work done more than fifteen years ago. They can arise from differences in junction potentials due to use of different cells. Penketh used an H cell while a Metrohm cell was used in this work.

### B. Precision of results

The precision of measuring the  $E_{init}$  values is estimated to be 8.6 mv for one standard deviation. This value was obtained from fifteen pairs\* of  $E_{init}$  measurements made during the course of this work. Voltage data ranged from 380 to 790 mv.

$E_{init}$  was obtained from the point of intersection of the steep slope of the wave and the residual current. This point was employed as a reproducible measure of the oxidation potential of phenolic antioxidants by Penketh (35). I agree with his findings and in addition I must point out that in some cases  $E_{\frac{1}{2}}$  would be difficult to determine. This is due to the current peak which occurs with some compounds such as hydroquinone at a stationary electrode. An example of this phenomenon is given in Figures 11 and 12 in the Appendix. It is due, according to Adams (2), to an increase in the diffusion layer thickness as the concentration of electroactive species decreases in the immediate vicinity of a stationary microelectrode. This leads to a drop in the current so a peak results.

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$$* \sigma = \sqrt{\frac{D^2}{2n}}$$

where D = difference between pair of values  
n = number of pairs

The PAR analyzer is capable of four modes of operation. They are: direct current (DC); sampled DC; pulse and differential pulse. The instrument manual indicates greater sensitivity can be achieved if pulse mode is employed in place of DC. This was tried on the  $1.1 \times 10^{-3} M$  2, 6-di-tert-butyl phenol in pH 2 buffer. As can be seen from curve 4 in figure 1, although the current flow was greater, the two waves were not resolved. Therefore, throughout the course of this work DC was employed exclusively.

C. Effect of Water on Decomposition Potential of N, N-Dimethylacetamide/  
Lithium Chloride

Decomposition\* of DMAC containing 0.94 M LiCl as an electrolyte occurs at  $\sim 760$  mv vs SCE. The decomposition is probably due to the oxidation of  $Cl^-$  to  $Cl^0$ . It is surprising that this occurs at such a low potential since it occurs at  $\sim 1100$  mv in water. As can be seen from the data in Table VII there is an increase in decomposition potential as water is added.

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\*Decomposition is defined as the intersection of the steep current rise with voltage and the baseline of little current change with voltage.

Table VII

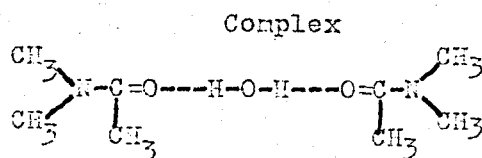
DMAC/0.94 M LiCl

Molarity of H <sub>2</sub> O	Mv vs SCE
0	760
2.86	810
3.92	855
4.43	860
4.94	875
5.43	895
5.92	900
6.40	920
27.76	990

The rate of increase is steep initially as can be seen from the plot of the data in Figure 2. The shape of the curve resembles a titration curve. The point which would correspond to the inflection point is at 4.94 M H<sub>2</sub>O. This corresponds to two moles of DMAC for each mole of water. At 9.07 M H<sub>2</sub>O, the rate of change of decomposition potential decreases abruptly. At 27.76 M H<sub>2</sub>O the decomposition potential is only 990 mv. Hydrogen bonded complexes such as those below might form as water was added. The Cl<sup>-</sup> ion would also become hydrated which would make it more difficult to oxidize.

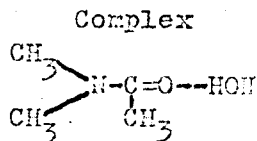
Moles DMAC/Moles H<sub>2</sub>O

2



Moles DMAC/Moles H<sub>2</sub>O

1



When excess water is present the Cl<sup>-</sup> would be completely hydrated and the increase in decomposition potential would be expected to level off.

D. It might be argued that the increase in decomposition voltage is due to dilution of the LiCl and not due to competition between complex formation between water and DMAC and hydration of Cl<sup>-</sup>. Accordingly, 10 ml of cyclohexane (0.0926 M) was added to 75 ml of DMAC/0.94 M LiCl and the decomposition potential was determined. No change (Figure 3) was seen for addition of cyclohexane. Cyclohexane concentration was calculated at 1.09 M in the final solution. At that concentration for water, it is seen from Figure II that decomposition potential had increased ~15 mv. For addition of 10 ml of water to 75 ml of DMAC (6.53 M) the decomposition potential had increased ~160 mv.

If the increase in decomposition potential with water is due to hydrogen bonding, then addition of a hydroxy compound should also have the same effect. Ethylene glycol was chosen because it is a hydrocarbon analog for water. The change in decomposition potential which occurs upon addition of ethylene glycol to DMAC/0.94 M LiCl is shown in Table VIII and Figure 4.

Table VIII

Addition of Ethylene Glycol to DMAC/0.94 M LiCl

M Ethylene Glycol	Decomposition Potential, Mv
0	740
2.25	870
3.99	915
5.39	930
Ethylene Glycol/0.94 M LiCl	990

The increase in decomposition potential is more rapid than for water. This may mean that the  $\text{Cl}^-$  complex is stronger.

Increased ionization of LiCl is apparently not involved in the mechanism of the increase since the dielectric constant of ethylene glycol/DMAC mixtures would be lower than that for water/DMAC mixtures as can be seen from Table IX.

Table IX.

Dielectric Constants of Solvents

Solvent	Dielectric Constant	Temperature
DMAC	37.8	—
Water	78.5	25°C
Ethylene Glycol	41.2	20°C



### E. Participation of Water in Anodic Oxidation of 2, 6-Di-Tert-Butyl-4-Methyl Phenol

Although the decomposition potential of a 1:1 DMAC, ethylene glycol, 0.47 M LiCl solution is 960 mv vs SCE, no wave is observed for 2, 6-di-tert-butyl-4-methyl phenol. The appearance of a wave was anticipated below 950 mv from the results which Penketh had obtained for this compound in methanol/water. A wave does appear, however, when water is added to the solvent. A  $1.2 \times 10^{-3}$  M solution of 2, 6-di-tert-butyl-4-methyl phenol was scanned at 5 mv/sec from zero mv to 960 mv vs SCE. Water was added in 5 ml increments to 75 ml of DMAC, ethylene glycol and the scan was repeated. As can be seen from Figure 5 and Table X, the wave gradually becomes more defined from the large current increase associated with solvent decomposition.

Table X

Oxidation of 2, 6-di-tert-butyl-4-methyl phenol vs H<sub>2</sub>O Curve

Total Water Added, ml	E <sub>init</sub> 2, 6-di-tert-butyl-4-methyl phenol
0	not observed
5	900
10	800
15	750
20	740

Initial Solvent: 75 ml DMAC, 1:1 Ethylene Glycol, 0.47 M LiCl

And as water content increases the E<sub>init</sub> decreases.

Therefore, water somehow participates in the mechanism of anodic oxidation of this phenol. It appears that it is through an increase in basicity and dielectric strength of the solvent which would lead to greater dissociation of the phenol. This would agree with the fact that E<sub>init</sub>

increases as pH decreases as shown by Penketh and others. Low values of pH would, of course, prevent dissociation of a hydrogen ion.

F. Formulation of Ternary Solvent N, N-Dimethylacetamide/Methylene Chloride/Water

Since it was found that water was a necessary constituent of the solvent, a mixture of 50 ml of DMAC and 25 ml H<sub>2</sub>O was prepared for polarographic scans. This was made 0.63 M in LiCl as electrolyte. This solvent had a decomposition potential of ~1000 mv, so it was felt that all anodic waves which might be encountered would be lower than solvent decomposition. Unfortunately, a number of the high molecular weight phenolic antioxidants for study were not soluble in this solvent. This was evidenced by cloudiness when a DMAC solution was added to the DMAC/ water mixture. In order to circumvent this problem a less polar solvent was added to help dissolve the phenolic antioxidants. It had to be miscible with DMAC and water. Methylene chloride fit all the requirements, so it was added to the stirred DMAC/ water mixture in increments until two phases formed. This occurred at ~13 ml. To be sure of a single phase methylene chloride was reduced to 10 ml combined with 50 ml DMAC and 25 ml of water. All of the phenolic antioxidants are soluble in this mixture. It has a decomposition potential of ~960 mv. Large quantities of solvent of the above proportions were prepared by mixing 652 ml DMAC, 87 ml methylene chloride, 260 H<sub>2</sub>O and 20 g LiCl.

### G. Examination of Potassium Perchlorate, Lithium Acetate and Magnesium Perchlorate as Alternate Electrolytes

In the course of scanning the antioxidants it was found that a few of them (for example: 2, 2' methylene-bis-(4-ethyl-6-tert-butyl phenol) and 4, 4' methylene-bis-(2,6-di-tert-butyl phenol) had waves which were barely discernable from solvent decomposition. It was therefore obvious that the solvent matrix would be improved if the decomposition potential could be increased. Penketh (33) had employed sodium acetate as a pH 2 buffer constituent and as can be seen from Fig. 1, the decomposition potential of the solvent is approximately 1010 mv.

Since lithium salts are generally more soluble than sodium or potassium salts in DMAC, lithium acetate was checked as an alternate electrolyte. As can be seen from Fig. 6, there is a gradual current rise for DMAC saturated with acetate which begins at ~600 mv and becomes steep at 1100 to 1200 mv. The shape of this decomposition wave would limit the utility of lithium acetate as an electrolyte because phenolic compounds with waves >800 mv would still be difficult to discern. Hydroquinone was scanned in the solvent with the resultant large poorly defined wave labeled 3 in Fig. 6. Use of this electrolyte was not pursued further.

Since the perchlorate anion is in a higher oxidation state than chloride, it was felt that a perchlorate salt would be a good electrolyte. Lithium perchlorate had been used by Popov and Geske (2) in acetonitrile. Unfortunately, lithium perchlorate was not available, so potassium and magnesium perchlorate were evaluated. Potassium perchlorate is not very soluble in DMAC, but a solution was prepared which was  $1.3 \times 10^{-2}$  M in

$\text{KClO}_4$  and 5 M in  $\text{H}_2\text{O}$ . This electrolyte had a decomposition potential of  $\sim 1200$  mv, but the current increase started to become steep at  $\sim 1000$  mv. Hydroquinone had a "normal" looking wave in this solvent, but as water was added the shape changed considerably as can be seen in Fig. 7. Magnesium perchlorate was much more soluble in DMAC and a  $1.8 \times 10^{-2}$  M solution was prepared and scanned. The decomposition potential was  $> 1400$  mv for this electrolyte. When methylene chloride and water were added to give the following composition: DMAC/ $\text{MeCl}_2$ / $\text{H}_2\text{O}$  65 ml/9 ml/20 ml, the decomposition potential only dropped  $\sim 100$  mv as shown in Fig. 8. This electrolyte was found to be very useful and a number of phenolic antioxidant waves were measured using it as a supporting electrolyte.

H. Relationship of Water Content of Solvent to Oxidation Potential of Hydroquinone, 2-Tert-Butyl-4-Methyl Phenol and 2, 6-Di-Tert-Butyl-4-Methyl Phenol

Water, as was shown in IV, E, has an effect on the oxidation potential of 2, 6-di-tert-butyl-4-methyl phenol. It was felt that it would be desirable to firmly establish the relationship between water and  $E_{\text{init}}$  for phenols which had different degrees of hindrance around the hydroxyl. Therefore, hydroquinone, 2-tert-butyl-4-methyl phenol and 2, 6-di-tert-butyl-4-methyl phenol were studied which represent no, intermediate, and complete hindrance around the hydroxyl. Current-voltage scans were made of each of the three compounds in various combinations of DMAC, water and methylene chloride. Water concentration was varied from  $\sim 12$  M to  $\sim 50$  M. This data is to be found in Tables XI-XIII in the appendix.

As was done earlier 100 mg of the phenol was dissolved in 25 ml of DMAC. Five ml of this solution was pipetted into 50-75 ml of solvent mixture in the polarographic cell. This resulted in a phenol concentration of  $\sim 1.5 \times 10^{-3}$  M. The resultant waves and exact solvent compositions are shown in Figures 9, 10, 11 and 12 for hydroquinone, Figures 13, 14 and 15 for 2-tert-butyl-4-methyl phenol and Figure 16 for 2, 6-di-tert-butyl-4-methyl phenol.

A number of approaches of plotting the data to give a linear plot of  $E_{init}$  vs water concentration were tried. It was found that a plot of  $E_{init}$  vs  $1/M \times 10^2, H_2O$  is linear for all three phenols as can be seen from Figures 17, 18 and 19. This is reasonable since Amis (5) established that a linear relationship exists between the standard potential of a galvanic cell and the reciprocal of the solvent dielectric constant.

The linear relationship enables one to put the  $E_{init}$  for phenolic antioxidants on a common basis by extrapolation to pure water even though they might not be soluble in it! All that need be known is the  $E_{init}$ , the molarity of water and the slope of the  $E_{init}$  vs  $1/M \times 10^2, H_2O$  line. The slopes of the compounds studied above were calculated from regression equations shown in Tables XI, XII, and XIII in the Appendix. As can be seen from the data in Table XIV, they are not radically different considering the extreme difference in substitution around the hydroxyl.

Table XIV

## Regression Slope for Phenols

Compound	Slope of $E_{init}$ vs $1/M \times 10^2, H_2O$
Hydroquinone	24.4
2-tert-butyl-4-methyl phenol	28.8
2, 6-di-tert-butyl-4-methyl phenol	41.1

## I. Anodic Oxidation of Commercially Available Phenolic Antioxidants

As can be seen from the structures given in Table VI in the Appendix, the phenolic compounds studied fall into one of three classes: no substitution in the 2, 6 position relative to hydroxyl; one substituent; or two substituents. Since the slopes of  $E_{init}$  vs  $l/M \times 10^2$ ,  $H_2O$  found in the previous section do not differ greatly for extremes in substitution around the hydroxyl, they have been used in finding  $E_{calc}$  rather than determining a slope for each compound. (This would not be possible in most cases anyway due to solubility considerations.)

Current voltage scans (5 mv/sec 0.050 ma) were made on 100 mg of the antioxidant dissolved in 25 ml of DMAC, 5 ml of which was pipetted into the cell. The ultimate solvent composition for each compound is given in Table XVII in the Appendix.  $E_{init}$  was determined from the curve and is also tabulated.  $E_{calc}$  was found by mathematical extrapolation to 55.5 M  $H_2O$ . The slopes given in Part H, Table XIV, were employed according to the class of substitution described above. Typical current voltage scans of the compounds are shown in Figures 20 - 26.

A number of variables were examined to determine their effect on the value of  $E_{init}$ . The variables and effects on  $E_{init}$  are shown in Table XV.

Table XV.  
Effect of Variables on  $E_{init}$

<u>Variable</u>	<u>Change or Adjustment</u>	<u>Effect on <math>E_{init}</math></u>	<u>Figure</u>
Scan rate	Set to 2, 5, 10, 20, mv/sec	not significant*	16, 27
Calomel Ref Electrode	~1.5 cm between ref and Pt vs ~4 cm separation	not significant	28
Calomel Ref Electrode	fresh calomel electrode vs one in use	no $\Delta$ solvent scan	29
Calomel Ref Electrode	Soak in DMAC before scan in solvent with $H_2O$	not significant	28
Platinum Electrode	freshly prepared vs in use	significant $\Delta$ first 5 or 6 scans then no significant $\Delta$	—
Platinum Electrode	Hold at 1150 mv (greater than solvent decomposition) for a few minutes	no significant $\Delta$ in next scan	28
Platinum Electrode	Wipe electrode with tissue between scans	not significant	28
Temperature	1.5°C $\Delta T$ between scans	~5 mv	—
Concentration of Phenol	1 x vs 2 x hydroquinone	not significant	11, 12

\*  $\Delta$ mv < 2 standard deviations

The reasons for the changes or adjustments are obvious for most of the variables in the table. Some clarification is offered here for those which may not be so obvious. Separation of the electrodes affects the cell resistance. Since no correction has been made for the IR drop across the cell, it was felt important to show  $E_{init}$  was independent of electrode position. However, to minimize the IR drop, electrodes were always placed within one cm or two cm from each other. Holding the electrode at 1150 mv tests for deposition of oxidation products on the surface of the electrode. This might, of course, happen after repeated scans. This did not appear to be the case but the electrode was rinsed with acetone and wiped with a tissue between scans since the behavior of all phenolics upon oxidation is not known.

## V. DISCUSSION

### A. Extrapolation of Measured Oxidation Potentials to Pure Water

The values of  $E_{calc}$  obtained by extrapolation to pure water agree fairly well with literature values. The agreement might be better if everyone employed the same solvent - water. A comparison of the  $E_{calc}$  is shown in Table XVII (Appendix) and conditions are summarized in Table XVIII

Water has a pH of  $\sim 5.6$  and water/DMAC 2:1 by volume has a pH of 5.5 due to dissolved  $CO_2$ .

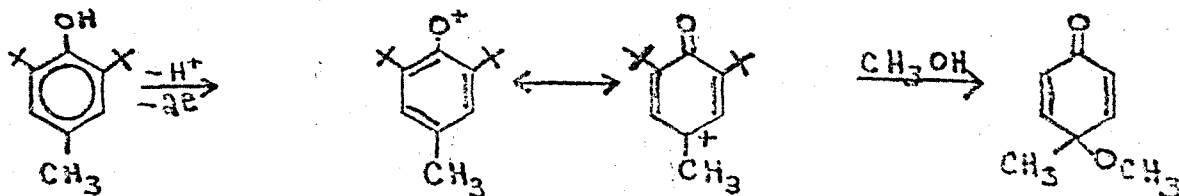


Table XVIII

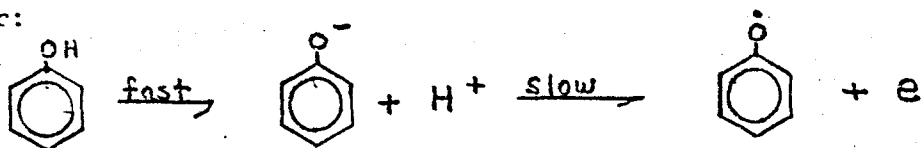
## Polarographic Conditions Used by Other Authors

Reference	Electrode	Extrapolation	Solvent
(33)	Platinum	pH = 0	Aqueous buffer/50% methanol
(2)	Carbon paste	-	Aqueous buffer
(22)	-	-	pH 2 buffer
(24)	Graphite	-	Methanol
(7)	Graphite	pH = 0	Aqueous buffer/50% methanol
(6)	Stationary Graphite	pH = 0	Aqueous buffer/alcohol
(18)	Rotating Graphite	pH = 0	Aqueous buffer/10% ethanol

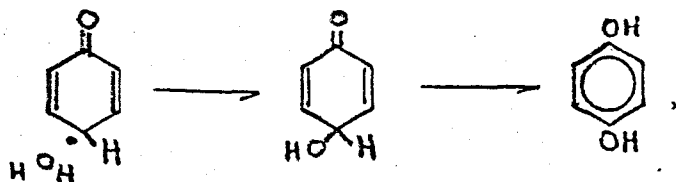
For comparison  $E^{\circ}$  values from the literature have been adjusted to 5.5 pH in the cases where authors have extrapolated to pH = 0. Typically, an equation of the form  $E(\text{observed}) = E^{\circ} - m(\text{pH})$  is reported for the phenols studied in the reference. When  $E^{\circ}$  is given in volts  $m$  is usually 0.050 to 0.060. In the case of ref (22) no value for  $m$  was given so I used the theoretical value of 0.059. On the average  $E_{\text{calc}}$  is  $\sim 100$  mv higher than OP reported by Penketh (33) for the same compound in water/methanol 1:1. However, good agreement is found with Gorkhovskii (18) who employed water/ethanol 10:1. The reason for this behavior may lie in the mechanism of anodic oxidation in the presence of methanol. It was shown in the text by Adams (2) that 2, 6-di-tert-butyl-4-methyl phenol is converted to 2, 6-di-tert-butyl-4-methyl-4-methoxy-cyclohexadienone in acetonitrile buffered by tetraethylammonium hydroxide in methanol. The following mechanism was proposed:



Hedenburg (20) proposes the following mechanism for oxidation of phenol in water:



In the case of phenol the free radical would probably be short lived and in dilute aqueous solution would add water.



