ELECTROPLATING OF POLYMETHACRYLATE

by

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I. INTRODUCTION

The development of new types and higher quality
steels, coppers, ceramics, and other similar materi-
als to meet severe material problems in industry,
even though still progressing, seems to be integra-
ting its interests with polymeric materials of
greater resistance to environmental conditions. Po-
lymer application in coatings is on the increase,
with rubber, polyethylene, polyvinylchloride and
fluoride coatings demonstrating great durability
against various weather and corrosion conditions.
The polymer family, with its thousands of various
polymer combinations, exhibits most of the physical
properties of all substances known to man. It may
generally be said that for any corrosion or electri-
cal insulation or abrasive resistance or structural
problem, there is a suitable polymer which will meet
job specifications. If it were possible to coat a
substance with any one of many polymers, the final
product would be limited in neither a physical or
chemical manner.

The problem of inducing a polymer to form on a

surface from an emulsion is one on which little information is available. From analogy which may be drawn between rubber and emulsions similar to latex, it is inferred that the mechanism is one of neutralizing ionic charges associated with the existance of particles in a disperse medium such as an emulsion. Neutralization of this ionic cloud has been accomplished both electrochemically and physically in the case of latex, with resulting deposition of gum rubber.

There are two methods which stimulate coagulation of polymers suspended in an emulsion. The first, electrodeposition of the rubber using the emulsion as the electrolyte, involves the neutralization of negative attached ions at the anode with the subsequent formation of crude rubber at that electrode. The second, coagulation of the rubber on a surface which has been coated with a positive ion releasing substance, function by the same principle as that of electrodeposition, in that the ion cloud surrounding the polymer globule is neutralized by positive ions and subsequent coating occurs. Since synthetic plastics may be prepared in emulsion form, it was considered desirable to determine if they could be deposited in a similar way.

The object of this investigation was to determine

if a synthetic plastic can be plated on a surface by electrodeposition.

II. LITERATURE REVIEW

A survey of available literature was made to determine the mechanism of plating a plastic electrochemically from an emulsion. Because direct literature was unavailable on this subject and incomplete on the electrodeposition of rubber, polymerization principles, colloid kinetics and structure, and rubber plating conditions were studied so that analogy with known principles and practices could be used to postulate possible situations in which some plastics would react as rubber is known to do in its emulsified state.

Polymerization Techniques and Mechanism

Polymerization is the linkage of many molecules together to form a high molecular weight product whose properties are determined by the nature of the parent molecules and the method employed to unite them.

Functionality in Polymerization. Functionality is the condition that Carothers (10) has placed on the occurrence of a polymerization reaction. Chemical reactions occur at functional positions of an organic molecule, and for a continuous chain build-up there must

be at least two positions in the molecule to which linkage may be made. A bifunctional molecule forms linear polymers, while a trifunctional or polyfunctional monomer forms a three dimensional network.

Free Radical Substitution Mechanism in Polymerization.

A free radical (2) is defined as an extremely short-lived molecular fragment believed to contain a single, unpaired electron that reacts readily with the unsaturated bond of a monomer molecule upon collision. "When these free radicals react with monomer molecules they cause the formation of new, larger free radicals which in turn react with other monomer molecules, thus propagating the polymer chain." The free radical reaction may take several hours to complete, depending on the method and reaction temperature, even though individual reactions take place almost instantaneously.

Emulsion Polymerization.

According to Groggins (7), liquid monomers are dispersed and suspended in a non-slovent liquid by an emulsifier. The resulting monomer globules have diameters of one to ten microns. "During polymerization under influence of heat and appropriate catalysts, the average particle size decreases about one tenth, and the polymer is obtained in the form of a very stable emulsion called a latex." The reaction proceeds very rapidly as compared with other polymerization techniques with a much

higher average molecular weight material produced. Polymerization occurs within the bulk of the emulsified globule, and the net effect of the emulsifier after polymerization is to furnish an accumulation of charge which prohibits precipitation of the polymer from solution.

Other Methods of Polymerization. Two other procedures are empolyed, solution and bulk. In solution polymerization, the monomer is dissolved in a suitable solvent along with a catalyst. The soltion is heated to reaction temperature at which polymerization occurs at a moderate and even rate. Temperature is controlled by the boiling point of the solvent as the reaction is exothermal. The average size of the polymer is a function of the solvent and concentration of the monomer used.

In bulk polymerization, homogeneous liquid or gas phases are brought into contact with a proper catalyst at reaction temperature where the reaction proceeds fairly rapidly.

Behavior of Rubber Latex

Crude rubber obtained as a latex from the rubber tree has been processed to yield a gum rubber through the action of an electric current.

Rubber Latex Emulsion Composition. According to
Schmidt and Marlies (10), natural latex is a dispersion
of 30.45 parts rubber hydrocarbon, 65.50 parts water,
2 parts protein, 1 part soaps and related compounds, 1
part carbohydrates, and 0.4 parts inorganic matter.

Szeqavri (5) prepared commercial emulsions suitable
for electrodeposition by stabilizing the emulsion with
ammonia and then raising the solids content to sixty per
cent by centrifuging, creaming, or evaporation.

Additions of Sulfur and Accelerators to Rubber
Latex. According to Sheppard and Eberlin (5), sulfur
and accelerators which enable the crude rubber to be
vulcanized can be added to the emulsion without break-
ing or separating from it. Selective deposition does
not occur upon electroplating, and the deposit has the
same composition at the suspension.

Accumulation of Crude Rubber at the Anode. Con-
tinued accumulation at the anode is not hindered by
increasing thickness of the collection, for intermi-
cellar liquid carries the charge directed from the
electrode to the outer surface of the deposit. Any
desired thickness may be built by varying the time of
electrode exposure.

Mechanism of the Electrodeposition of Rubber from
a Latex. Szeqavri (11) studied the process in detail

and concluded that the migration effects of the col-
loid particles of rubber to the anode have little effect
on electrodeposition. Coagulation emanates from the sur-
face of the anode and radiates toward the latex compound.
Szeqavri observed the same deposition phenomenon when
he placed a coagulating agent on the surface of a metal
and dipped it into a solution used previously to electro-
plate rubber. The coagulant liberated positive ions
which served, as the electric current, to dissipate nega-
tive surface charges.

Surface Charges and Rubber Latex Configuration.
According to Schmidt and Marlies (10), latex colloids
are 0.2 microns in diameter. There are three distinct
layers to each particle. The center consists mainly
of lower molecular weight rubber; over this, there is
a skin of higher molecular weight rubber sufficiently
strong to resist penetration by a needle; the third
is a layer containing mainly proteins and probably soaps.
The materials of the third or sorbed layer act as emul-
sifying agents, and their ionization imparts a negative
charge which prevents precipitation in solution and
which is neutralized at the anode.

Reaction of the Anode. According to Mantel (9),
an anode which undergoes anodic corrosion and whose

oxidation product is compatible with that of the deposit
is the most desirable. A copper anode is oxidized to
cuprous ions which are incompatible and cause breakdown
of the deposited rubber. A zinc anode, however, causes
no decomposition.

Formation of a Plastic Emulsion

In preparing an emulsion (3), there are a number
of balancing effects which must be considered for the
emulsion to exhibit desired properties. In general,
there are at least five constituents which make up the
colloidal suspension. Monomer, surfactane, initiator,
buffer, and protective colloid which all must be chosen
for desired results.

Monomer. The physical and chemical characteristics
of a polymer are determined mainly from the beginning
monomer. If two or three characteristics are demanded,
then a co-polymer may be synthesized, and selection of
two different monomers of the desired polymer made.
As stated in (11), acrylate polymers exhibit excellent
film forming characteristics, but lack hardness. A
tough film can be formed by co-polymerizing the acrylate
monomer with either vinyl acetate or styrene. In this

example cited, the addition of the co-polymer adds to
the property of the final product.

Surfactants. Surfactants reduce the interfacial
tension between the monomer phase so that the monomer
can be dispersed in the solvent. It is the choice of
surfactants and rate of agitation which determine the
stability of the emulsion.

"Surfactants are of three types: anionic, cationic,
and nonionic. . . . In general, the anionic ones are
more easily used and tend to give smaller particle size
than nonionics ... . . a small amount of an anionic
surfactant is added to obtain better mechanical stability
and smaller particle size than can be obtained using
the nonionic types alone."

Initiators. Initiators are the source of free
radicals and are usually water soluble and depend on
a thermal decomposition into free radicals. They are
normally used at the reflux temperatures of the monomers,
and employed in concentrations of one-hundredth to two
tenths of a per cent. Typical initiators are potassium
persulfate, ammonium persulfate, and hydrogen peroxide.

Buffers. A buffer is normally added to an emulsion
reaction mixture to maintain the pH of the batch in the
four to five range. Buffers often employed are salts of

weak acids.

Protective Colloids. Protective colloids are employed to prevent agglomeration of the polymer particles. Attaching themselves to the surface of the polymer globules, they protect against agglomeration by enveloping the polymer. These colloids tend to increase the solution sensitivity of a polymer film, and should be held to a minimum. Some protective colloids are hydroxyethyl cellulose, gelatin, starches, polyvinyl alcohol, methyl cellulose, sodium polyacrylate, gum arabic etc. The colloid may be added at the beginning or end of the polymerization reaction.

Factors Affecting Electrodeposition of Synthetic Resins

Fink and Feinleib (6) in their study of the electrochemical deposition of Saran, polyvinyl chloride, and a styrene-butadiene co-polymer from commercial emulsions evaluated the effects of cathode diaphragms, voltage, and current density.

Cathode Compartment and Diaphragm. During the electrochemical reaction in an aqueous emulsion, the liberation of hydrogen gas and the formation of hydroxyl ions was observed when a noncorrosive cathode was used or when the decomposition voltage of water was surpassed

for a corrodible cathode. The cathode compartment was
one containing sodium chloride in a porous clay diaphragm,
so as to maintain the pH in the anionic compartment
by prohibiting migration of hydroxyl ions. The diaphragm
also prohibited the hydrogen from being deposited jointly
with the plastic. If this had occurred, the final deposit
would have been hard and brittle.

Current Density and Voltage Variations. Using a
zinc anode, a copper cathode, and a porous clay diaphragm,
the maximium energy yield was obtained within a total
cell voltage of one volt and current densities of the
order of four milliamperes per square centimeter. Under
these conditions, a deposit thickness of one millimeter
plated in about twenty minutes. At higher current
densities, deposits over three millimeters thick plated
quite rapidly.

At higher voltages, a higher density deposit was
obtained.

III. EXPERIMENTAL

The experimental section includes the purpose of this investigation, plan of experimentation, materials and apparatus used in the investigation, method of procedure, data and results obtained, and a sample of the calculations.

Purpose of Investigation

The purpose of this investigation was to determine if a synthetic plastic could be plated on a surface by electrodeposition. Any phenomena observed during the plating operation were analyzed, if possible, and sound experimental procedure for future investigation was developed.

Plan of Experimentation

A study was made to determine conditions favoring electrodeposition of natural rubber from a stabilized latex so as to duplicate this situation with an emulsified plastic. Rubber is coagulated on an anode when the negative surface charge of each colloid particle is neutralized by positive ions emanating from the anode. The experimental investigation of this thesis was founded on the belief that neutralization of this surface charge would lead to formation of a plastic film at the source of positive ions.

Emulsions of polymethacrylate were prepared from a methyl acrylate monomer. Emulsions having from 30 to 40 weight per cent solids content were prepared and the electrochemical behavior studied when anionic surfactant concentrations of 6, 12, 20, 25, and 30 grams per 1250 grams and 800 grams of water and methyl acrylate were used respectively. These varying amounts of anionic surfactants were employed to study the effect of charge magnitude upon the quantity of methyl acrylate plated from emulsion. The behavior of a single nonionic emulsion was observed to allow comparision and yield a cross check on any proposed mechanism.

Materials

The following list includes all chemical materials used during the course of the entire project.

Ammonium Persulfate. Certified reagent grade; lot No 713070. Obtained from Fisher Scientific Co. Inc., Silver Spring, Md. Used as catalyst in the polymerization reactions.

Igepal. CO 890. Manufactured by General Aniline and Film Corp., Philadelphia, Pa., and obtained as a sample. Used as nonionic surface active agent in emulsion VI.

Methyl Acrylate. Inhibited with 1000 ppm hydroquinone; lot No 8862. Obtained from Rohm and Haas, Philadelphia 5, Pa. Used as monomer in polymerization reactions.

Sodium Chloride. Certified reagent grade; lot No 90204. Manufactured by J. T. Baker Chemical Co., Phillipsburg, N. J. Used as electrolyte in cathode compartment.

Tergitol. Anionic surfactant; sample No 3A 8881. Manufactured by Union Carbide Chemicals Co., Charleston, W. Va. Used as anionic surface active agent.

Water. Distilled. Obtained from the Dept. of
Chemical Engineering, Virginia Polytechnic Institute,
Blacksburg, Va. Used in the emulsion preparation.

Apparatus

The following list includes all apparatus used
to prepare the emulsions or to electrodeposit poly-
methacrylate.

Buret. Laboratory, 50 ml, 0.1 ml graduations.
Obtained from Fisher Scientific Co. Inc., Silver
Spring, Md. Used to feed the aqueous catalyst solu-
tion into the reaction kettle.

Cable. No 14TW, 600 volts. Manufactured by
Rome Cable Co. Inc. Obtained from the Dept. of Che-
mical Engineering, Virginia Polytechnic Institute,
Blacksburg, Va. 2¾ inch sections used as anode in
the electroplating cell.

Carbon Rod. 17.5 mm dia-115 mm length with elec-
trical connection fitting. Salvaged from a Burgess
1½ volt dry cell battery. Used as the cathode in the
electroplating cell.

Condenser. Allihn, jacket length 40 cm, 5 bulb,

24/40. Obtained from Fisher Scientific Co. Inc.,
Silver Spring, Md. Used to condense vapors from the
reaction kettle.

Container. 15 qt. tin. Obtained from the Dept.
of Chemical Engineering, Virginia Polytechnic Institute,
Blacksburg, Va. Used as a water bath for the reaction
kettle.

Decanter. 500 ml with ground glass stopcock.
Obtained from Fisher Scientific Co. Inc., Silver Spring,
Md. Used to control the flow of methacrylate into the
reaction kettle.

Flasks. 1000 ml. Obtained from Fisher Scientific
Co. Inc., Silver Spring, Md. Used to store emulsions.

Generator. 90 ampere - 108 volts DC; serial No
726. Manufactured by L. J. Lund, New York, N. Y. Used
to supply current to the plating cell.

Heater. Chrome steel, ring type immersion, 2000
watts. Obtained from Fisher Scientific Co. Inc., Sil-
ver Spring, Md. Used to control the temperature of
the water bath.

Micrometer. 0 - 1.000 inch, 0.001 inch gradua-
tions. Manufactured by Central Tool Co., Auburn, R.I.
Used to measure the diameter of each deposit.

Milliampere Meter. 0 - 100 ma, type NX-35, style WG-41610-5. Manufactured by Westinghouse Co. Inc., East Pittsburg, Pa. Used to measure the flow of current through the electroplating cell.