It could also dimerize as evidenced by polymeric film formation on electrodes in non-aqueous media.

In a system of water/methanol 1:1 by volume there are ~16 moles of methanol to 23 moles of water so it is difficult to decide how the oxidation is occurring.

Since electrolytic oxidations are pH dependent and the pH scale is based on water it seems reasonable to extrapolate to water and avoid the complications of other solvents which can participate in the reaction.

#### B. Relationship of Oxidation Potential to Induction Period

Numerous authors have related oxidation potential to induction period increase or other measures of antioxidant efficiency. Penketh (33) related the induction period increase of saturated gasoline to the oxidation potential of simple phenols. He found that antioxidant activity was related to  $(\text{CP})_0$  as shown in Table XIX

Table XIX

## Antioxidant Activity vs Voltage of Wave

(OP) <sub>0</sub>	(OP) <sub>0</sub> Adjusted to 5.6 pH + 100 mv	Antioxidant Activity
>0.80	>0.575	slight to none
>0.70 < 0.80	>0.475 < 0.575	fair
<0.70	<0.475	good

These values have been adjusted to 5.6 pH to relate the antioxidant activity to  $E_{calc}$  in this thesis. Since there is ~100 mv difference remaining after this treatment (see Table XVII Appendix), 100 mv was added to the result. Almost all of the substituted phenols were effective if (OP)<sub>0</sub> was less than 0.70 v with the exception of hydroquinone. There is a point at which a compound is so easily oxidized that it reacts directly with molecular oxygen. This was pointed out by Lloyd (24) who studied the relationship between  $E_{1/2}$  and induction periods in Cumene and *d* methyl styrene. As can be seen from a comparison of induction periods in these substrates with those in gasoline used by Penketh (Table XX Appendix) the order of effectiveness can be reversed. Most antioxidants studied in this thesis (Table I Appendix) would fall into the fair to good category with the possible exception of 2, 6-bis-(2'-hydroxy-3'-tert-butyl-5'-methyl-benzyl) - p cresol. It would be very difficult to predict the increase in induction period induced by addition of an antioxidant to a particular substrate from the oxidation potential. However, all of the antioxidants which met the oxidation potential criteria given in Table XIX produced a significant increase in the induction periods of the various substrates in Table XX. The measurement of oxidation potential is therefore a very valuable tool for rapidly screening antioxidants.

## SUMMARY

Anodic oxidation is a rapid method for screening antioxidants. Phenolic compounds with an oxidation potential between 0.5 and 0.6 volts have been found to be efficient antioxidants as shown by an increase in the induction period of oxygen uptake in peroxide free radical oxidation of hydrocarbons.

Numerous investigators have measured oxidation potentials in buffered methanol/water mixtures and then extrapolated their results to zero pH.

Many of the higher molecular weight antioxidants which are suitable for use in polymeric systems are not soluble in water/methanol mixtures. Binary and ternary solvent systems of dimethylacetamide (DMAC)/water and DMAC/water/methylene chloride ( $\text{MeCl}_2$ ) were developed to dissolve these antioxidants so that their oxidation potentials could be measured at a stationary platinum electrode.

In the course of measuring the oxidation potentials, it was observed that the value in addition to being related to the structure of the compound, was related to the molarity of the water present in the system. A plot of oxidation potential versus the reciprocal of

the molarity gives a straight line for molarities greater than 12.

The slope of the plot is 41.1 for the hindered 2, 6-di-tert-butyl-4-methyl phenol 28.8 for 2-tert-butyl-4-methyl phenol and 24.5 for hydroquinone. Since all of the antioxidants studied are substituted phenols, their oxidation potentials were adjusted to the same relative basis by extrapolation to 55.5 molar water using the appropriate slope.

Table VI

## Phenolic Antioxidants Studied


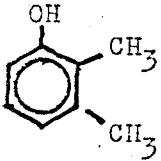
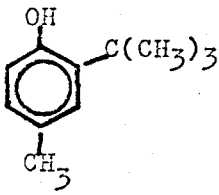
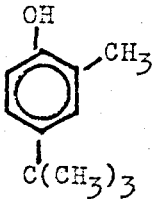
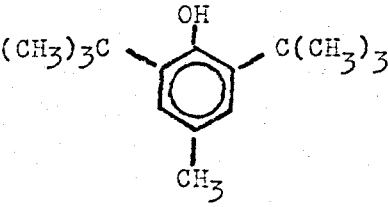
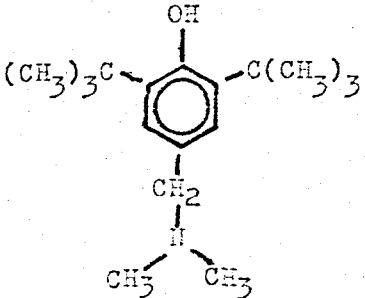
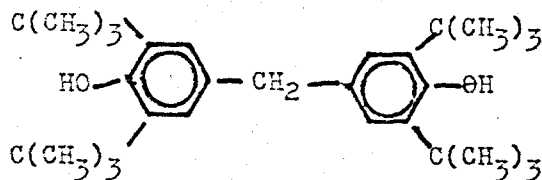
<u>Compound</u>	<u>Structure</u>	<u>Source</u>
Hydroquinone		Phipps and Bird
2, 3-dimethyl phenol		Aldrich Chemical Co.
2-tert-butyl-4-methyl phenol		Aldrich Chemical Co.
4-tert-butyl-2-methyl phenol		Aldrich Chemical Co.
2, 6-di-tert-butyl-4-methyl phenol		Aldrich Chemical Co.
4 hydroxy-3,5-di-tert-butyl-benzyl-dimethyl-amine (Ethyl 703)		Ethyl Corp., New York N.Y.

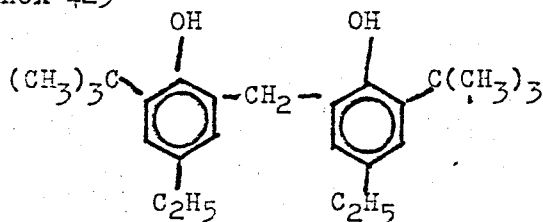
Table VI Cont.

4, 4'-methylene-bis-  
2, 6-di-tert-butyl  
phenol



American Cyanamid Co.  
Bound Brook, N.J.

2, 2' methylene-bis-  
(4 ethyl-6-t-butyl  
phenol) or Plastanox 425



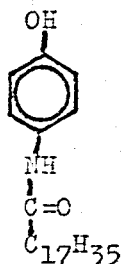
American Cyanamid Co.  
Bound Brook, N.J.

Irganox 565

hindered phenol;  
no structure available

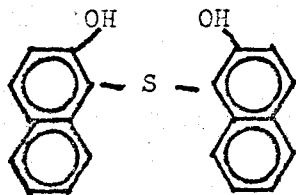
Geigy Chemical Corp.  
Ardsley, N.Y.

p-hydroxy-stearanilide  
(Succinox 18)



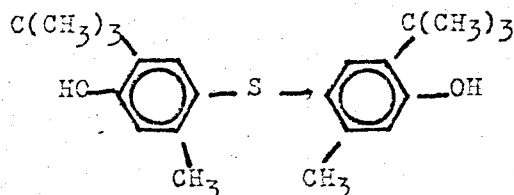
Miles Laboratories, Inc.  
Elkhart, Indiana

1, 1'-thio-bis-(2  
hydroxy-naphthalene)  
Plastanox 61 or  
Catalin CAO-30



American Cyanamid or  
Catalin Corp., New York,  
N.Y.

4, 4'-thio-bis (6-tert-  
butyl-m-cresol) or  
Santowhite Crystals



Monsanto Chemical Co.  
St. Louis, Mo.

Table VI Cont..

2, 6 bis (2' hydroxy-  
3'-tert-butyl-5'-  
methyl benzyl)-p-cresol  
or Plastanox 80

American Cyanamid Co.  
Bound Brook, N.J.

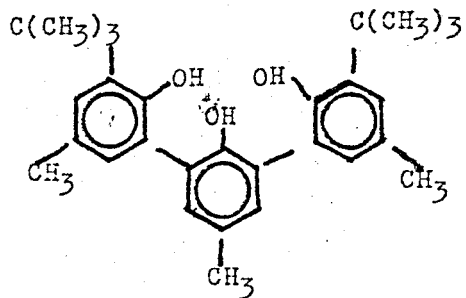




TABLE XI

Slope of  $E_{init}$  vs  $1/M \times 10^2$  for hydroquinone

$$\text{Slope} = \frac{n\sum XY - (\sum X)(\sum Y)}{n\sum X^2 - (\sum X)^2} = 24.4$$

$\frac{Y}{E_{init}, \text{ mv}}$	$\frac{X}{1/M \times 10^2}$		
		$\sum Y$	= 3868
380	1.84	$\sum X$	= 33.887
400	1.84	$n\sum XY$	= 167325
530	7.11	$(\sum X)^2$	= 1715.62
510	5.97	$n\sum X^2$	= 2006.72
495	5.23		
510	4.71		
520	7.36		
523	7.36		

$$r = 0.95$$

TABLE XII

Slope of  $E_{init}$  vs  $1/M \times 10^2$  for 2-tert-butyl-4methyl phenol

$$\text{Slope} = \frac{n \sum XY - (\sum X)(\sum Y)}{n \sum X^2 - (\sum X)^2} = 28.8$$

$$\frac{Y}{E_{init}, \text{ mv}} \quad \frac{X}{1/M \times 10^2}$$

745	7.41	$n \sum XY = 348938.0$
713	6.20	$\sum X = 49.59$
725	5.27	$(\sum X)^2 = 2459.17$
718	4.70	$\sum Y = 6861$
685	3.98	$(\sum Y)^2 = 47073321$
670	3.55	$(\sum X)(\sum Y) = 340236.99$
735	7.33	$n \sum X^2 = 2761.72$
600	3.10	$n \sum Y^2 = 47391430$
565	1.93	
705	6.12	

$$r = \frac{n \sum XY - (\sum X)(\sum Y)}{[n \sum X^2 - (\sum X)^2]^{\frac{1}{2}} [n \sum Y^2 - (\sum Y)^2]^{\frac{1}{2}}}$$

$$r = 0.89$$

TABLE XIII

Slope of  $E_{init}$  vs  $1/M \times 10^2$  for 2,6-di-tert-butyl-4-methyl phenol

$$\text{Slope} = \frac{n\sum XY - (\sum X)(\sum Y)}{n\sum X^2 - (\sum X)^2} = 41.1$$

$\frac{Y}{E_{init}, mv}$	$\frac{X}{1/M \times 10^2}$
--------------------------	-----------------------------

790	7.20	$n\sum XY$	= 599549.52
740	6.90	$\sum X$	= 70.43
760	7.20	$\sum Y$	= 8382
620	3.84	$\sum X^2$	= 432.03
720	6.60	$(\sum X)^2$	= 4960.38
620	3.84	$(\sum X)(\sum Y)$	= 590344.26
747	7.38	$\sum Y^2$	= 5888534
705	6.24	$n\sum Y^2$	= 70662408
700	6.24	$(\sum Y)^2$	= 70257924
670	5.49		
660	4.95		
650	4.55		

$$r = \frac{n\sum XY - (\sum X)(\sum Y)}{\left[ n\sum X^2 - (\sum X)^2 \right]^{\frac{1}{2}} \left[ n\sum Y^2 - (\sum Y)^2 \right]^{\frac{1}{2}}}$$

$$r = 0.968$$

TABLE XVI

COMPOUND	SOLVENT COMPOSITION *					$E_{init}$	M H <sub>2</sub> O	1/M H <sub>2</sub> O x 10 <sup>2</sup>	$E_{calc}$
	ml DMAC,	ml H <sub>2</sub> O,	ml MeCl <sub>2</sub> ,	Electrolyte Molarity					
2,3-dimethyl phenol	57.24	17.76	0	Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.027	765	13.16	7.60	598
2-tert-butyl-4-methyl phenol	57.24	17.76	0	Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.027	740	13.16	7.60	573
4-tert-butyl-2-methyl phenol	57.24	17.76	0	Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.027	730	13.16	7.60	563
2,6-di-tert-butyl-4-methyl phenol	53.91	19.57	6.52	LiCl	0.44	790	13.59	7.36	568
4-hydroxy - 3,5 - di-tert-butyl-benzyl-dimethyl-amine Ethyl 703	53.95	19.52	6.53	LiCl	0.44	520	13.54	7.38	291
4,4-methylene-bis-2,6-di-tert-butyl phenol	53.95	24.52	6.53	LiCl	0.42	740	16.01	6.25	557

\* calculated to nearest 0.01 ml where a large quantity of solvent was prepared and then 65 - 80 ml used in polarographic cell

TABLE XVI Cont..

COMPOUND	SOLVENT COMPOSITION					$E_{init}$	M $H_2O$	$1/M H_2O \times 10^2 E_{calc}$	
	ml DMAC,	ml $H_2O$ ,	ml $MeCl_2$ ,	Electrolyte Molarity					
2,2' methylene -bis-(4-ethyl- 6-tert-butyl phenol) Plastanox 425	53.95	19.52	6.53	LiCl	0.44	830	13.54	7.38	601
	53.95	21.52	6.53	"	0.43	790	14.57	6.86	582
Irganox 565	58.95	19.52	6.53	"	0.42	510	12.74	7.84	262
p-hydroxy-stearanilide Succinox 18	53.95	19.52	6.53	"	0.45	620	13.54	7.38	484
	58.95	19.52	6.53	"	0.42	630	12.74	7.84	483
1,1' thio-bis-(2-hydroxy-naphthalene) Plastanox 61 or CAO-30	53.95	19.52	6.53	"	0.44	520,650	13.54	7.38	359,489
4,4' -thio-bis-(6-tert-butyl-m-cresol) Santowhite Crystals	53.95	19.52	6.53	"	0.44	600	13.54	7.38	439
	53.95	19.52	6.53	"	0.44	590	13.54	7.38	429
2,6-bis-(2'-hydroxy-3'-tert-butyl-5'-methyl-benzyl)-p-cresol Plastanox 80	60.97	19.02	0.0	$Mg(ClO_4)_2$	0.10	325	13.20	7.58	87

## Comparison of Voltage for Polarographic Waves Obtained by Other Authors

Compound	$E_{calc}$	O.P. (33)*	$E_{p/2}$ (2)	$E_{\frac{1}{2}}$ (18)	$E_0$ (6)	$E_{\frac{1}{2}}$ (22)	$E_{\frac{1}{2}}$ (24)	$E_{\frac{1}{2}}$ (7)
Hydroquinone	389	263	300	345	-	-	-	-
2, 6-di-tert-butyl-4-methyl phenol	568	312, 422	-	-	-	-	303	331
2-tert-butyl-4-methyl phenol	568	441	-	606	-	-	472	-
2, 3-dimethyl-phenol	598	531	-	-	-	-	-	-
2-methyl-4-tert-butyl phenol	563	451	-	-	-	-	527	-
2, 2'-thio-bis-6-tert-butyl-o-cresol	434	-	-	-	295	500	-	-
4, 4'-methylene-bis-2, 6-di-tert-butyl phenol	557	-	-	-	-	474	-	-

\*Reference

TABLE XX

## Antioxidant Efficiency

Compound	E <sub>calc</sub>	(33)* P 195 RMP (36)**		t <sub>i</sub> cumene HRS 126.5°C (24)	t <sub>i</sub> d Methylstyrene 81°C (24)***	Pentaplast 190°C t <sub>i</sub> min (22)	AO Rating	
							Tetralin	3 <sup>108</sup>
Hydroquinone	389	0	-	-	-	-	-	-
2, 6-di-tert butyl-4-methyl phenol	568	70	76	23.5	22.3	-	163	48
2-tert-butyl-4- methyl phenol	568	95	37.5	33	24.7	-	84	71
2, 3-di-methyl phenol	598	25	-	-	-	-	-	-
2-methyl-4-tert- butyl phenol	563	-	14.5	16.2	11.4	-	80	22
2, 2'-thio-bis-6- tert-butyl-p- cresol	434	-	-	-	-	360	-	-
4, 4'-methylene- bis-2, 6-di-tert- butyl phenol	557	-	-	-	-	290 min	-	-

\* reference

\*\* relative molar potency

\*\*\*induction period increase

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- 47) Turner, W. Richard, and Elving, Philip J., Analytical Chemistry, 37, No. 4, p. 467-469, (1965).
- 48) Vermillion, T. J., and Pearl, I. A., Journal of Electrochemical Society, 3, p. 1392, (1964).

## AUTOBIOGRAPHY

I, Mark Anthony Forte, was born on July 8, 1940 in Waterbury, Connecticut. I grew up in Queens, New York where I attended Newtown High School and was graduated in 1958. From 1958 to 1962 I attended City College of the City University of New York, where I majored in Chemistry. While a student at City College, I was a member of the Young Men's Christian Association and president of Compton '62, a social club. I was graduated in June, 1962 with the degree of Bachelor of Science.

I was then employed as an analytical chemist by E. I. du Pont de Nemours and Company, Incorporated and assigned to the Pioneering Research Laboratory at the experimental station in Wilmington, Delaware. In February, 1965 I was transferred to the Spruance Textile Fibers Plant in Richmond, Virginia in the analytical research group. While at du Pont I have worked on numerous products including Nylon, Nomex,\* Tyvek,\* Teflon\* and Kevlar.\* My current professional level is senior chemist.

\* registered Dupont trademark

In 1968, I was married to Mary Louise Moschler. Mary Lou is a 1964 graduate of Westhampton College of the University of Richmond. She is a teacher at A. M. Davis Elementary School in Chesterfield County.

In 1969, I enrolled in the evening graduate program at the University of Richmond, where I am currently a candidate for the degree of Master of Science in Chemistry.

I am a member of Sigma Xi, honorary research society; The American Chemical Society; The Society for Applied Spectroscopy. I am a member of the Episcopal Church of the Redeemer; Bon Air Community Association; and the Richmond Ski Club.

My recreational interests include skiing, fishing, traveling and photography.