Motor. Variable speed, 115 volt AC, 60 cycle, type NSI-18, No 1546117. Obtained from Central Scientific Co., Chicago, Ill. Used as stirrer in emulsion preparation apparatus.

Porous Cup. Battery, 24mm dia - 76 mm height. Obtained from Fisher Scientific Co. Inc., Silver Spring, Md. Used to seperate the anode and cathode compartments in the electroplating cell.

Reaction Kettle. 1000 ml, Reaction, Pyrex brand glass, $ 24/40, 24/40, 24/40, and 34/45 ground glass joints. Obtained from Fisher Scientific Co. Inc., Silver Spring, Md. Used to house polymerization reaction components.

Resistors. Variable, 112 - 2, 113 - 2, 156 - 1.4, and 450 ohm - 1 ampere. Obtained from the Dept. of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to regulate electroplating cell current.

Stirrer. Mercury seal, Pyrex brand glass with $ 34/45 joint. Obtained from Fisher Scientific Co. Inc.,

Silver Spring, Md. Used to agitate the polymerization reaction mixture.

Stopper. Rubber, No 9. Obtained from Fisher Scientific Co. Inc., Silver Spring, Md. Used to seal emulsions in 1000 ml flasks.

Thermometer. Laboratory, 0 - 100°C. Obtained from Fisher Scientific Co. Inc., Silver Spring, Md. Used to measure the temperature in the reaction kettle.

Timer. 0.1 - 10,000 seconds, "Time-it". Obtained from the Dept. of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to time the passage of current through the electroplating cell.

Procedure

This investigation proceeded in three steps: (1) preparation of emulsified polymethacrylate; (2) observation of the effects of surface charge and cell voltage on the colloidal particle in the electrochemical cell; and (3) investigation of the character of the deposit obtained from different emulsions.

Preparation of Emulsions. As a basis for the emulsion preparation segment of this experiment, the

procedure (4) for paint emulsion production was followed with respect to time and temperature of the reaction mixture, the methods of addition of monomer, water, surfactant, and catalyst as well as all mechanical operations involved.

Inhibitor Removal from Monomer. Methacrylate inhibited with 1000 parts per million of hydroquinone was processed to reduce the inhibitor concentration to between ten and twenty parts per million. Celanese Corporation's recommendation (1) for removal by washing was followed. 2500 grams of methyl acrylate at 20-25°C was washed twice with 50 grams of a solution containing 5 grams of sodium hydroxide and 62 grams sodium chloride per 100 grams of aqueous solution, and then was again washed three times with 125 grams of water at room temperature of 20-25°C. Monomer losses up to five weight per cent of the wash water resulted from foregoing procedure.

Design of Process Equipment and Mechanical Operations. Process equipment was designed and assembled in which the batch emulsion polymerization reaction could be carried out, tempera-

ture controlled, agitation rate varied, and mono-
mer added continuosly.

Methods of Addition of Components during Ope-
ration. Water, surfactant, catalyst, and monomer
were added in varying quantities and fashions.
Table 1, page 27, lists the total quantities of the
reaction components. Methods of addition of the
individual components were:

Water. 1200 grams of water was charged
into the reaction kettle at room temperature.

Surfactant. The entire amount of "Ter-
gitol" or "Igepal" was added directly to the
1200 grams of water at room temperature, and
the mixture heated to 60°C and held there for
10 minutes while an agitation rate of 350 rpm
was employed.

Catalyst. 3.2 grams of ammonium persul-
fate dissolved in 50 grams of water was add-
ed to the water and surfactant mixture when
the temperature of the latter had been lo-
wered from 60°C to 30°C.

Monomer. 80 grams of methylacrylate
was added along with the entire 50 ml of am-
monium persulfate solution after the kettle

had cooled to 30°C. The kettle temperature
was raised to 80-82°C and held for 2 hours
while the remaining 720 grams of methacry-
late was added evenly over this period.
Agitation was maintained at 350 rpm.

Temperature Increase. To insure com-
plete polymerization, the reaction vessel
was heated to 90°C and its contents agi-
tated at the rate of 350 rpm for 10 min-
utes following the complete addition of the
monomer.

Solids Content Determination. 15 to
20 grams of each emulsion was heated at
90°C for 40 to 60 hours to determine the
solid content of each.

Electrochemical Behavior of the Colloid Particles.
The following procedure was employed to survey the ef-
fects of varying amounts of surface active agents.

Charge Distribution. Six emulsions were
prepared to compare the net effect of charge dis-
tribution surrounding an emulsified polymethacry-
late globule. Tergitol, the anionic surface ac-
tive agent was employed in quantities of 6, 12,
20, 25, and 30 grams per batch of emulsion. 30

grams of Igepal, the nonionic surfactant was used
in the preparation of only one emulsion.

Electroplating Cell. Since gases were libe-
rated at the cathode when colloidal particle were
coagulated, a porous battery cup, 24 mm in dia-
meter—76 mm in height, was used to separate the
2¾ inch section of 14TW copper wire and emulsion
from the cathode compartment. The cathode com-
partment contained 0.5 normal sodium chloride
solution and a 17.5 mm diameter - 115 mm length
carbon cathode.

Measurement of Cell Current. The cell
current was measured with a 0.0 - 100.0
milliampere meter.

Line Resistance. Four resistors of 112,
113, 156, and 430 ohms were placed in series,
so as to reduce the cell current for genera-
tor voltages of 25, 35, 50, 75, and 90 with-
in the range of the 0 - 100 milliampere
meter. The line resistance was held constant
throughout all tests at 811 ohms.

Generator Voltage. The only parameter
in the electroplating cell other than the
line resistance which could be held constant

was the supply voltage. Five generator volt-
ages of 25, 35, 50, 75, and 90 were used for
the five anionic emulsions. Voltages of 25,
50, 90, and 108 were used for the nonionic
emulsion.

Measurement of Cell Voltage. The only
accurate method of measuring the voltage
across the cell would have been to use a
vacuum tube volt meter. However, one was
not employed, and no cell voltages were ob-
tained.

Cell Current - Time Measurement. A
"Time-it" clock was used to measure various
time intervals at the end of which the cell
current was recorded.

Character of the Deposit. After the cell current
had been stopped, the coated anode was removed from
its position, dried, weighed, measured, and observed.

Removal of Water from Deposit. The deposit
was dried at 90°C in an electric oven for periods
of 40 to 60 hours.

Weight of Deposit. Each anode was weighed
before deposition and after drying. The weight
of the deposit was determined by difference.

Deposit Length and Thickness. The length of each deposit was measured with a 1/32 inch division rule, while the thickness of the deposit was obtained by measuring the diameter of the plated anode with a 0.01 inch graduated micrometer.

Miscellaneous. Any noticeable differences in color or adhesive character of a deposit from normal were recorded for future clarification and correlation.

Data and Results

The data and results obtained from the investigation are presented in this section. They are described under the following headings: (1) emulsion preparation and stability, (2) operating conditions of the electroplating cell, and (3) physical characteristics of the deposits.

Emulsion Preparation and Stability. The total amounts of water, methyl acrylate, ammonium persulfate, and Tergitol or Igepal for each one of the six emulsions prepared are listed in Table 1, page 27. Method of addition of each component has been explained on pages 21 to 22 in the discussion of experimental procedure. The dry solids content as determined by drying 10 to 18 grams of emulsion for 40 to 60 hours at $90^{o}C$ is listed in the bottom row of this table.

Table 2, page 28 contains data of time-stability studies on emulsions I, II, and III. 0.1 grams of 0.253 normal hydrochloric acid, 0.5 grams of glycerine, and 0.2 grams of 0.23 normal sodium hydroxide solution were added to emulsion I and the quantity of coagulant estimated at 18 hours, 7 days, 14 days,

TABLE 1

Total Component Amounts in Emulsions

Substance	Emulsion No					
	1	2	3	4	5	6
	Total Amount, gm					
Water	1250	1250	1250	1250	1250	1250
Methacrylate	800	800	800	800	800	800
Ammonium Persulfate	3.2	3.2	3.2	3.2	3.2	3.2
Tergitol	6	12	20	25	30	—
Igepal	—	—	—	—	—	20
Total Dry Solids %[a]	30.3	35.4	35.8	39.1	36.1	36.1

(a) Determined by heating 10-18 grams of emulsion @ 90°C in an oven

   for 40 - 60 hours.

TABLE 2

Coagulation and Settling Properties of Modified Emulsions.

Additive	Emulsion Comments						
	I				II		III
	Observation Time						
	18 hr	7 day	14 day	42 day	7 day	35 day	28 day
None	0.01[f]	0.01	0.02	0.02;2	0.02	0.02; 3	0.00; 3
Hydrochloric acid [a]	0.005	0.01	0.1	0.13;2	- -	- - -	- - -
Glycerine [b]	0.005		1.0	3.0	0.0	0.05; 3	- lost -
Sodium Hydroxide							
1[c]	0.0	0.001;1	0.001;1	0.01;2	0.02	0.02; 3	0.00; 3
2[d]	- -	- -	- -	- -	0.0	0.01; 3	0.0
3[e]	- -	- -	- -	- -	0.005	0.1 ; 2	0.25; 4

(a) 0.1 gm of 0.253N HCl added to 35 ml of emulsion.

(b) 0.5 gm of glycerine added to 35 ml of emulsion.

(c) 0.2 gm of 0.23N added to 35 ml of emulsion.

(d) 0.3 gm of 0.23N added to 35 ml of emulsion.

(e) 0.4 gm of 0.23N added to 35 ml of emulsion.

(f) Thickness of top layer, in.

1 Slightly thinner than raw emulsion.

2 Small quantities of white creamy precipitate.

3 Trace of white creamy precipitate.

4 1/16 in layer of white creamy precipitate.

and 42 days after these additions. In all cases the
coagulated polymethacrylate appeared as a surface
layer. All samples were observed in a 40 ml "screw
cap" test bottle.

Sodium hydroxide was seen to be a stabilizing
agent below the concentration of 0.4 grams of 0.230
normal in 35 milliliters of emulsion. Glycerine and
hydrochloric acid were observed to be coagulants.

Conditions for Deposition of Polymethacrylate.
Electroplating cell currents were measured for all
tests, and the total quantity of current was com-
puted by graphical integration of the time-current
graph. Table 3, page 30 lists the total deposit
weight, the total current passed, and the calcu-
lated gram equivalent weight for all voltage and
emulsion combinations.

Gram Equivalent Weight. The gram equiva-
lent weight for emulsions II to V as listed in
Table 3, page 30, for which Tergitol concentra-
tion of 12, 20, 25, and 30 grams per batch of
emulsion were used, showed a general decrease
for generator voltages of 25, 35, 50, and 75.
The average equivalent weight of these four
emulsions was observed to be 7,320, 5,460,

TABLE 3

Conditions for Deposition of Polymethacrylate

Emulsion No	Weight of Deposit gm Generator Voltage, volts						Current Passed coulombs Generator Voltage, volts						Gram Equivalent Weight gm/ Faraday Generator Voltage, volts					
	25	35	50	75	90	108	25	35	50	75	90	108	25	35	50	75	90	108
I	0.436	0.391	0.248	0.173	0.154		12.09	9.85	6.79	4.42	4.59		3,480	3,830	3,530	3,780	3,240	
II	0.251	0.246	0.135	0.137	0.104		3.16	3.32	1.67	1.25	3.03		7,620	7,150	7,800	10,300	3,310	
III	0.485	0.373	0.170	0.190	0.079		10.32	6.79	2.88	3.61	1.16		4,530	5,310	5,700	5,260	6,570	
IV	0.479	0.322	0.178	0.109	0.125		9.85	6.25	3.13	1.65	2.17		4,700	4,900	5,490	6,610	5,560	
V	0.000	0.193	0.245	0.141	0.147		16.10	4.03	5.71	3.06	3.06		0.000	4,610	4,140	4,450	4,640	
VI	0.013		0.148		0.291	0.347	4.60		13.90		15.90	17.00	273		1,030		1,765	1,975

5,440, and 4,500 grams/Faraday. Gram equivalent
weight for all tests of emulsion I averaged 3,560
grams per Faraday. Reasons for this phenomenon
are explained in the discussion section of this
report on pages 60 to 61.

Electroplating Cell Current and Anode Sur-
face Current Density. Tables 4 to 8, pages 32
to 36 list the cell current of emulsions I thru
V at corresponding test times. Because the anode
surface was a variable in all tests, anode sur-
face current density was used as the base for
comparision of current flow at different voltage
conditions. The current density was calculated
from both the exposed anode surface area and the
total current flow. Table 9 to 13, pages 37 to
41 list the anode surface current density. At
the test voltage conditions of 25, 35, 50, 75,
and 90, the average initial current density for
the five anionic emulsions were observed to be
70, 100, 150, 220, and 290 milliamperes per
square inch of anode surface.

Table 14, page 42 lists the current density
for emulsion VI at generator voltages of 25, 50,
90, and 108. Initial density for these four

TABLE 4

Current Through Electroplating Cell

at a Generator Voltage of 25

as a Function of Time.

Time sec	Electroplating Cell Current ma				
			Emulsion No		
	I	II	III	IV	V
0	25.0	26.0	26.0	28.0	21
20	24.7	26.0	25.0	27.5	
40	24.7	26.0	25.0	27.2	
60	24.7	25.0	24.9	27.0	
80	24.7	24.5	24.7	27.0	
90		22.0			
100	24.7	21.0	24.7	27.0	
110		19.0			
120	24.7	17.0	24.7	27.0	
125		14.0			
130		11.0			
140	24.7	7.0	24.6	27.0	
145		6.0			
160	24.7		24.0	27.0	21
180	24.7		23.9	26.8	
200	24.5		23.7	26.8	
220	24.0		23.7	26.5	
240	24.0		23.5	25.8	
260	24.0		23.3	25.2	
280	23.5		23.1	24.9	
300	23.0		23.1	24.0	
305	21.0				
310	17.0				
320	15.0		23.0	23.4	
330	14.9				
340	15.0		23.0	23.4	
350	15.1			23.2	
360	15.1		22.8	22.7	
370	15.4			20.0	
380	15.7		22.3	7.0	
385	15.7			5.2	
390	15.7			5.0	
400	16		21.1	4.5	
410			20.6		
420			18.9		
430			12.5		
440			12.0		
450			11.0		
460			9.0		
470			8.0		

TABLE 5

Current Through Electroplating Cell

at a Generator Voltage of 35

as a Function of Time.