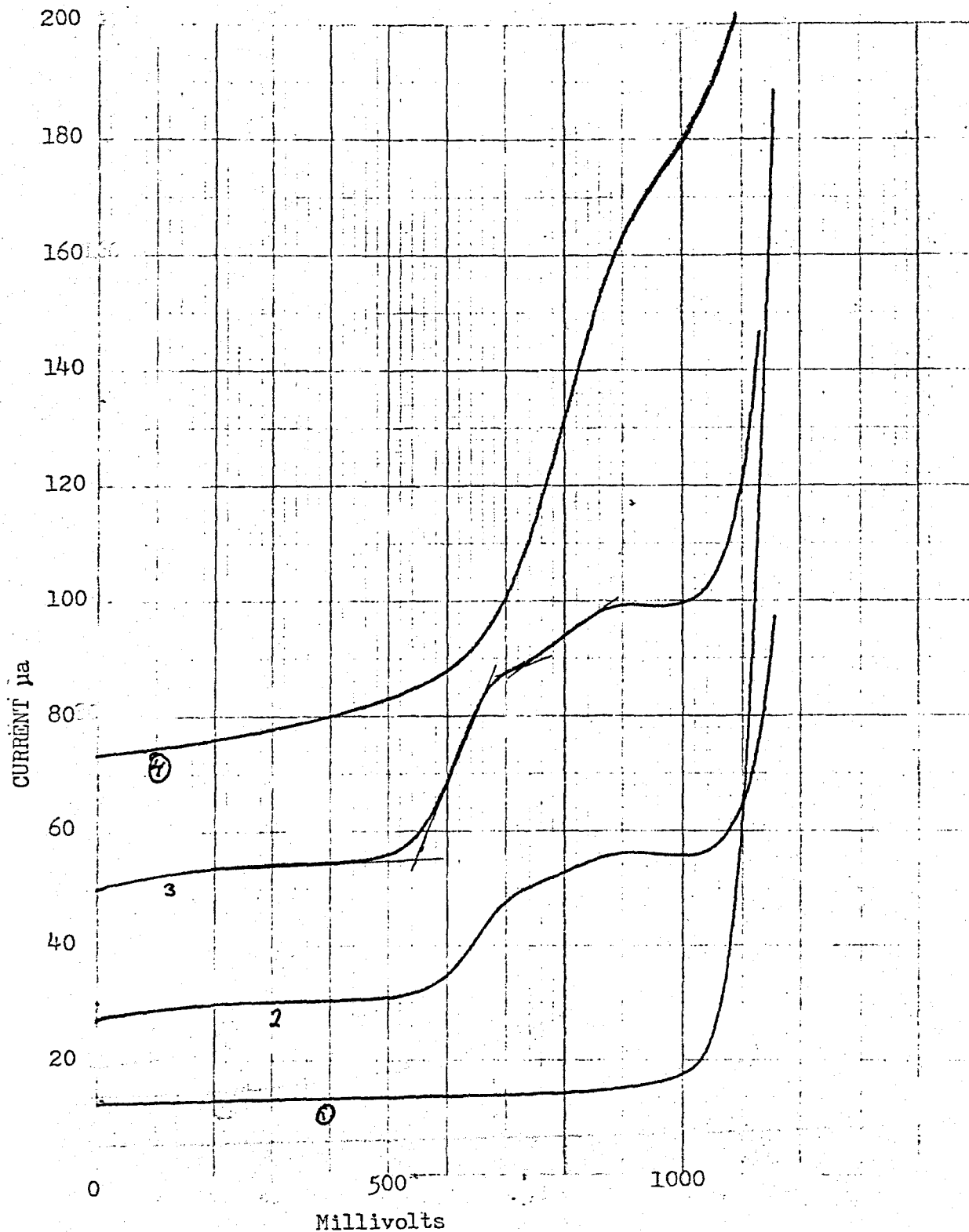
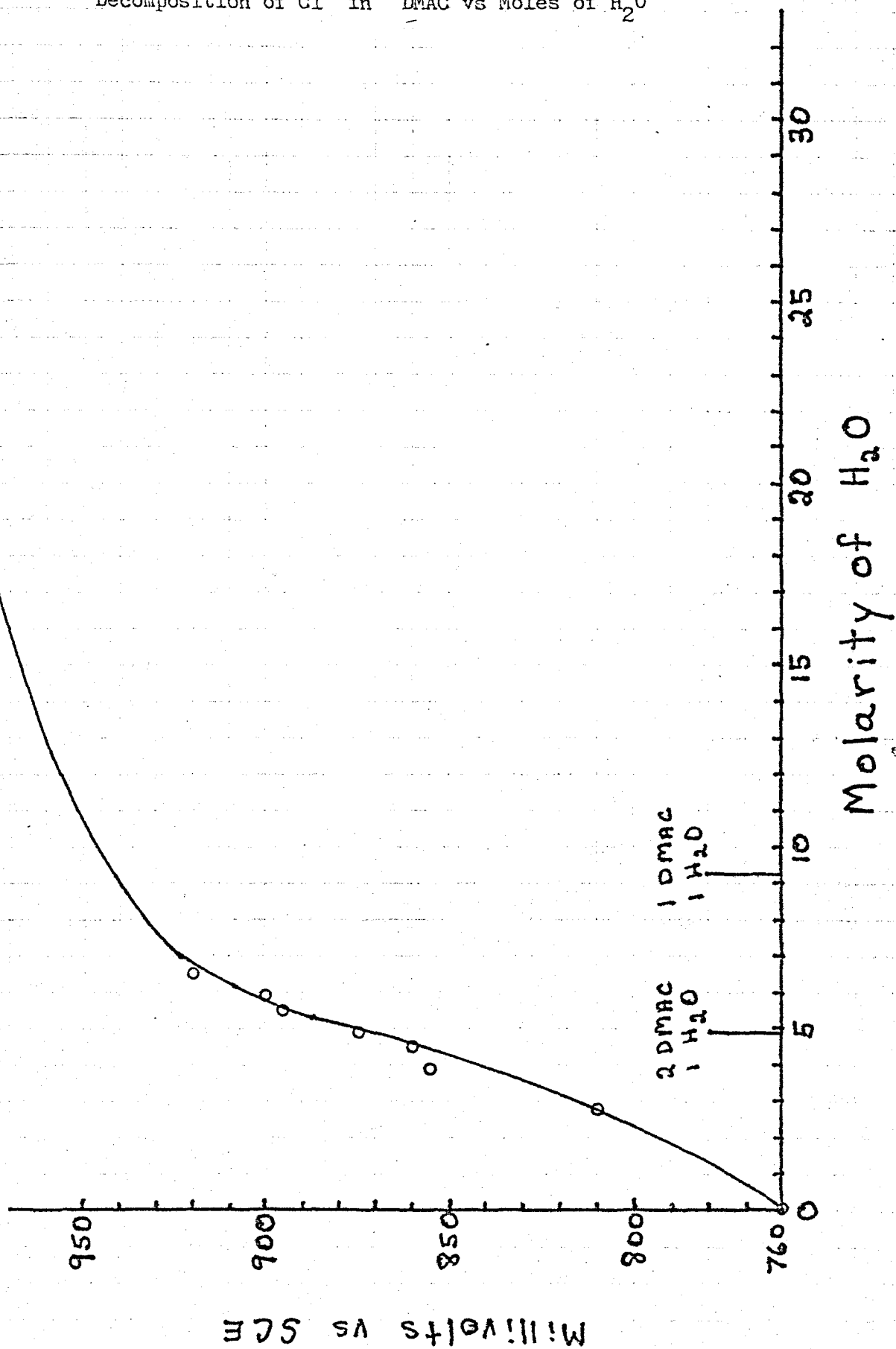


Figure 1. 2,6-di-tert-butyl-4-methyl phenol pH 2 buffer  
 (1) buffer scan at 5mv/sec  
 (2)  $1.1 \times 10^{-3}$  M 2,6-di-tert-butyl-4-methyl phenol  
 (3) same as (2)  
 (4) pulse polarography

Figure 2

Decomposition of  $\text{Cl}^-$  in DMAC vs Moles of  $\text{H}_2\text{O}$



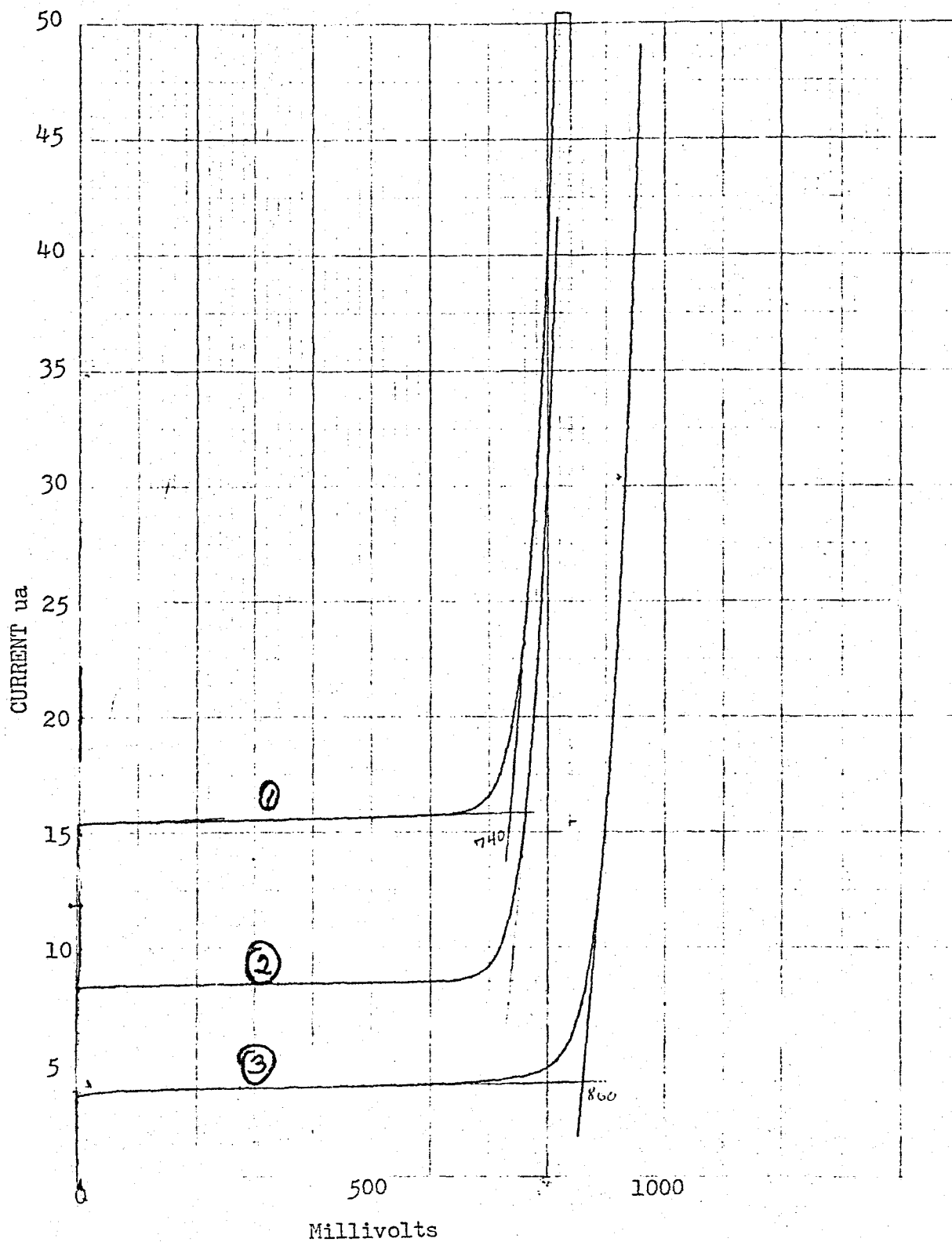


Figure 3. Solvent decomposition potential

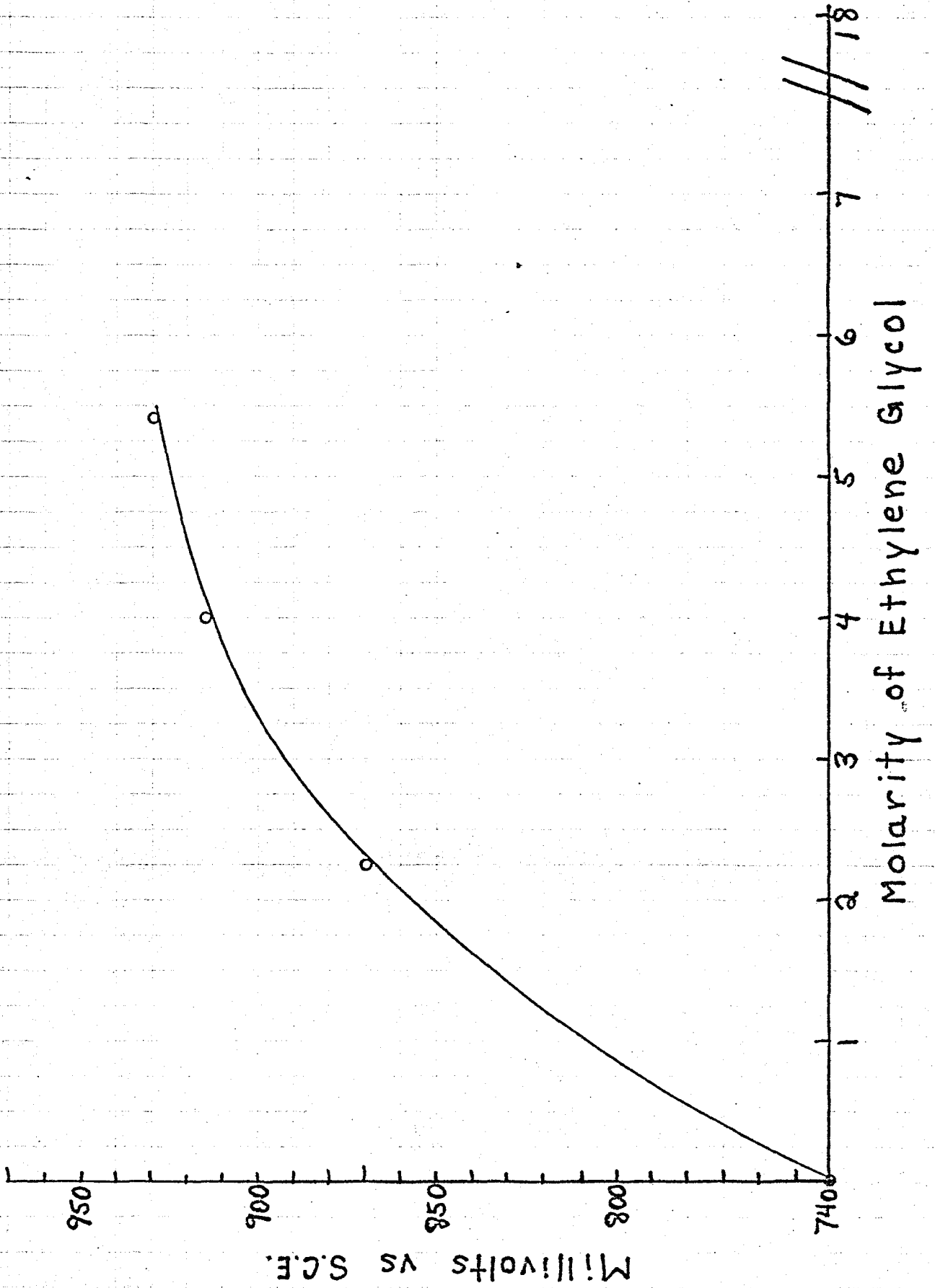
(1) DMAC/0.94 M LiCl 75 ml

(2) DMAC/ 0.94 M LiCl + 10 ml cyclohexane

(3) Solution (2) + 10 ml H<sub>2</sub>O

Figure 4

Decomposition of  $\text{Cl}^-$  in DMAC vs Moles of Ethylene Glycol





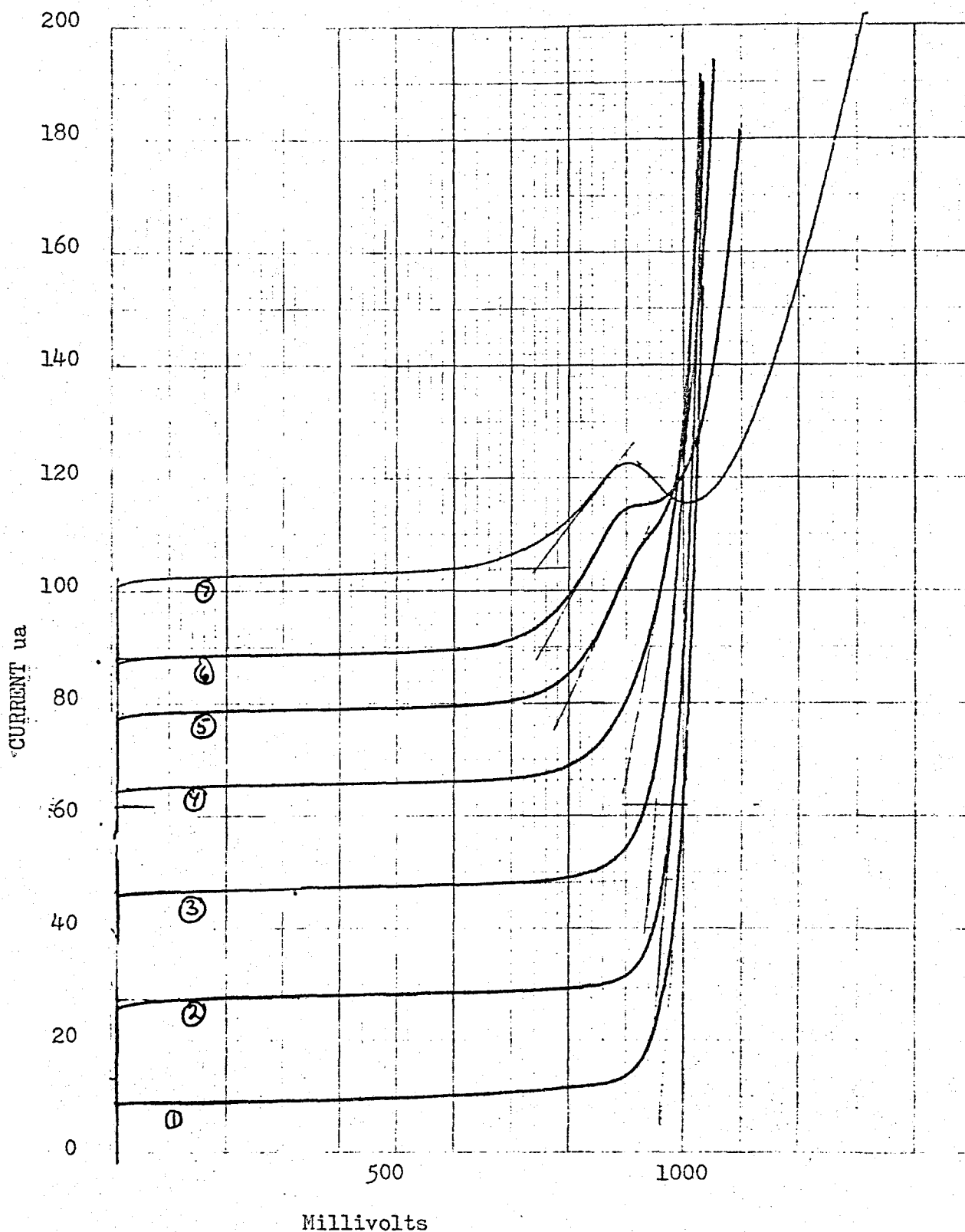


Figure 5. Polarographic waves for 2,6-di-tert-butyl-4methyl

phenol in DMAC/Et(OH)<sub>2</sub> 1 : 1 as water is added

- (1) 70 ml DMAC/Et(OH)<sub>2</sub> 1:1 2% LiCl
- (2) repeat (1)
- (3)  $1.2 \times 10^{-3}$  M 2,6-di-tert-butyl-4-methyl phenol
- (4) - (7) add water in 5ml increments

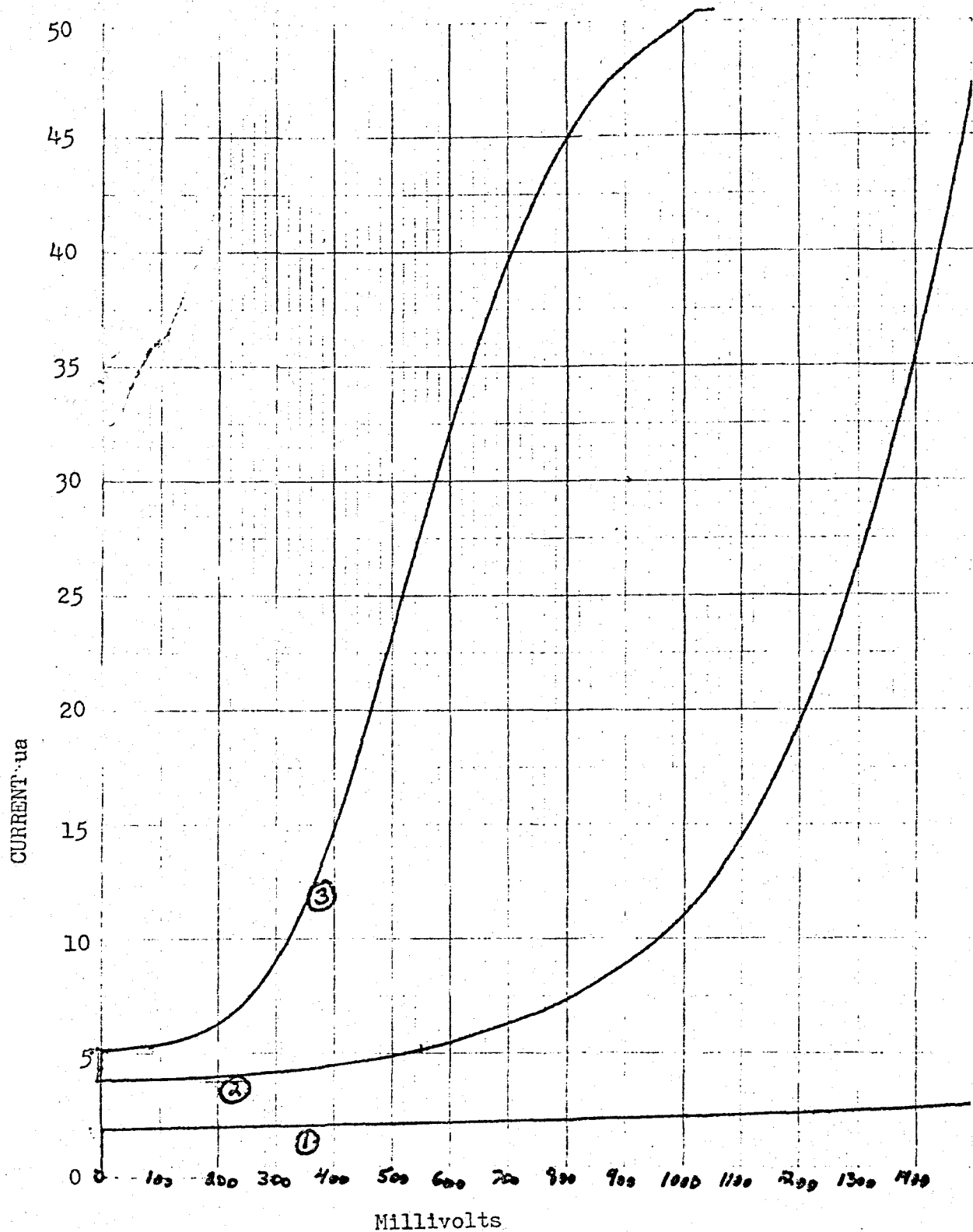


Figure 6. DMAC with Lithium acetate as electrolyte

- (1) DMAC no electrolyte - 50 ml
- (2) DMAC saturated with lithium acetate
- (3) Add 4ml 100 mg./25 ml hydroquinone

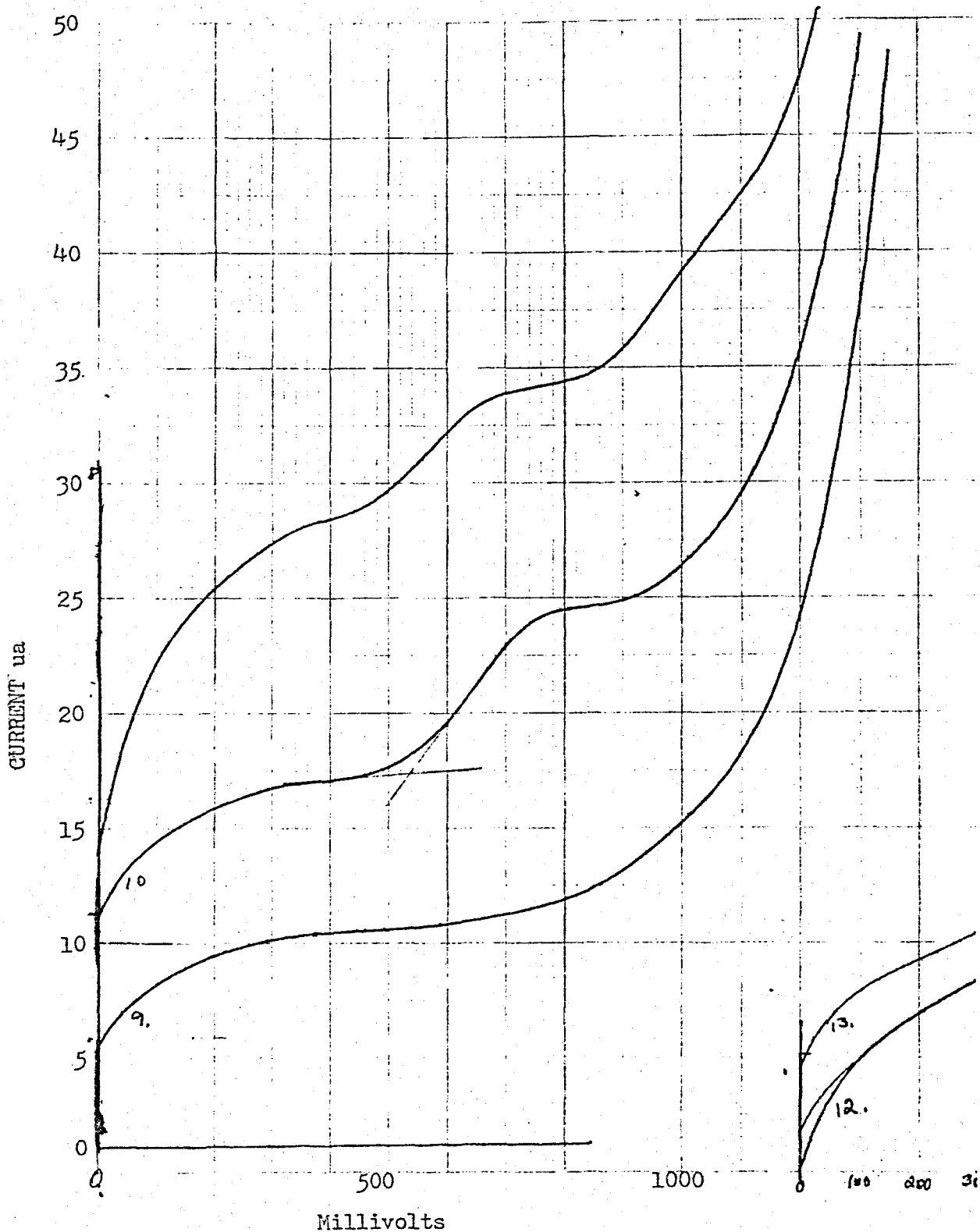


Figure 7. DMAC with Potassium perchlorate electrolyte

- (1) DMAC  $1.3 \times 10^{-2}$  M in  $KClO_4$  5 M in  $H_2O$  55ml total vol.
- (2) Add 1ml 100 mg./25 ml DMAC Hydroquinone
- (3) Add 5ml  $H_2O$

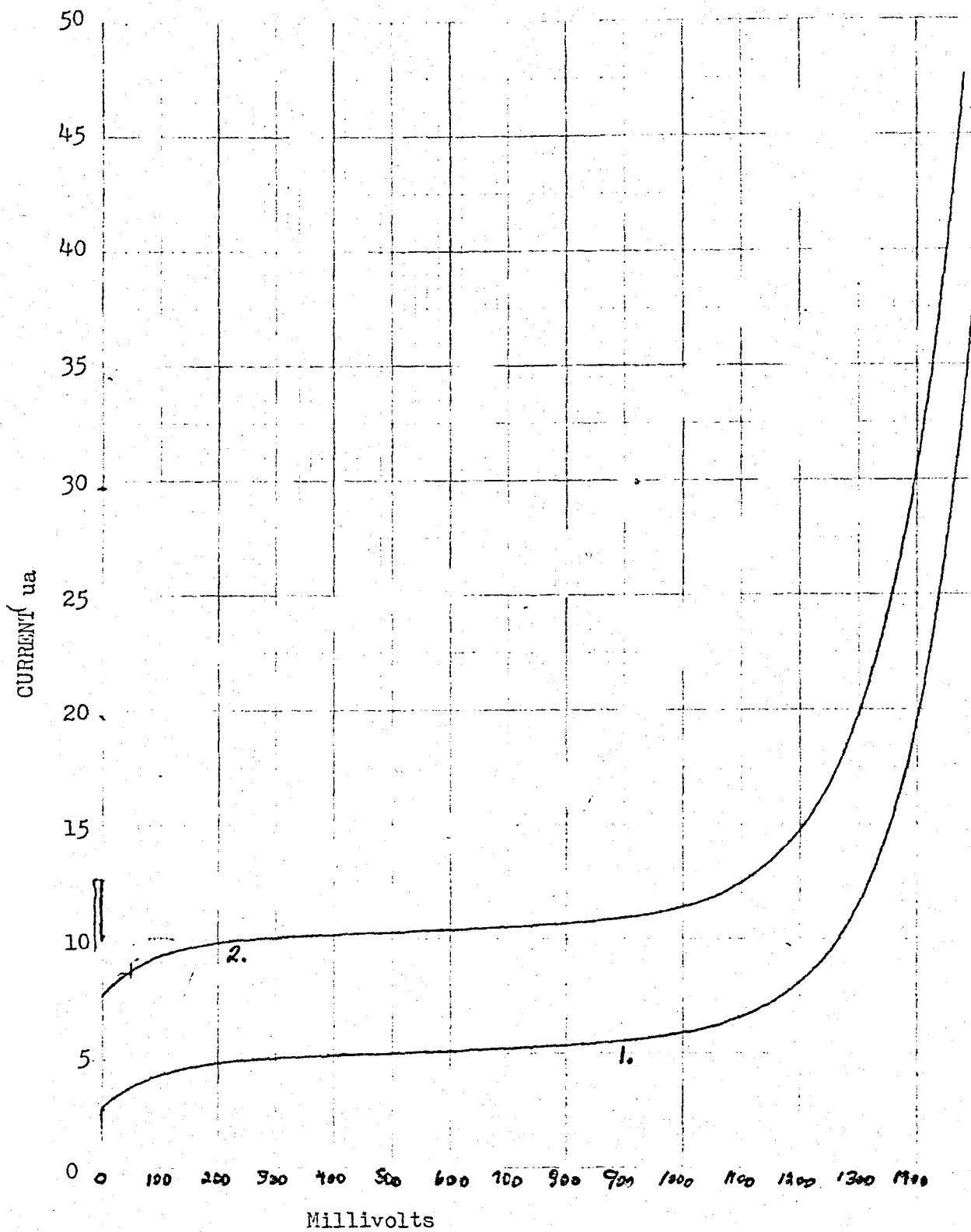


Figure 8. DMAC with Magnesium perchlorate electrolyte

(1) DMAC  $1.2 \times 10^{-2}$  M  $Mg(ClO_4)_2$  total vol. = 65 ml

(2) Add 9 ml.  $MeCl_2$  , 20 ml  $H_2O$

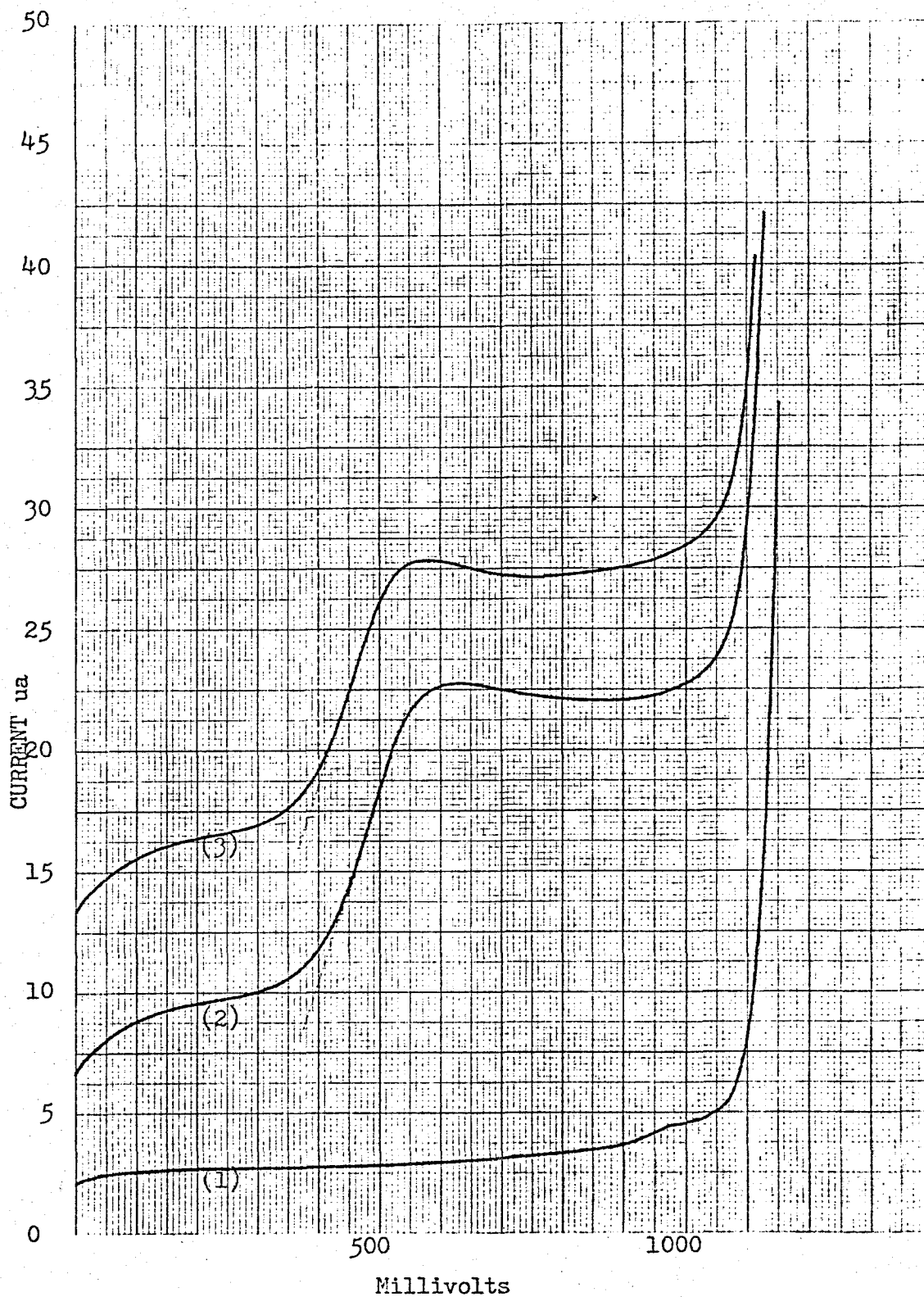


Figure 9. Hydroquinone wave vs water concentration in DMAC

(1) water,  $4.7 \times 10^{-1}$  M LiCl

(2) Add 2 ml 100 mg./25 ml DMAC of Hydroquinone

(3) Repeat scan (2)

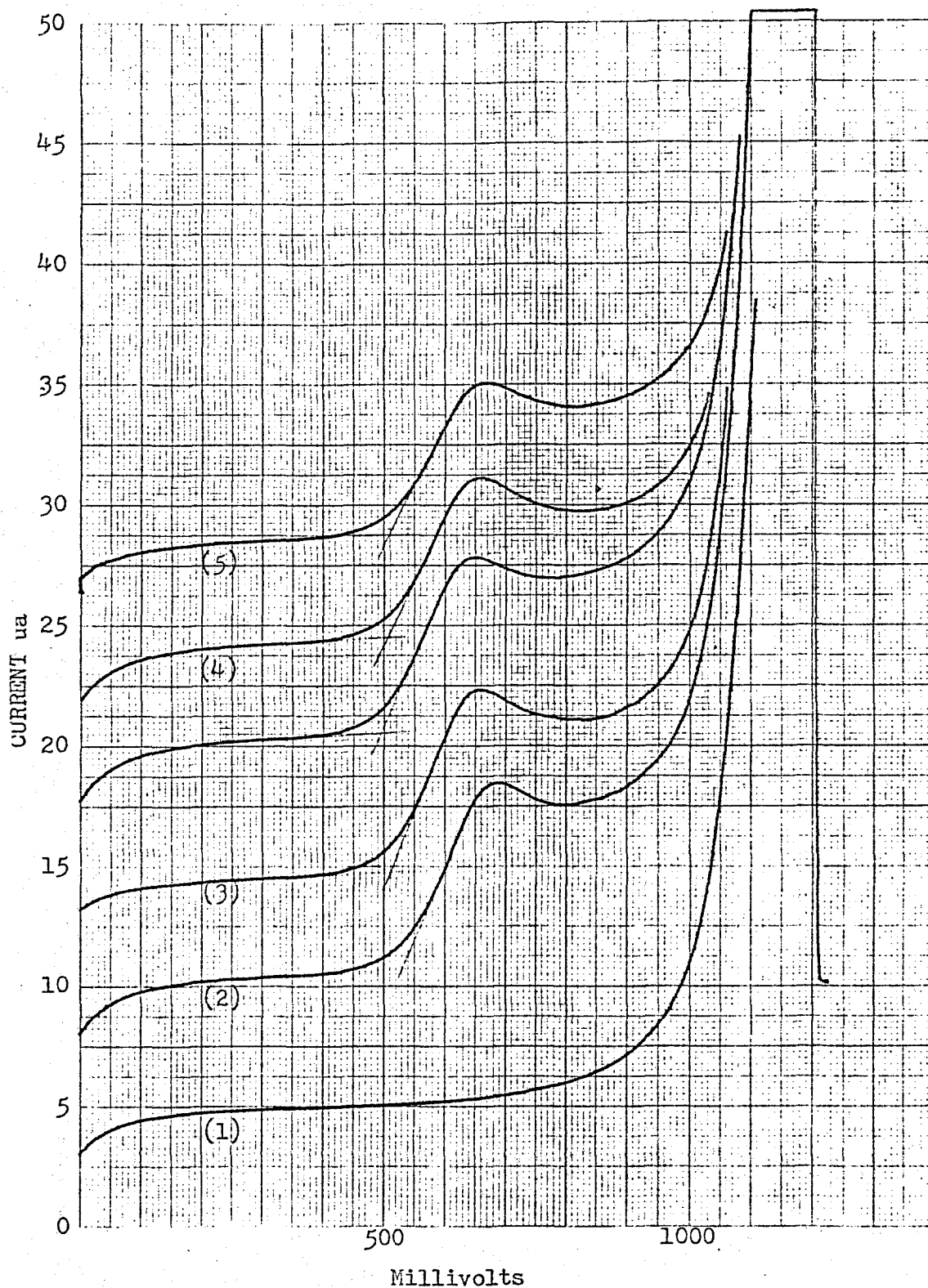


Figure 10. Hydroquinone wave vs water concentration in DMAC

- (1) Solvent DMAC/ $\text{MeCl}_2$ / $\text{H}_2\text{O}$  652/87/260 - 70 ml
- (2) Add 2 ml 100 mg./25 ml DMAC of hydroquinone
- (3) Add 5 ml  $\text{H}_2\text{O}$
- (4) Add 5 ml  $\text{H}_2\text{O}$
- (5) Add 5 ml  $\text{H}_2\text{O}$