Time sec	Electroplating Cell Current milliampere				
			Emulsion No		
	I	II	III	IV	V
0	36.5	35.1	38.0	37.0	38.0
20	35.7	34.9	36.7	37.0	37.0
40	35.4	34.0	36.1	36.7	35.0
60	35.4	32.0	36.0	36.0	35.0
70	35.4	31.0	35.9	35.8	33.0
80	35.4	29.0	35.7	35.5	33.0
85		26.0			
90		21.0			31.5
95		15.0			
100	35.0	11.0	35.1	35.1	30.0
105		7.5			
110		6.0			24.0
120	35.0	4.0	35.1	34.0	8.0
130		3.0			7.0
140	34.7		34.0	33.0	6.0
150		2.0		32.1	
160					
165				18.0	
170				13.5	
180	27.0		30.0	12.8	
190			26.0	10.0	
200	27.0		16.0	9.0	
210			9.0	8.0	
220	25.5		7.0		
240	24.0				
260	23.0				
280	21.5				
300	20.0				
320	32.0				
340	17.4				
360	17.0				
370	12.0				

TABLE 6

Current Through Electroplating Cell

at a Generator Voltage of 50

as a Function of Time

Time Sec	Electroplating Cell Current milliamperes				
			Emulsion No		
	I	II	III	IV	V
0	55.0	52.0	53.0	54.0	53.0
20	53.5	49.0	51.0	52.0	52.5
25		45.0			
30		27.0			
35		11.0			
40	52.5	8.0	49.0	50.0	51.5
50		6.0	38.0	46.0	
55		5.0	20.0	28.0	
60	51.4		11.0	14.0	50.0
70			8.0	9.0	
80	49.0		6.0	7.0	48.5
90				6.3	
100	44.0				43.0
110	41.5				15.0
120	38.0				11.5
130	32.0				9.0
140	19.0				
145	12.0				
150	8.0				6.0
160	4.0				

TABLE 7

Current Through Electroplating Cell
at a Generator Voltage of 75
as a Function of Time

| Time sec | Electroplating Cell Current milliampere | | | | |
| | Emulsion No | | | | |
	I	II	III	IV	V
0	84	82	85	85	84
10		79		82	
15		57		77	
20	82	11	82	35	82
25		7	79	14	
30	80	5	75	9	78
35			38	7	67
40	75		15	6	21
45			12	5	10
50	67		9	4	8
55			8	3.8	7
60	25		5		
80	4				
90	3				

TABLE 8

Current Through Electroplating Cell
at a Generator Voltage of 90
as a Function of Time

Time sec	Electroplating Cell Current milliampere				
			Emulsion No		
	I	II	III	IV	V
0	102	100	102	102	102
5		99	95	100	
10	100	85	35	97	100
15		13	13	94	
20	98	7	7	73	97
25	96	4	5	19	93
30	90	3	4	8	24
35	85			6	11
40	68				8
45	47				
50	33				6
55	25				
60	23				
65	21				
70	18				
75					
80	15				

TABLE 9

Current Density at Anode Surface

at a Generator Voltage of 25

as a Function of Time.

| Time sec | Anode Surface Current Density ma/sq.in. | | | | |
	I	II	III	IV	V
			Emulsion No		
0	72	67	59	78	75
50	72	60	57	75	
100	72	50	57	75	75
110		45			
120		41			
125		33			
130		26			
145		14			
150	72		55	75	
200	72		55	74	75
250	69		55	71	
300	66		55	66	75
350	45		55	63	
360				62	
370				56	
375				47	
380				28	
385				15	
395				13	
400			48		75
425			39		
450			25		
460			20		
470			14		75

TABLE 10

Current Density at Anode Surface
at a Generator Voltage of 35
as a Function of Time

| Time sec | Anode Surface Current Density ma/sq.in. | | | | |
| | Emulsion No | | | | |
	I	II	III	IV	V
0	91	85	121	114	108
50		85	115	114	102
80		71			93
90		51			
100	86	27	112	108	85
105		20			
110		15			68
120		10			23
130		7			20
140					17
150	76	5	106	99	
160				87	
165				56	
170				43	
175				41	
180			96	37	
185				31	
190			85		
200	67		51	28	
210			29	25	
220			22		
250	57				
300	49				
350	42				
370	36				

TABLE 11

Current Density at Anode Surface

at a Generator Voltage of 50

as a Function of Time

Time sec	Anode Surface Current Density ma/sq.in.				
			Emulsion No		
0	156	135	170	160	147
10		133	166	158	
20		127	163	155	
25		117	160		
30		71		152	
40		21	157	149	
50	150	15	121	123	142
55		13	64	78	
60			35	39	136
70			26	27	
,80	139			19	21
90					19
100	125				119
110					42
120	108				31
140	54				
150	23				10
160	11				

TABLE 12

Current Density at Anode Surface

at a Generator Voltage of 75

as a Function of Time

Time sec	Anode Surface Current Density ma/sq.in.				
			Emulsion No		
	I	II	III	IV	V
0	225	193	205	229	243
10		186	205	220	
15		134	203	207	
20		26	200	94	237
25		17	190	37	
30		12	180	24	226
35			87	19	194
40	201		33		61
45			23		
50	172		15	11	23
55			12	10	20
60	61		5		
80	11				
90	8				

TABLE 13

Current Density at Anode Surface

at a Generator Voltage of 90

as a Function of Time.

Time sec	Anode Surface Current Density ma/sq. in.				
			Emulsion No		
	I	II	III	IV	V
0	275	235	294	360	312
5		232	275	354	
10	268	200	86	347	
15		33	38	332	
20	258	16	20	258	298
25		9	14	67	285
30	236	7	11	28	74
35	223			21	34
40	179				
45	124				
50	89				18
55	67				
60	62				
65	57				
70	48				
80	40				

TABLE 14

Current Density at Anode Surface as a

Function of Time and Generator

Voltage for Emulsion VI

Time sec	Anode Surface Current Density ma/sq in			
	Generator Voltage			
	25	50	90	108
0	53.5	202	224	302
50	53.5	202	219	266
100	53.5	202	201	261
150	53.5	198	81.4	169
200	53.5	193	34.5	132
250		191	17.3	97
300		189	14.8	68
350			14.8	

conditions were 53.5, 202, 224, and 302 milliamperes respectively.

Figures I to VI, pages 44 to 49 are graphical representations of Tables 8 to 14. The rate of change of the surface density with respect to time was, for practical purposes, infinite during the second portion of the curves for generator voltages of 75 and 90 for emulsion I; of 90 and 75 for emulsion II; of 90, 75, 50, and 35 for emulsions III and IV; and of 90, 75, and 50 for emulsion V. The second portion of the curves in Figure VI, page 49, for emulsion VI have slopes of four at the higher voltage tests of 90 and 108. At the two lower voltages of 25 and 50, the cell sensed only slight depression of the current density throughout the entire tests.