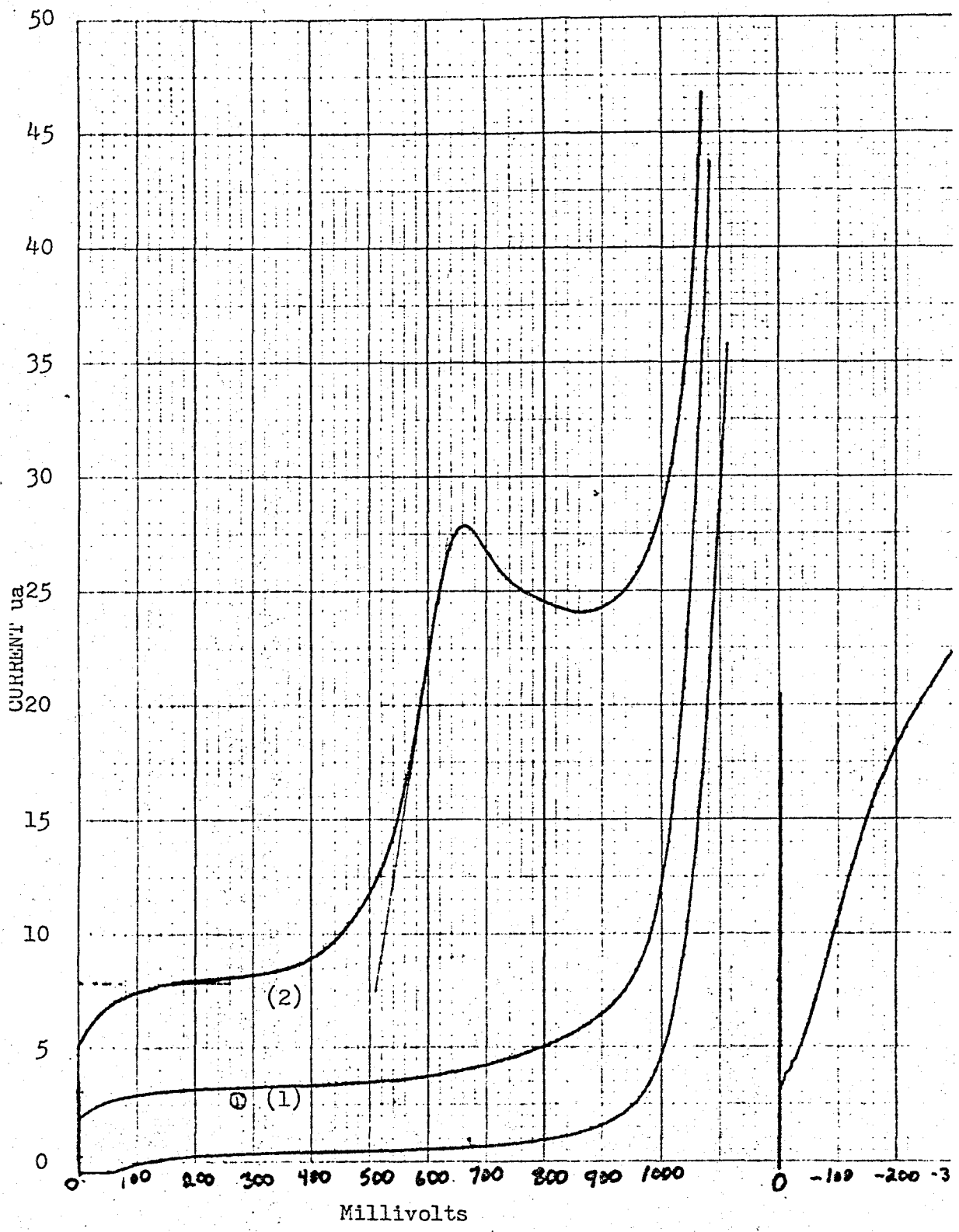


Figure 11. Hydroquinone wave vs water concentration in solvent  
 (1) Solvent  $\text{DMAC}/\text{MeCl}_2/\text{H}_2\text{O}$  75/10/30 - 75 ml  
 (2) Add 5 ml 100 mg./25 ml DMAC of hydroquinone

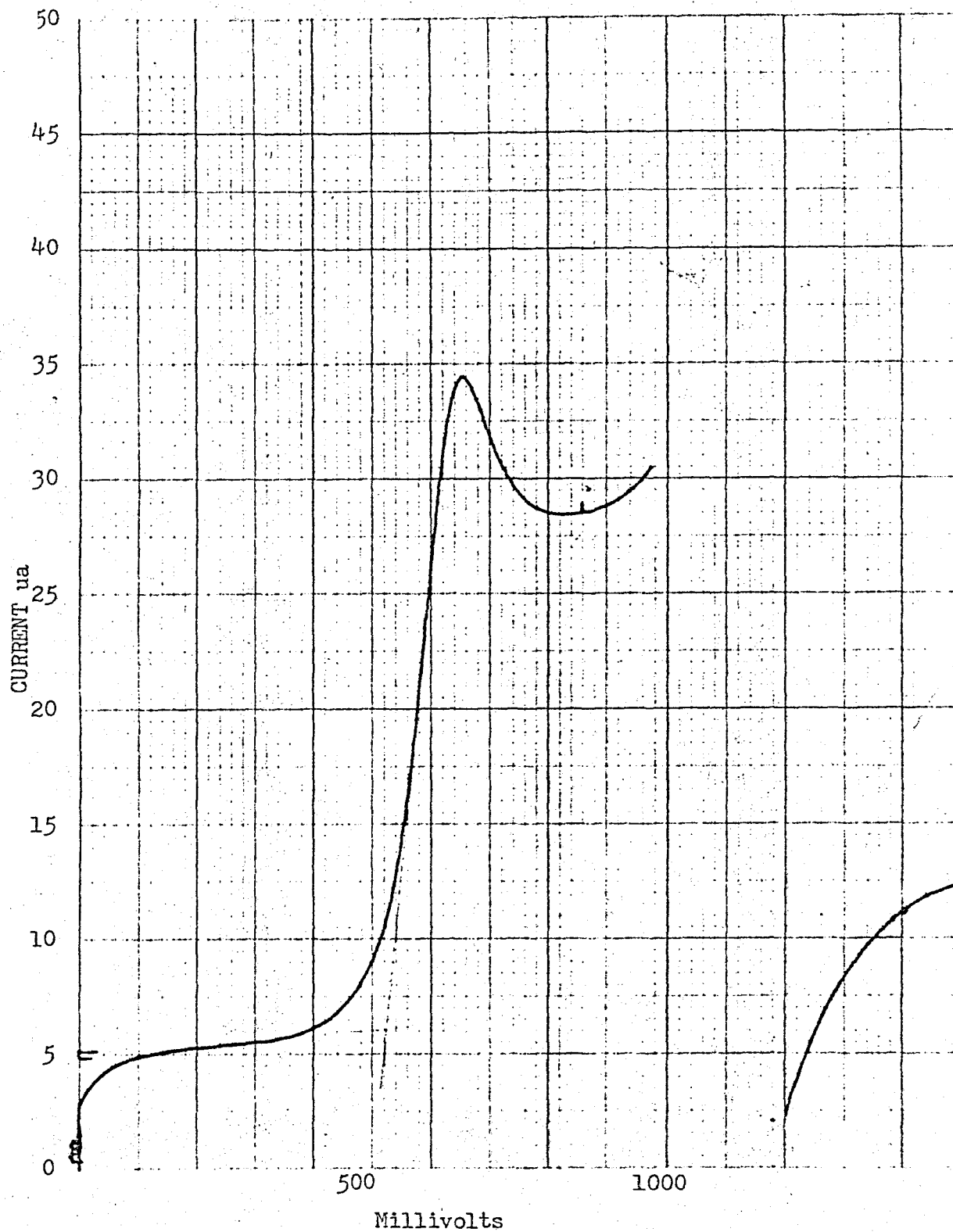


Figure 12. Hydroquinone wave vs water concentration in DMAC

(1) Add 2 ml of 100 mg./25 ml DMAC of hydroquinone to solution (2), figure 11.



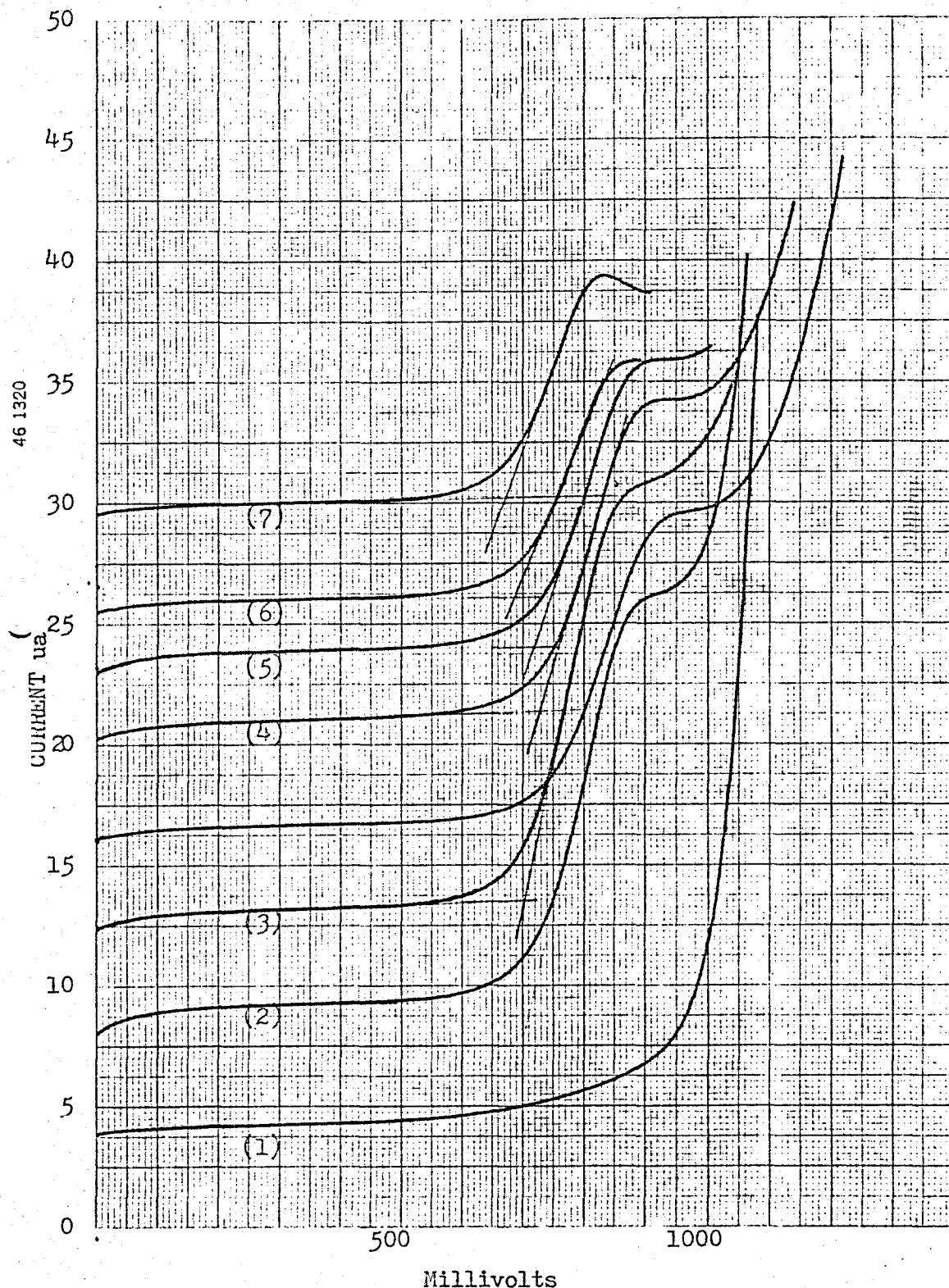


Figure 13. Wave for 2-tert-butyl-4-methyl phenol vs  $H_2O$  in DMAC

- (1) Solvent  $DMAC/MeCl_2/H_2O$ , 652/87/260 - 70 ml
- (2) Add 5 ml 100 mg./25 ml DMAC 2-t-butyl-4-methyl phenol
- (3) Add 5 ml  $H_2O$
- (4) Add 5 ml  $H_2O$
- (5) Add 5 ml  $H_2O$
- (6) Add 10 ml  $H_2O$
- (7) Add 10 ml  $H_2O$

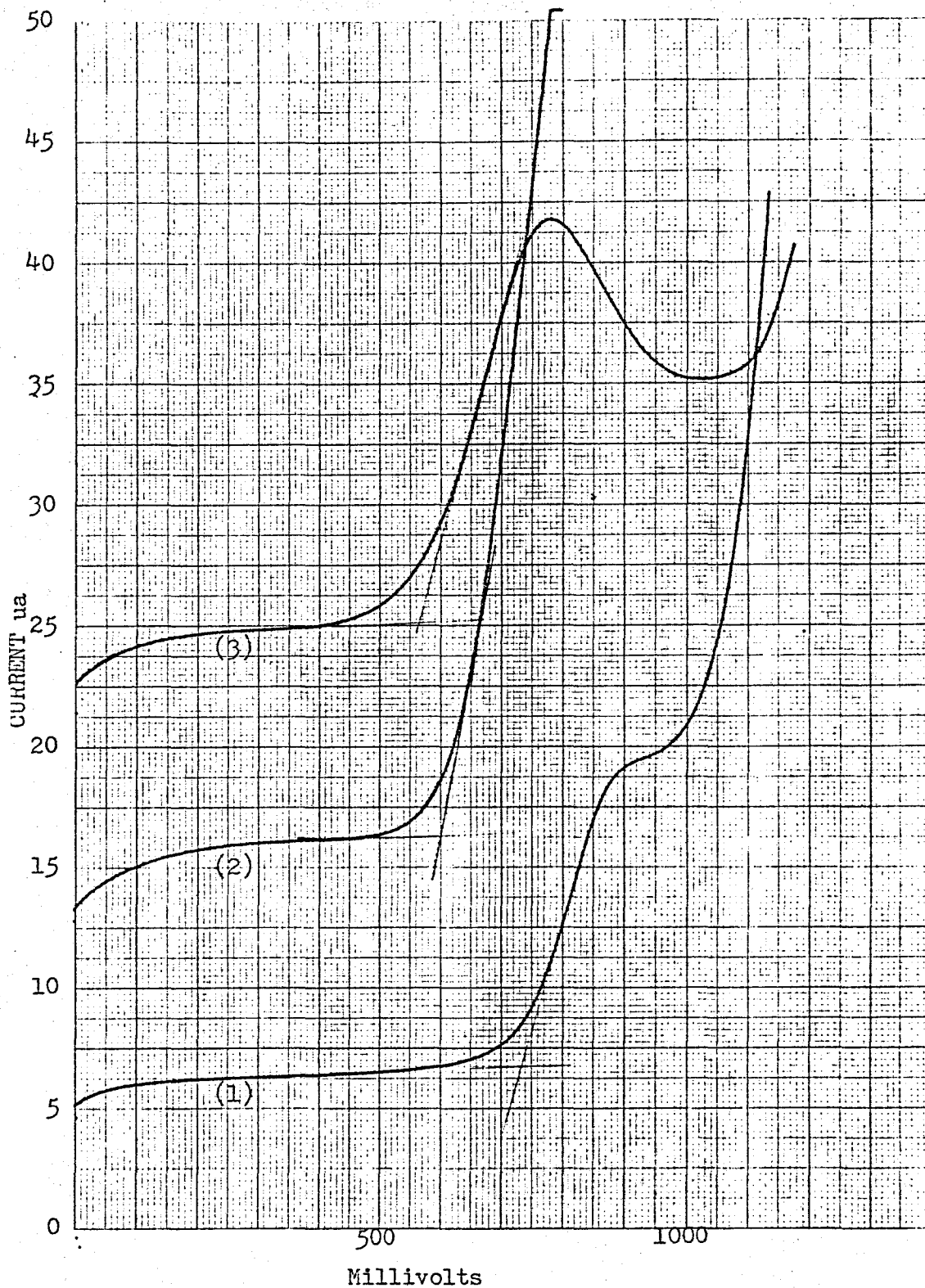


Figure 14. Wave for 2-tert-butyl-4-methyl phenol vs  $H_2O$  in DMAC

- (1) Solvent DMAC/ $MeCl_2$ / $H_2O$  , 652/87/260 - 50 ml  
plus 3 ml 100 mg./25 ml DMAC of 2-tert-butyl-4-methyl phenol
- (2) Add 2 ml of the phenol and 45 ml of  $H_2O$
- (3) Water , 2% LiCl plus 5 ml of the phenol in DMAC

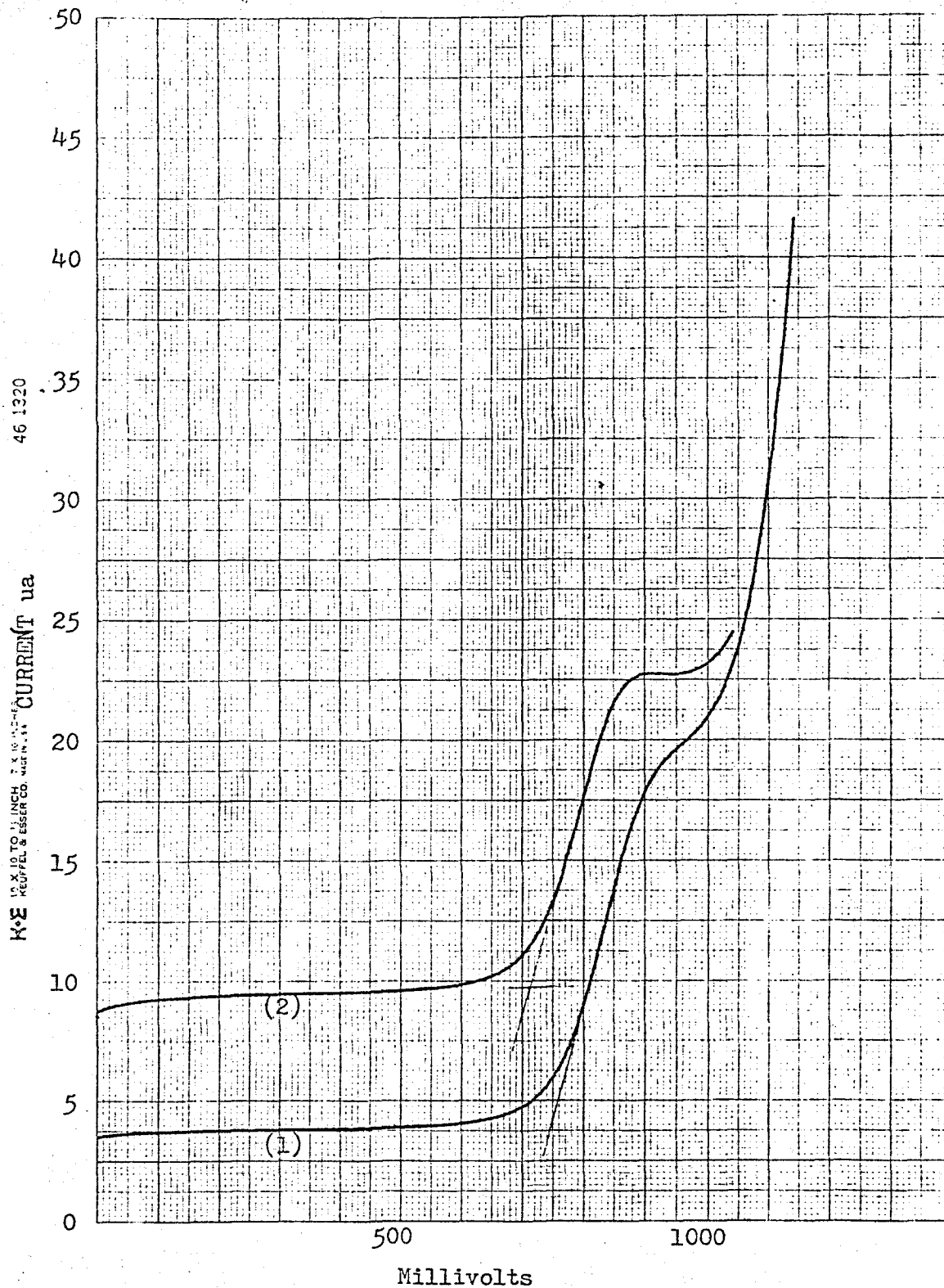


Figure 15. Wave for 2-tert-butyl-4-methyl phenol vs  $H_2O$  in DMAC  
 (1) Solvent  $DMAC/MeCl_2/H_2O$ , 652/87/260 - 70 ml plus  
 5 ml of 100 mg./25 ml DMAC of 2-tert-butyl-4-  
 methyl phenol  
 (2) Add 5 ml of  $H_2O$  to (1)

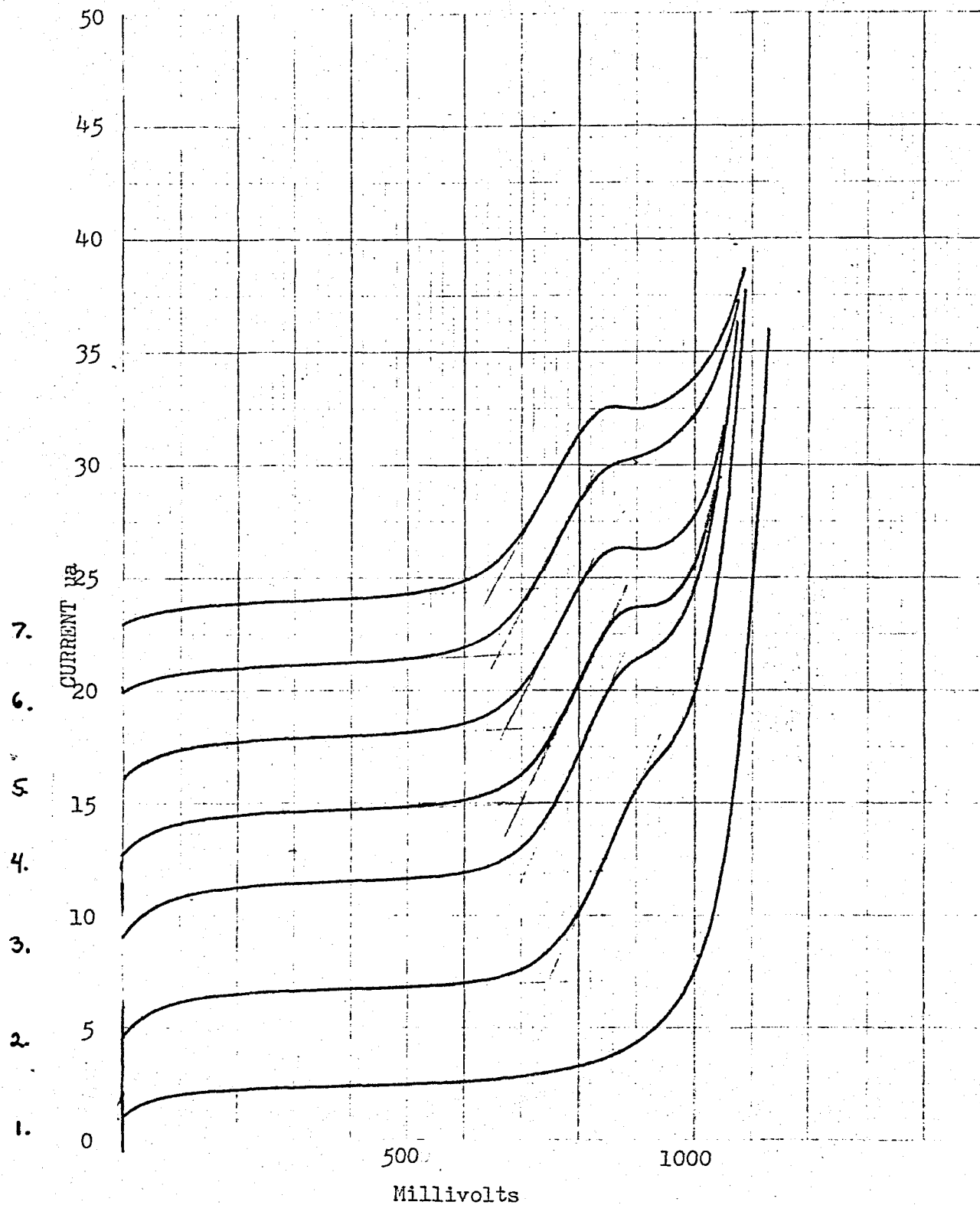


Figure 16. Waves for 2,6-di-tert-butyl-4-methyl phenol vs  $H_2O$  in DMAC

- (1) Solvent  $DMAC/MeCl_2/H_2O$  , 652/87/260 - 75 ml
- (2) Add 5ml of 100 mg./25 ml DMAC of 2,6-di-tert-butyl-4-methyl phenol
- (3) Add 5 ml of  $H_2O$  to (2)
- (4) Add 5 ml of  $H_2O$  to (3)
- (5) Add 5 ml of  $H_2O$  to (4)
- (6) Add 5 ml of  $H_2O$  to (5)
- (7) Add 5 ml of  $H_2O$  to (6)

Figure 17

$E_{init}$  vs  $1/M \times 10^2$  for Hydroquinone

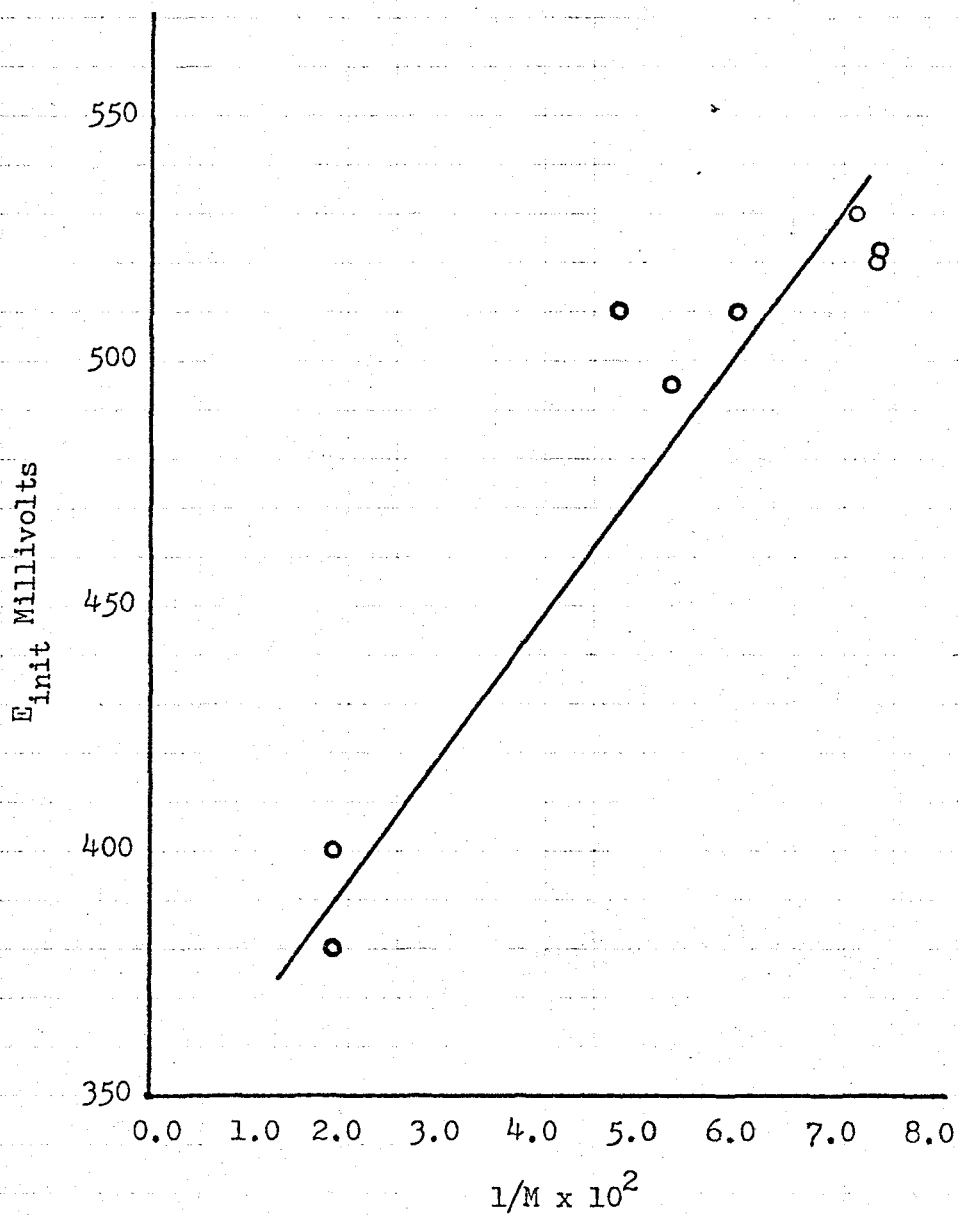


Figure 18.

$E_{init}$  vs  $1/M \times 10^2$  for 2-tert-butyl-4-methyl phenol

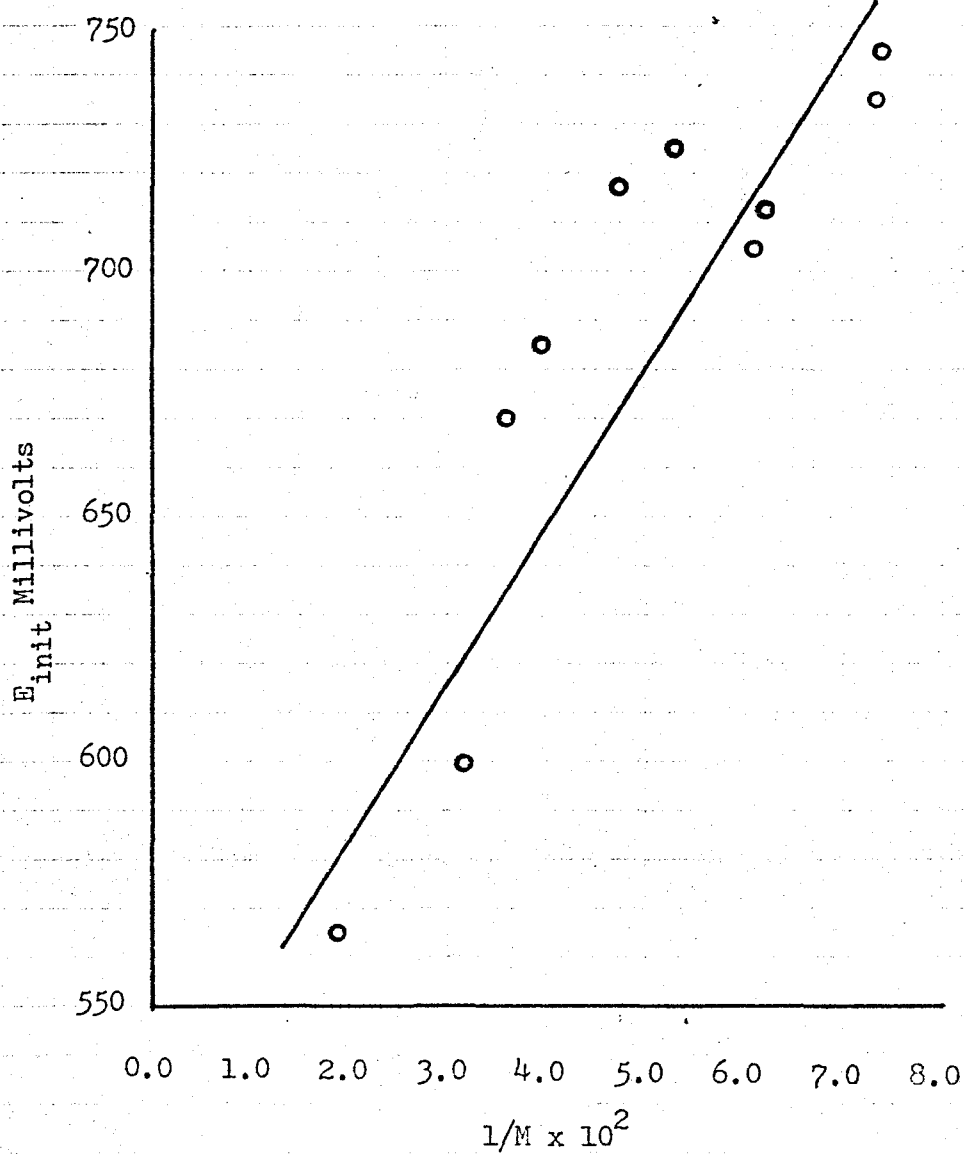
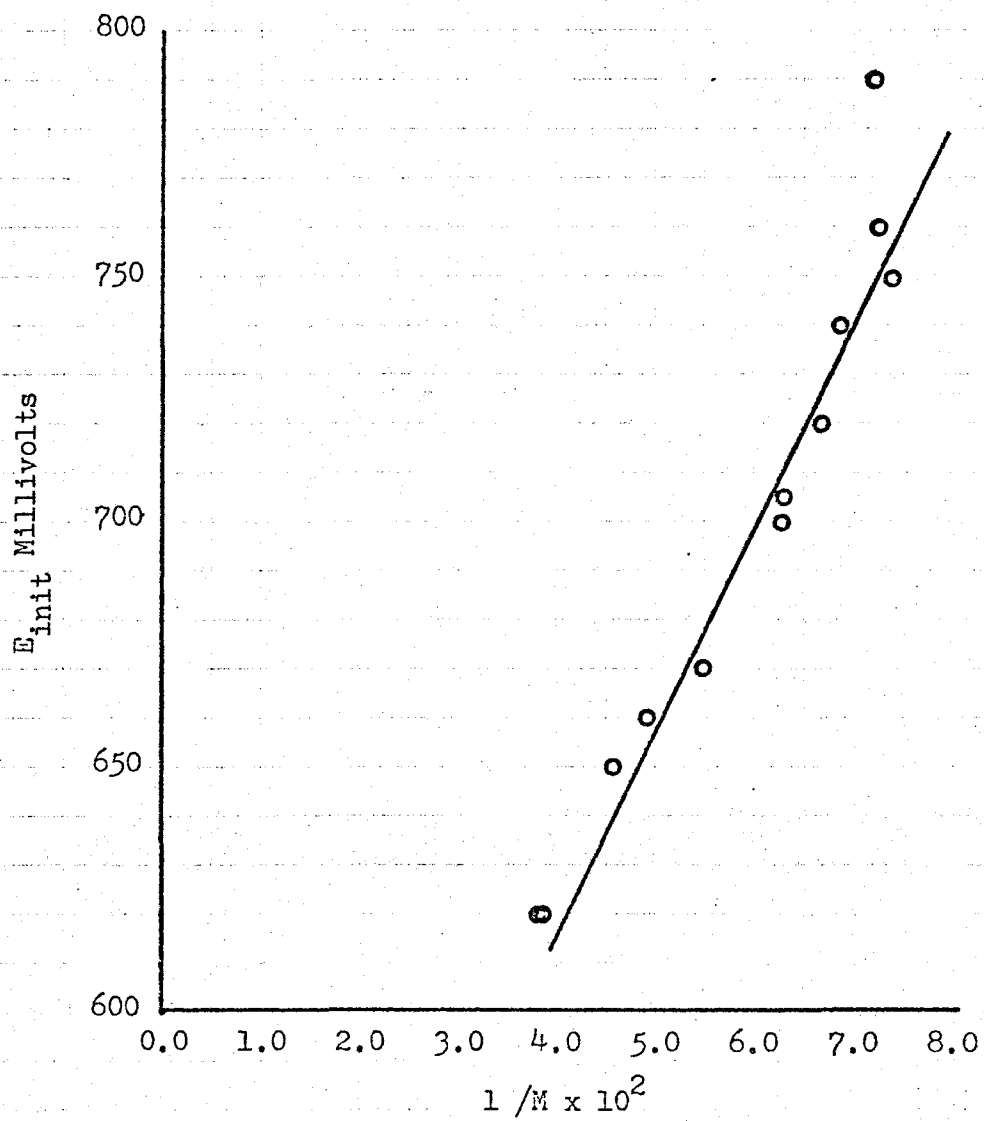


Figure 19.