Physical Characteristics of the Deposits. Table 15, page 50 contains measurements of the linear weight, diameter of the deposit and 0.066 inch copper anode, and the density after drying. The linear weight and thickness of all deposits decreased with increasing voltages while no trend was observed in the deposit density.
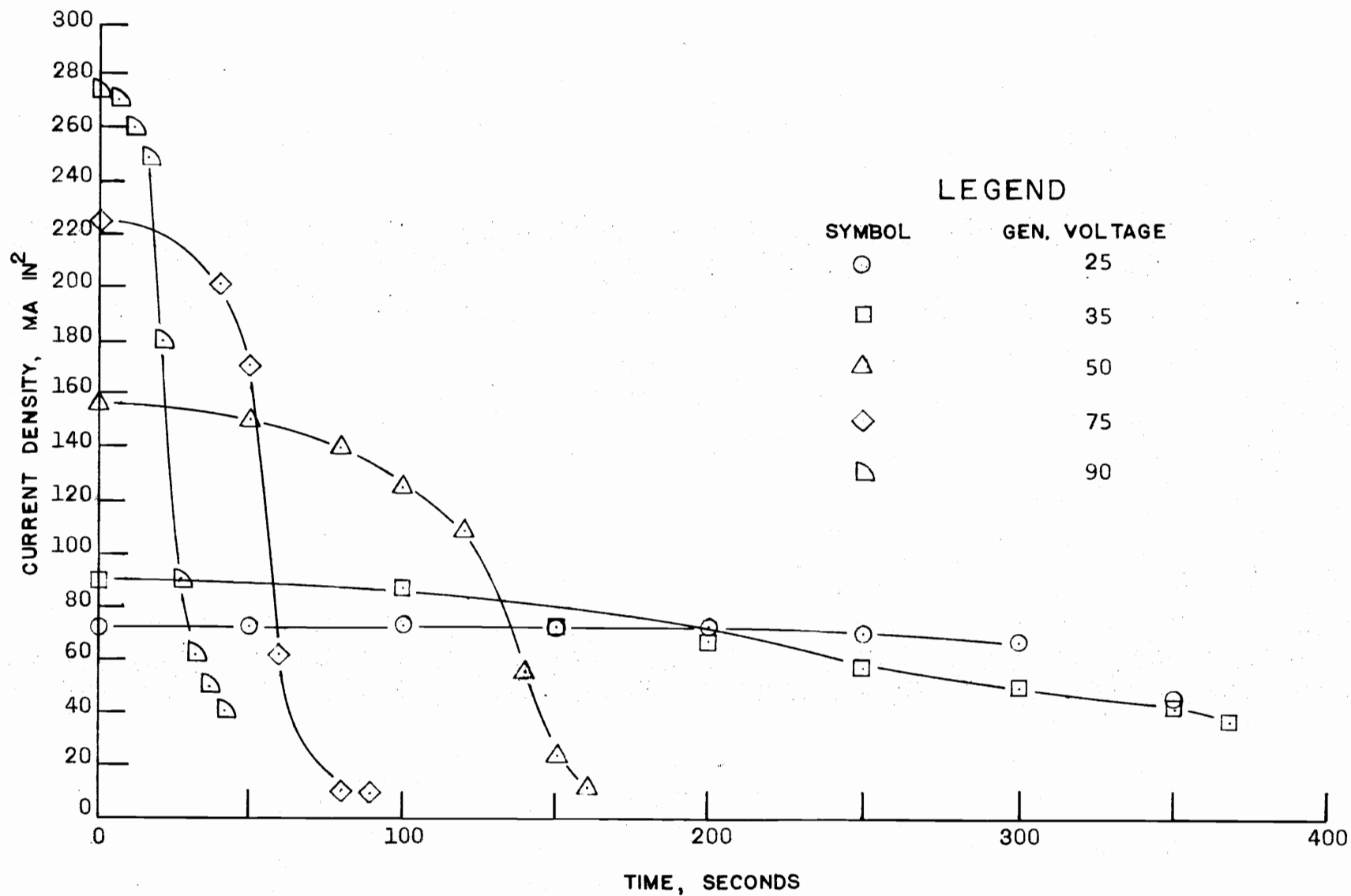
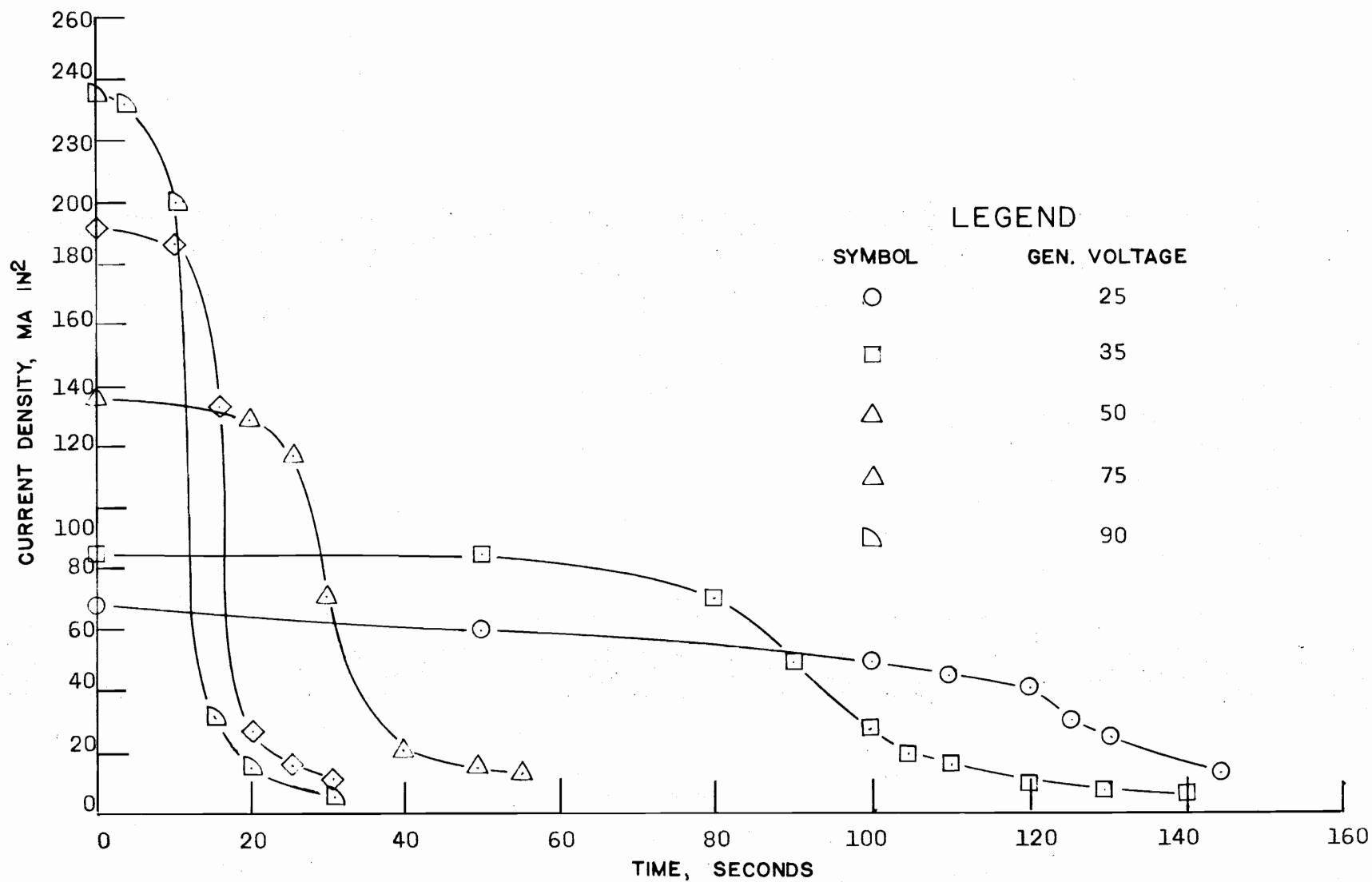FIGURE I. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION I