$E_{init}$  vs  $1/M \times 10^2$  for 2,6 di-tert-butyl-  
4-methyl phenol



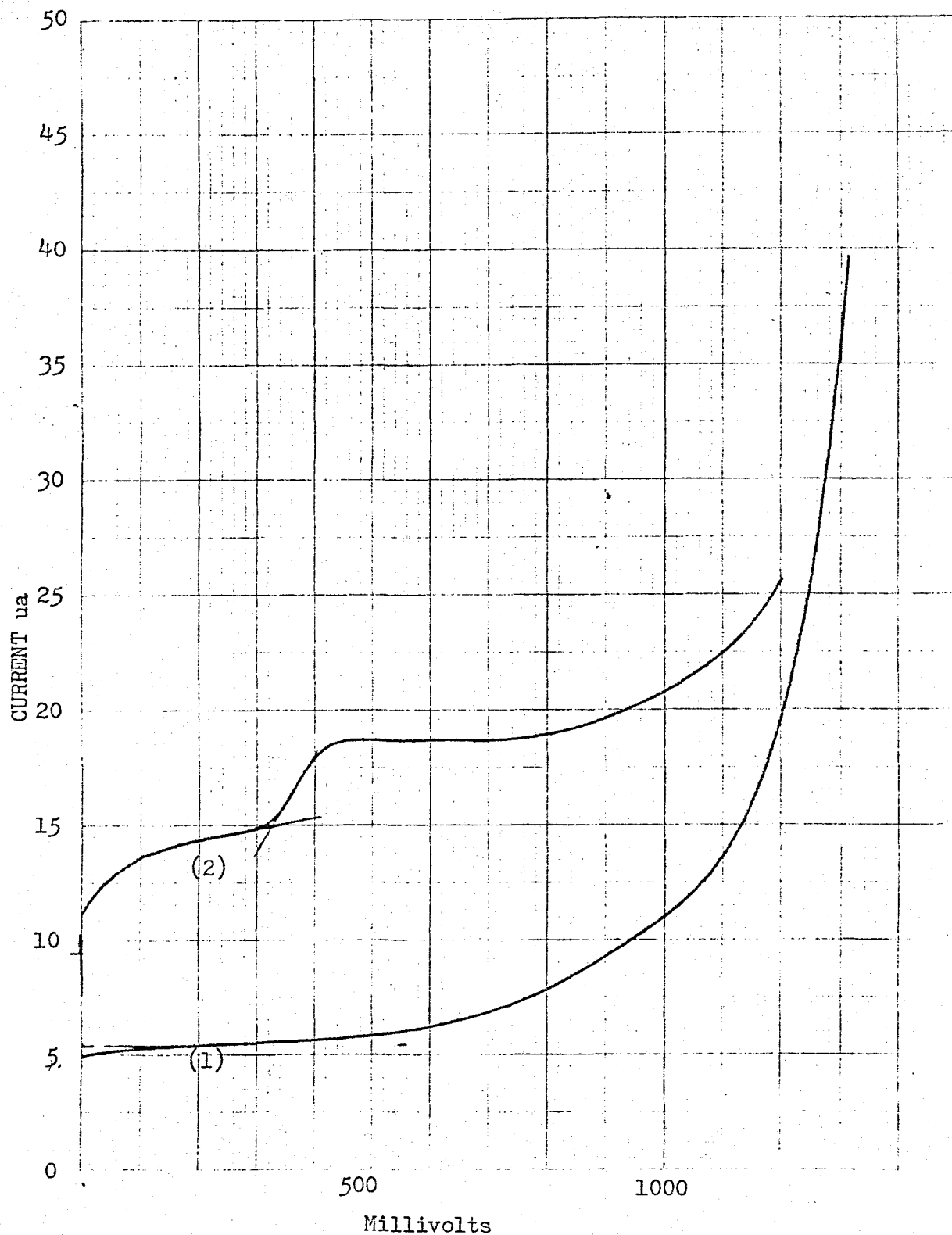


Figure 20. Wave for 2,6-bis (2'-hydroxy-3'-tert-butyl-5'-methyl benzyl)-p-cresol

(1) Solvent DMAC/H<sub>2</sub>O 500/170 Mg(ClO<sub>4</sub>)<sub>2</sub> 0.10 M - 75 ml

(2) Add 5ml of compound 100 mg./25 ml of DMAC



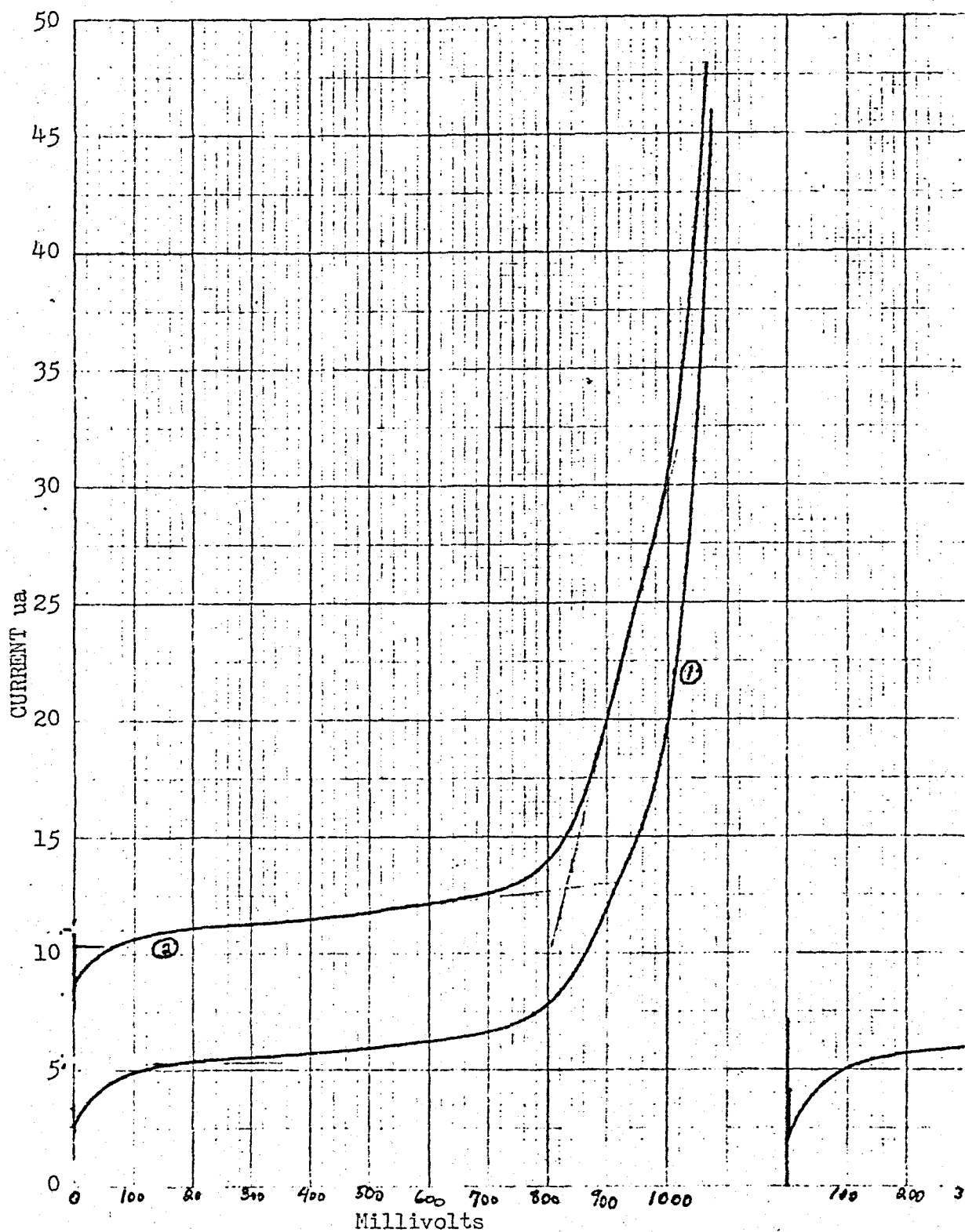


Figure 21. Wave for 2,2'-methylene-bis-(4-ethyl-6-tert-butyl phenol)  
 (1) Solvent DMAC/MeCl<sub>2</sub>/H<sub>2</sub>O 652/87/260 LiCl 0.44M - 75 ml  
 (2) Add 5 ml of compound 100 mg./25 ml DMAC

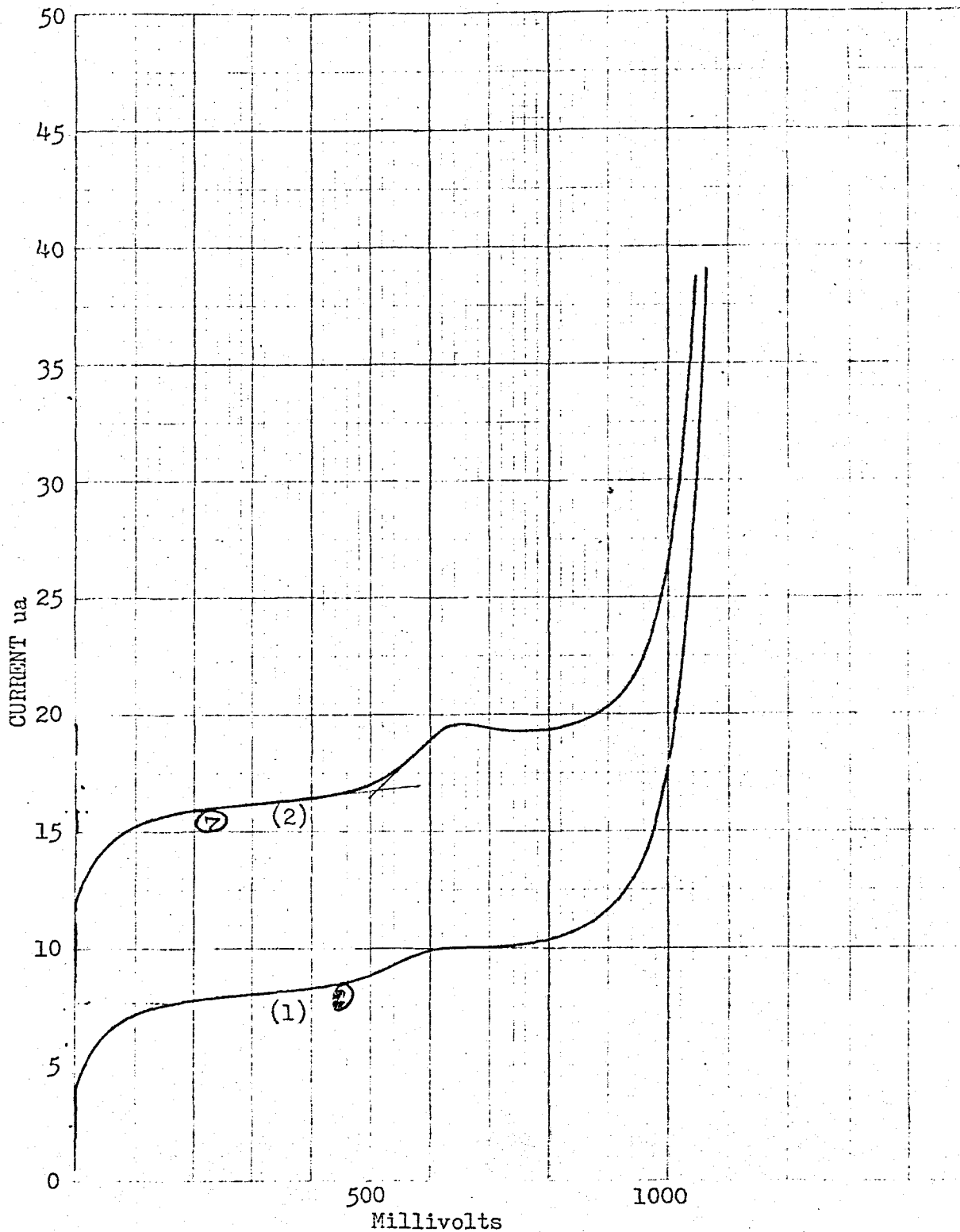


Figure 22. Wave for Irganox 565 structure unknown

(1) Add 5 ml of compound 100 mg./25 ml DMAC to solvent employed in Figure 21.

(2) Add 5 ml of compound to (1)

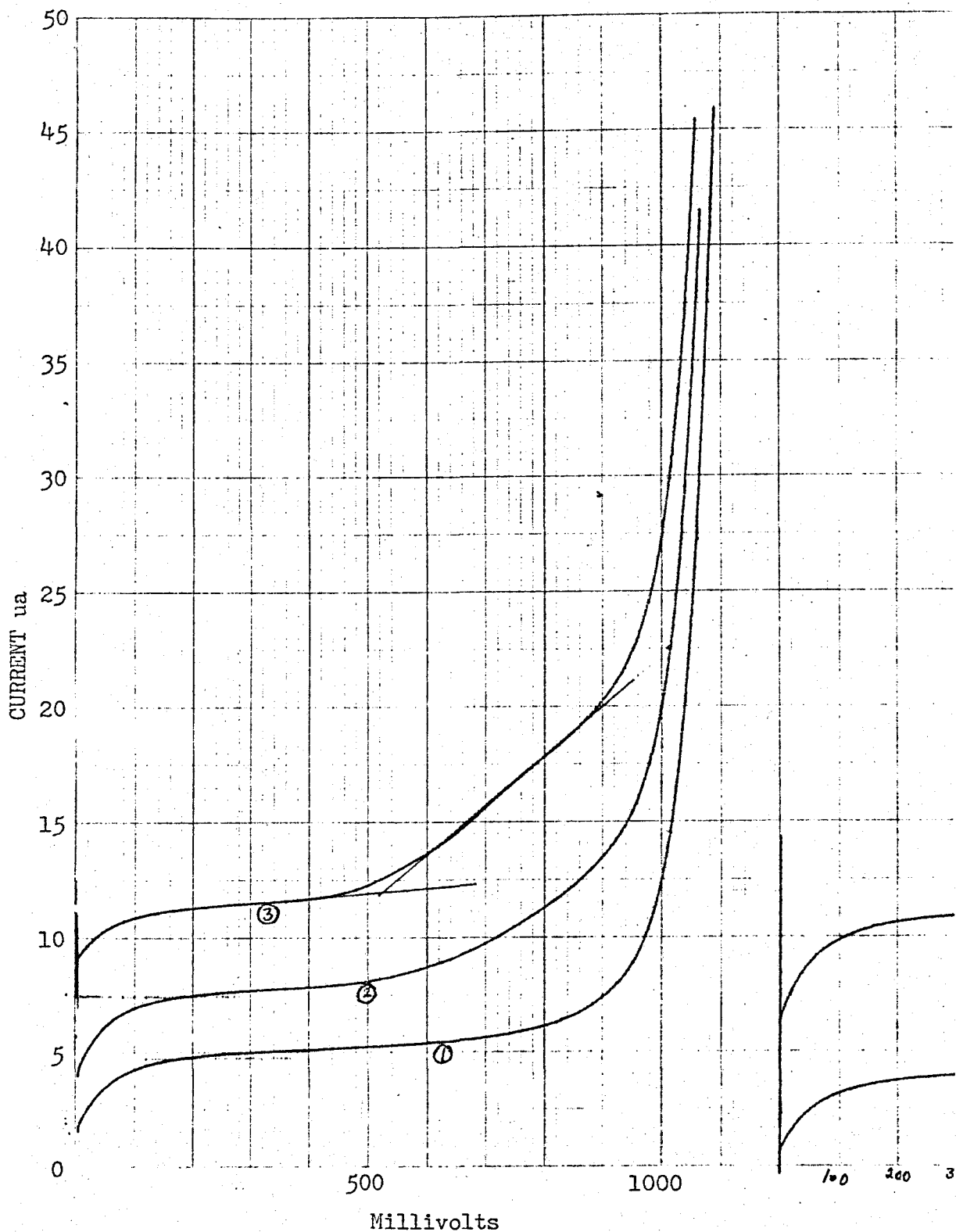


Figure 23. Wave for 4 hydroxy-3,5-di tert butyl benzyl dimethyl amine

- (1) Solvent  $\text{DMAC}/\text{MeCl}_2/\text{H}_2\text{O}$  652/87/260 LiCl 0.44 M - 75 ml
- (2) Add 5 ml of compound 100 mg./25 ml of DMAC
- (3) Repeat addition of compound

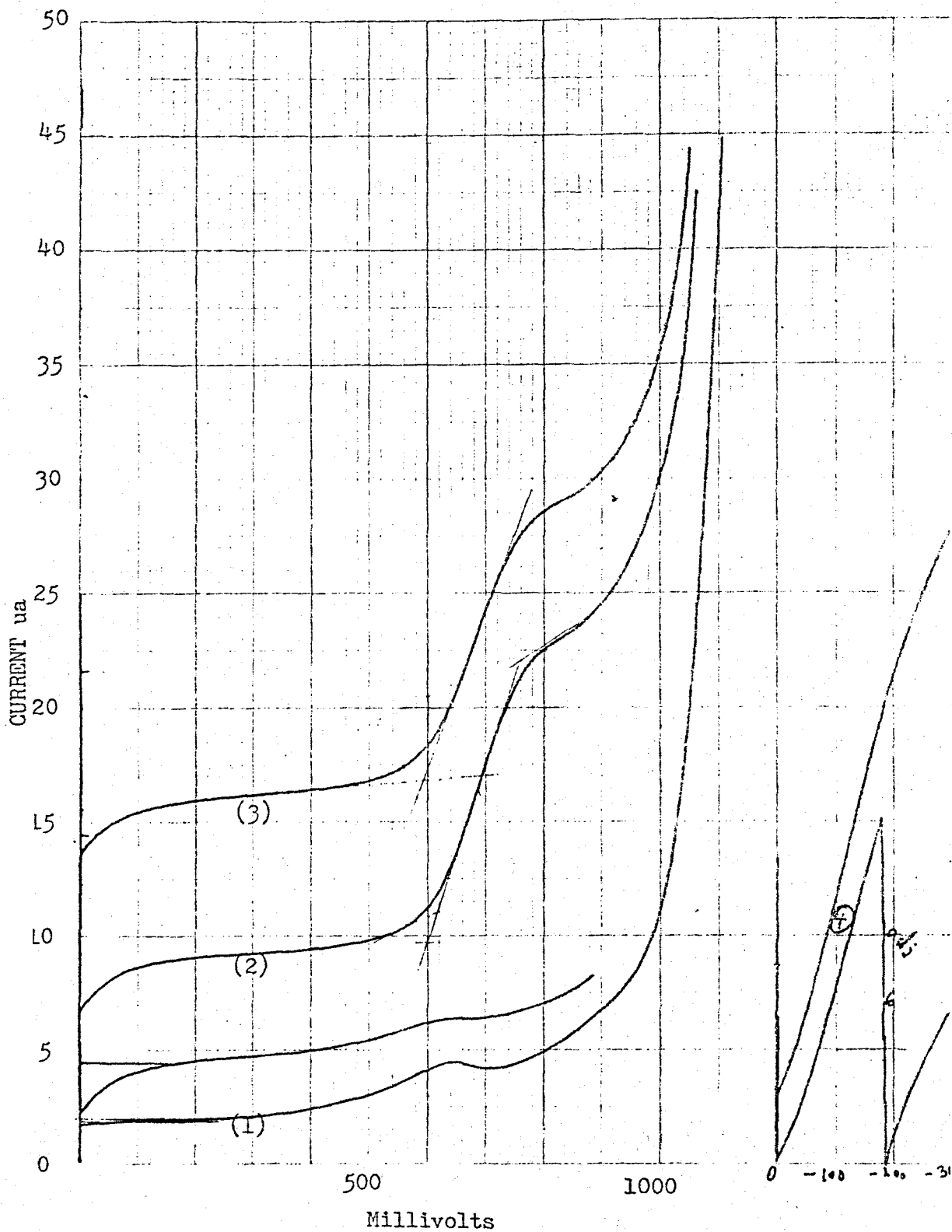


Figure 24. Wave for 4,4' thio-bis (6 tert butyl-m-cresol)

- (1) Solvent DMAC/MeCl<sub>2</sub>/H<sub>2</sub>O 652/87/260 LiCl 0.44 M - 75 ml
- (2) Add 5 ml of compound 100 mg./25 ml of DMAC
- (3) Repeat scan