FIGURE 2. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION II
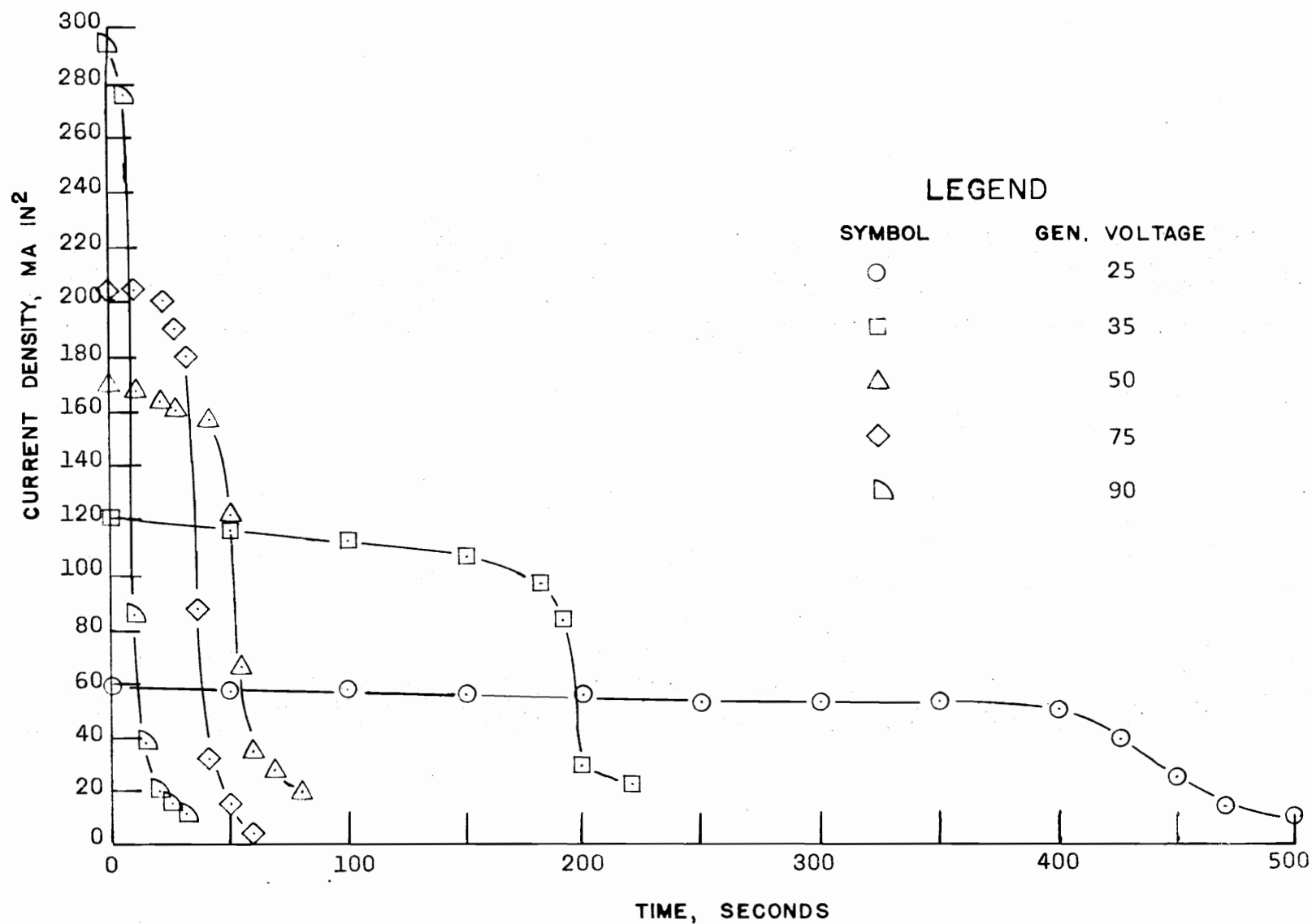
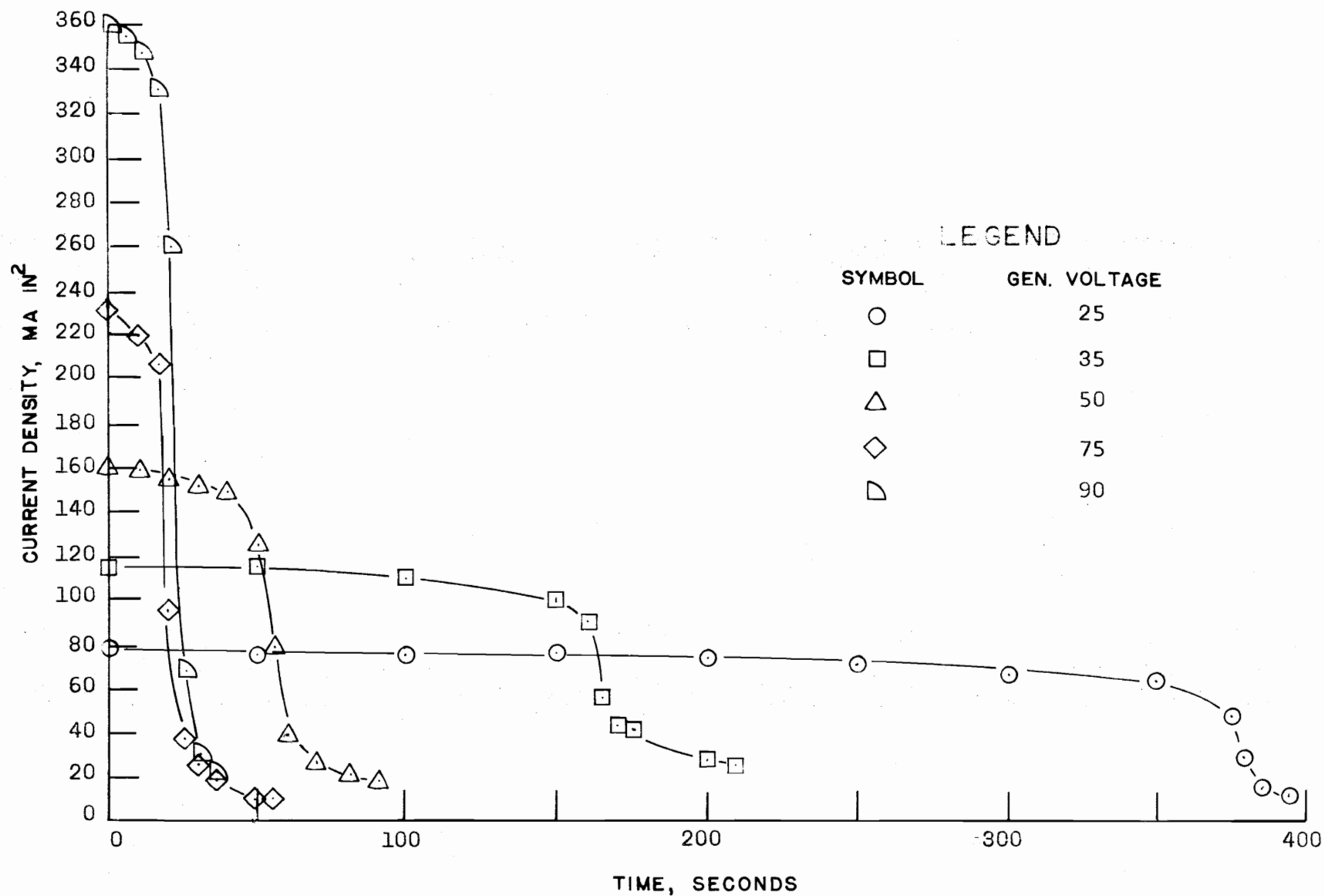FIGURE 3. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION III