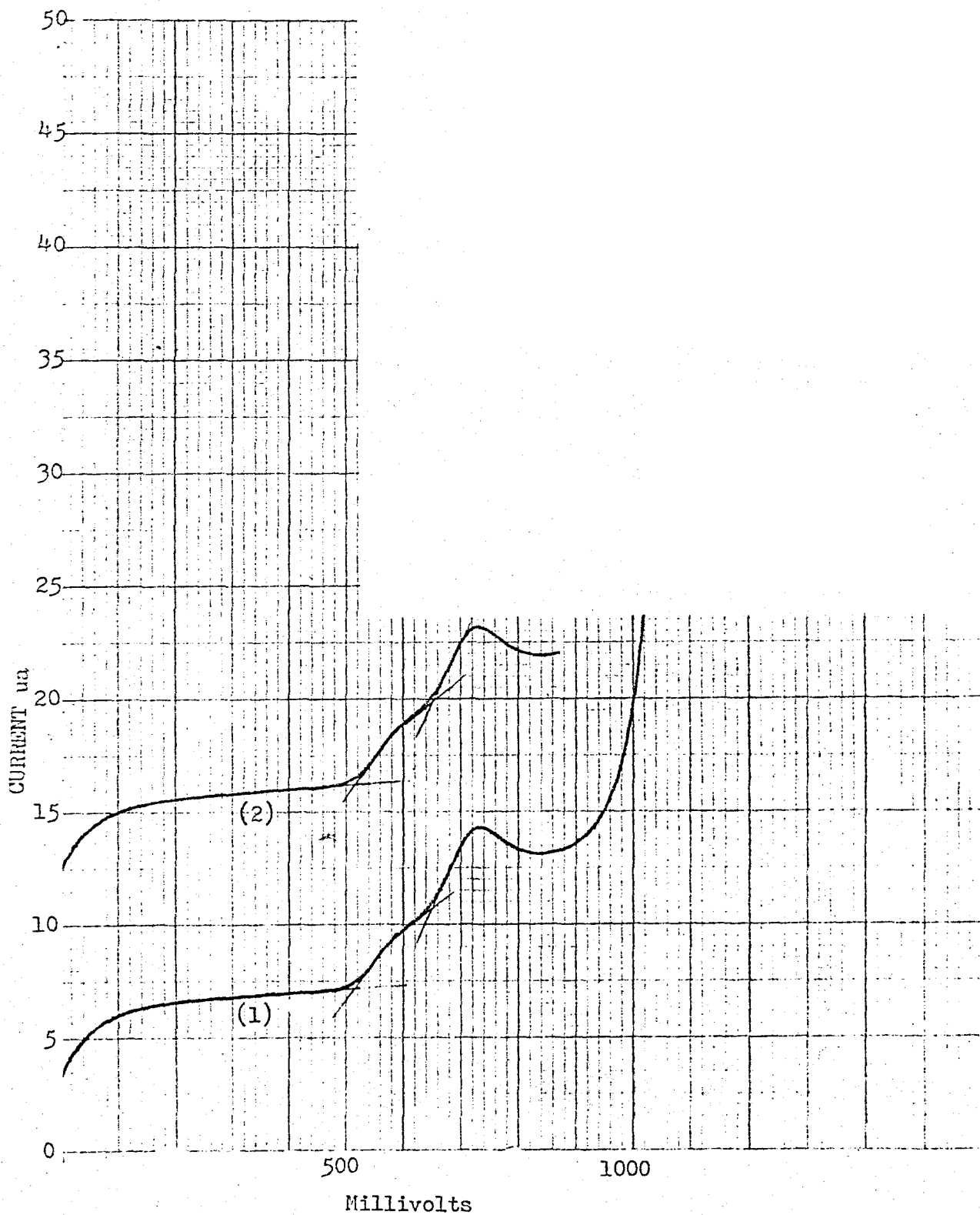


Figure 25. Wave for 1,1-thio-bis (2-hydroxy naphthalene)

(1) 5 ml of compound 100 mg./25 ml of DMAC added to 75 ml of  
DMAC/MeCl<sub>2</sub>/H<sub>2</sub>O 652/87/260

(2) Repeat scan to check for double wave

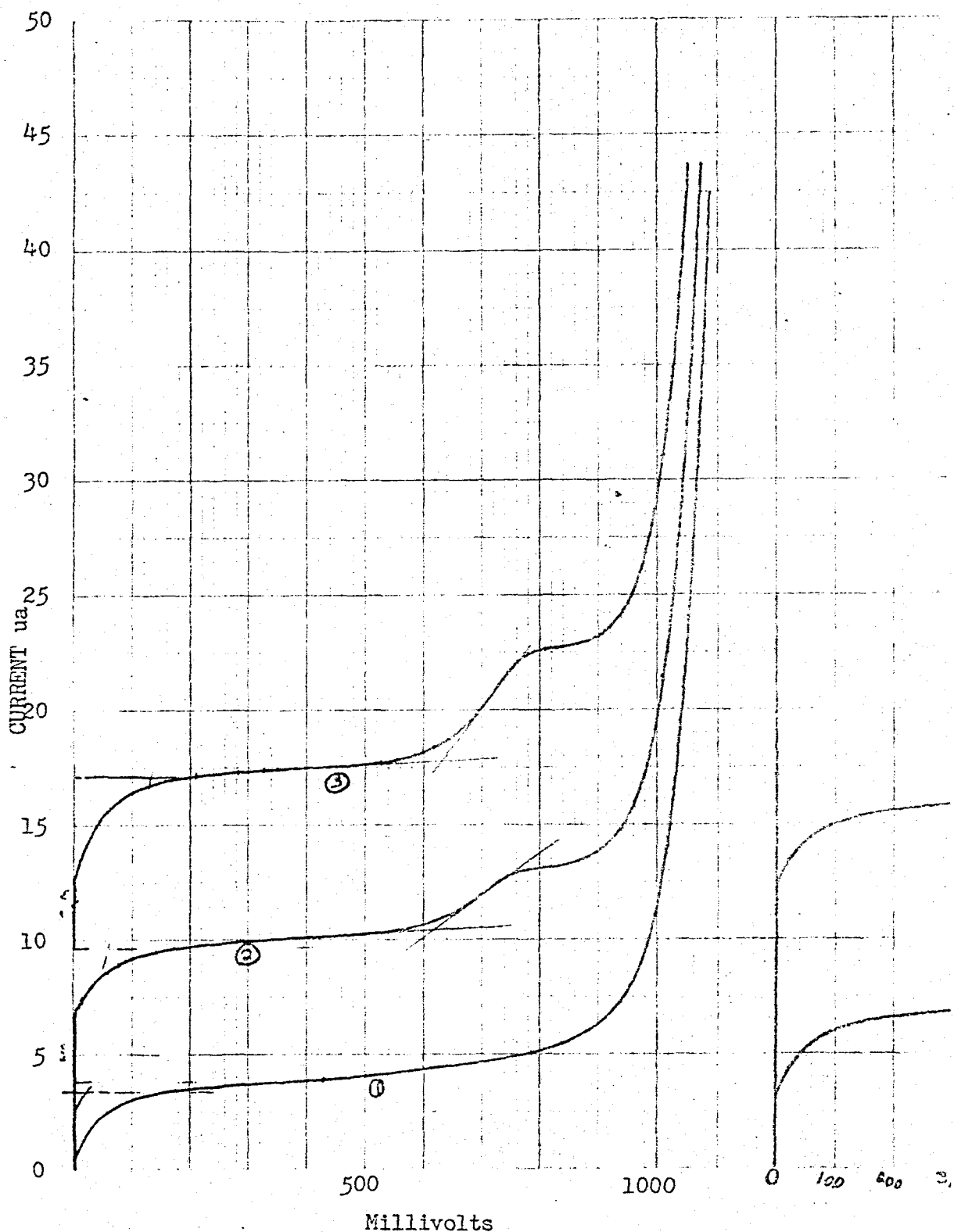


Figure 26. Wave for p-hydroxy stearanilide

- (1) Solvent DMAC/MeCl<sub>2</sub>/H<sub>2</sub>O 652/87/260 LiCl 0.44 M - 75 ml
- (2) Add 5 ml of compound 100 mg./25 ml of DMAC
- (3) Add 5 ml of compound 100 mg./25 ml of DMAC

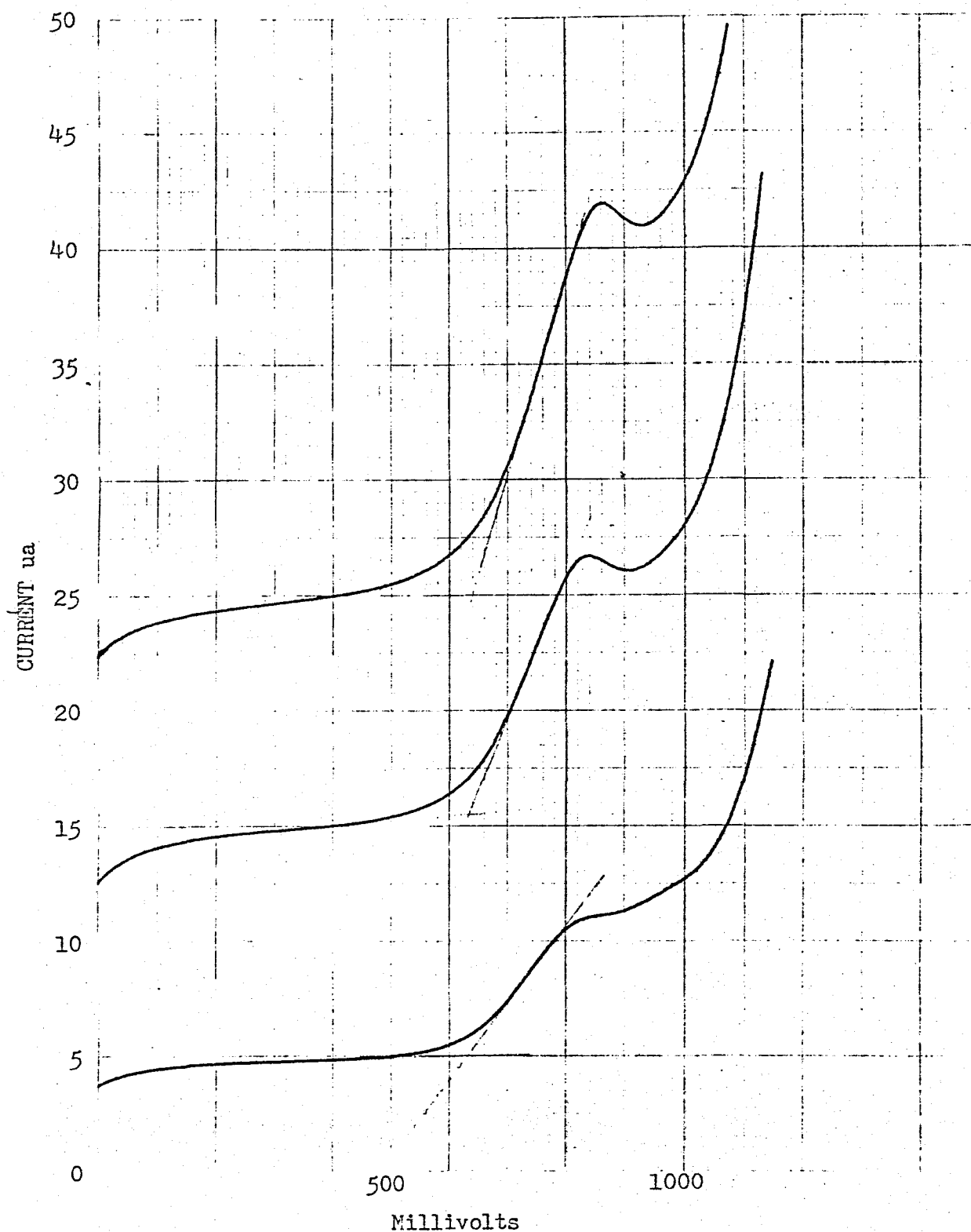


Figure 27. Effect of scan rate on  $E_{init}$  for 2,6 di tert butyl 4 methyl phenol

- (1) Scan at 2 mv/sec  $E_{init} = 630$
- (2) Scan at 10 mv/sec  $E_{init} = 637$
- (3) Scan at 20 mv/sec  $E_{init} = 647$

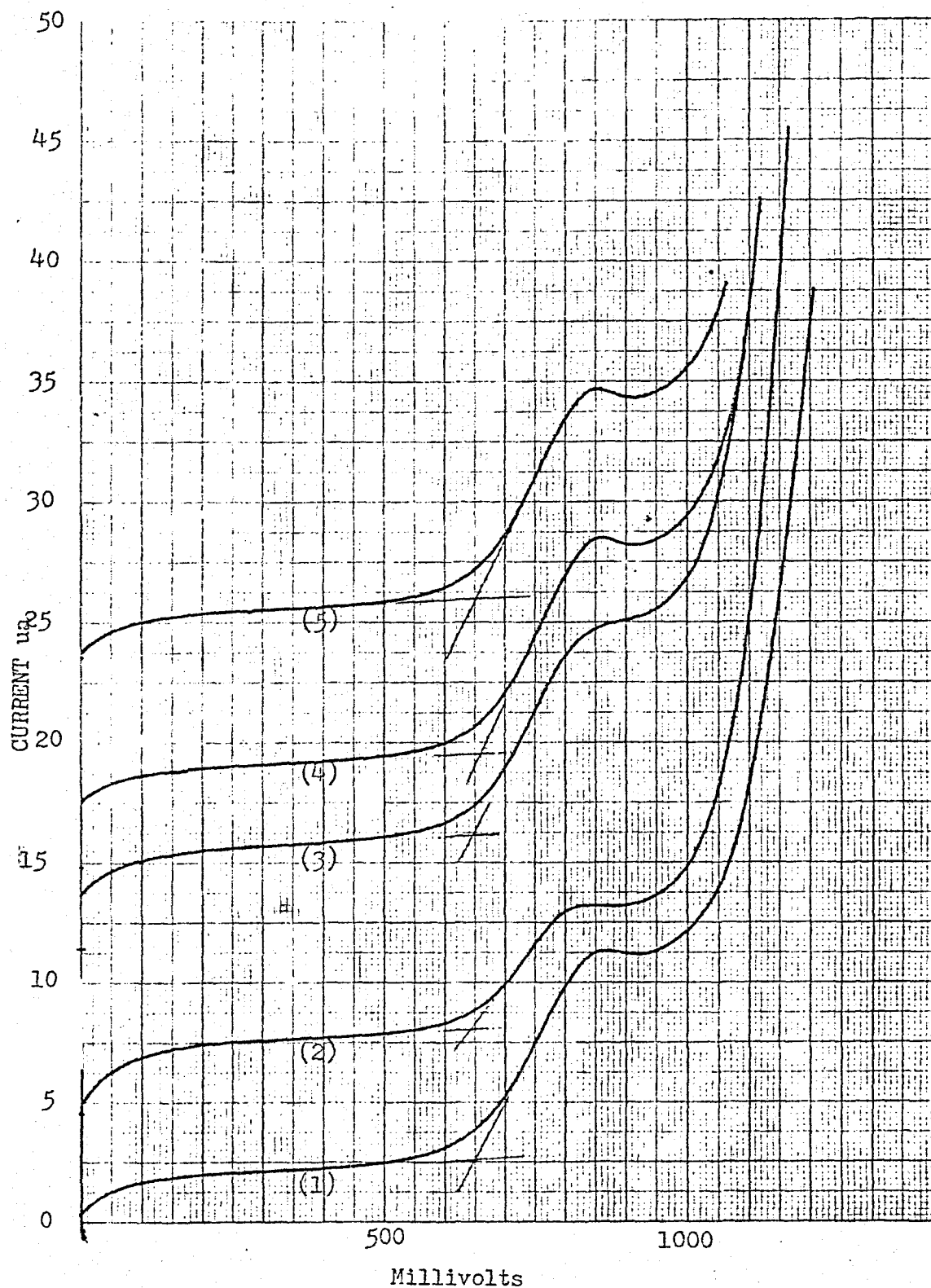


Figure 28. Study of effect of electrode changes on  $E_{\text{init}}$

- (1) Wipe electrode with tissue before scan
- (2) Only platinum tip of electrode dipping in solvent four cm. between electrodes
- (3) Platinum tip of working electrode 1.5 cm. from reference electrode
- (4) Working electrode held at 1150 mv before scan
- (5) Soaked reference electrode in DMAC before scan



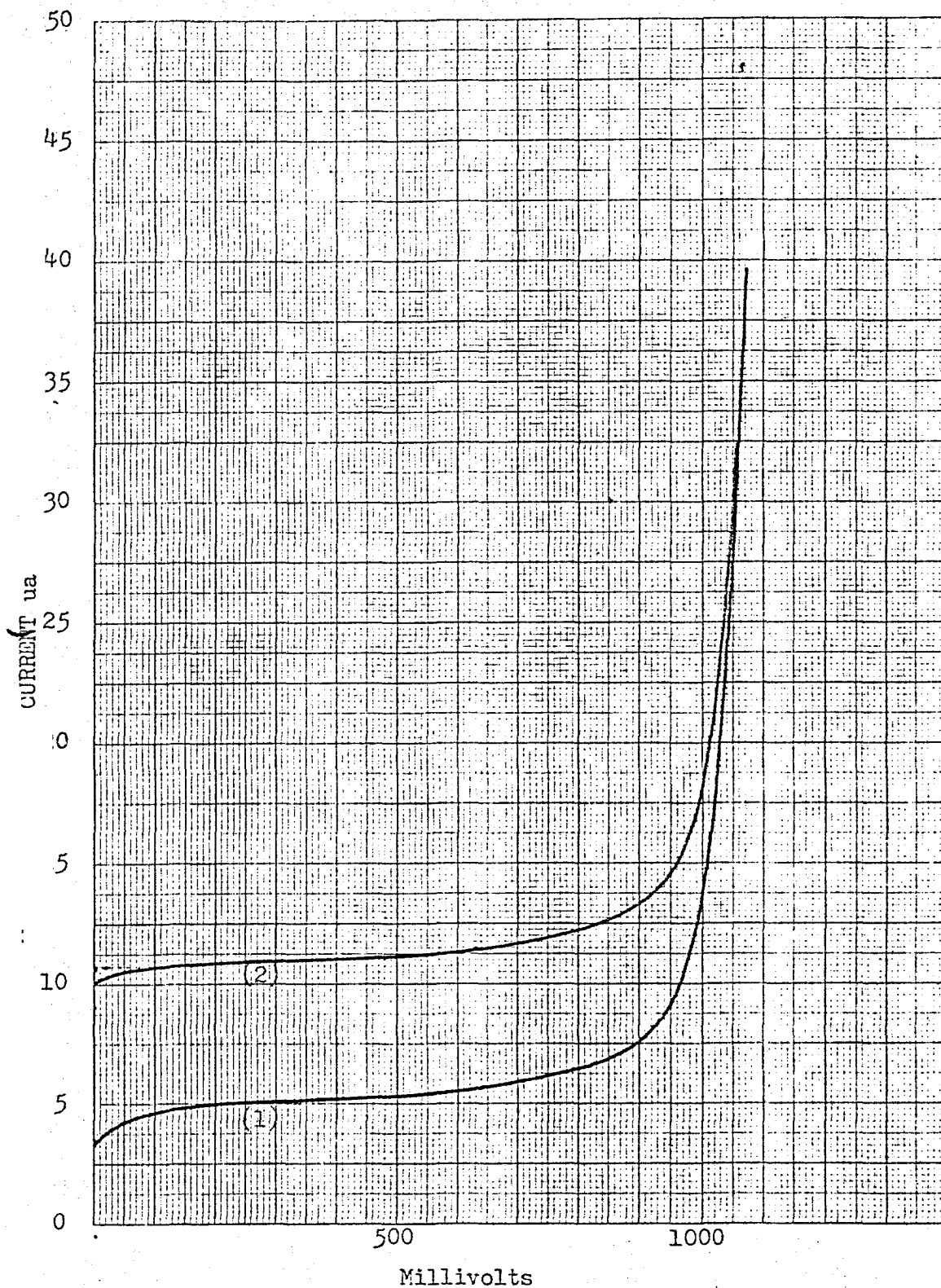


Figure 29. Comparison of two reference electrodes

- (1) Electrode # 1 scan at 5 mv/sec solvent -  
DMAC/MeCl<sub>2</sub>/H<sub>2</sub>O 652/87/260
- (2) Electrode # 2 same conditions as (1)