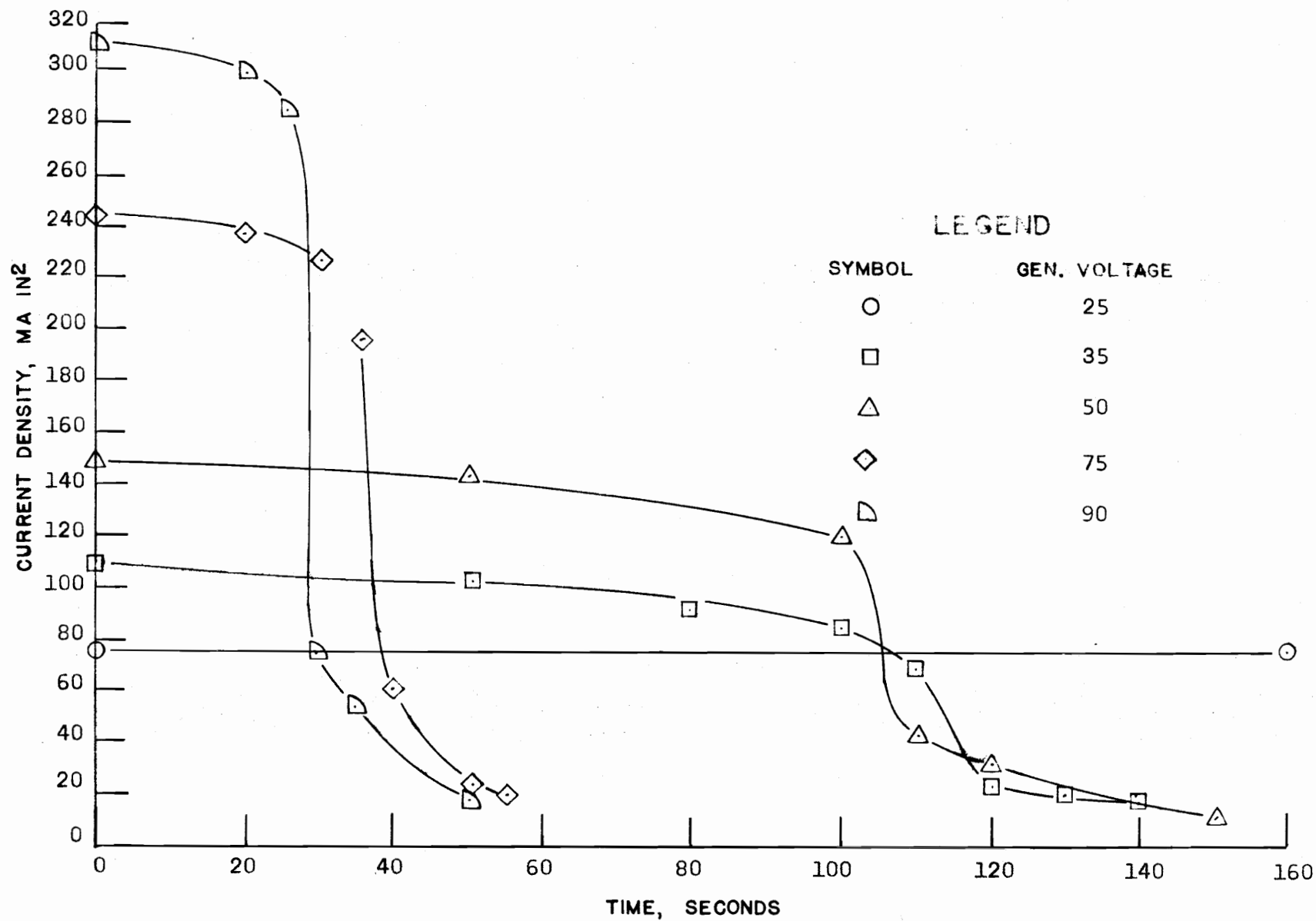FIGURE 4. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION IV

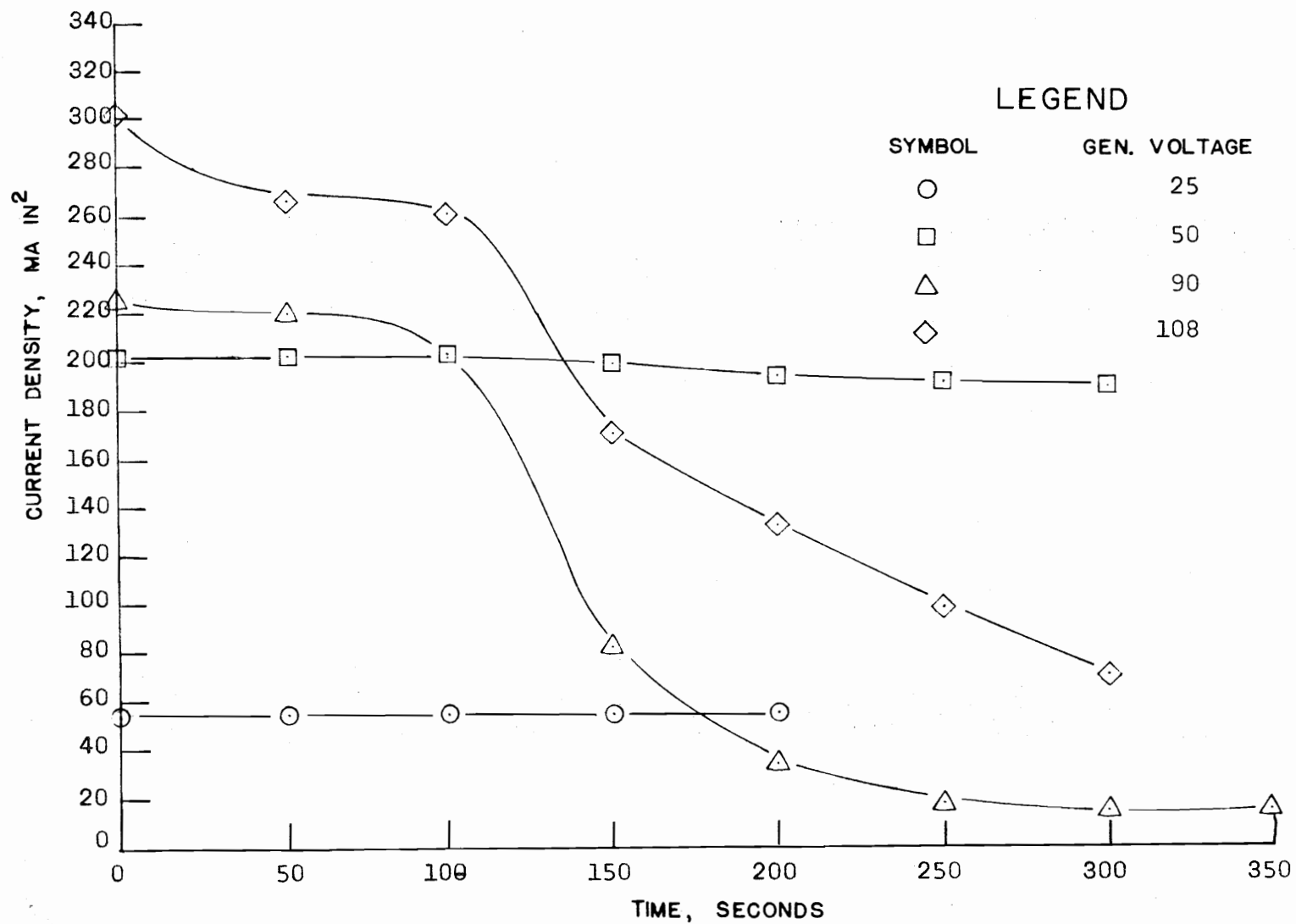FIGURE 5. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION V

FIGURE 6. ANODE CURRENT DENSITY DURING ELECTRODEPOSITION OF EMULSION VI

TABLE 15

Characteristics of Deposited Films

Emulsion No	Generator Voltage volts	Linear wt gm/in	Diameter of Deposit and Anode, in	Density gm/in^3
I	25	0.263	0.139	22.3
	35	0.201	0.130	20.5
	50	0.147	0.110	23.7
	75	0.097	0.100	21.9
	90	0.0865	0.095	23.5
II	25	0.126	0.110	21.1
	35	0.124	0.104	24.4
	50	0.0732	0.094	20.8
	75	0.0675	0.086	29.1
	90	0.0512	0.084	24.1
III	25	0.232	0.112	36.0
	35	0.249	0.138	21.8
	50	0.113	0.107	20.2
	75	0.0996	0.100	22.5
	90	0.0478	0.083	24.0
IV	25	0.278	0.141	23.2
	35	0.206	0.126	22.7
	50	0.1035	0.099	24.2
	75	0.1065	0.089	24.9
	90	0.0589	0.085	26.1
V	25	no deposit	- - -	- -
	35	0.114	0.105	21.8
	50	0.142	0.105	27.1
	75	0.0851	0.100	19.2
	90	0.094	0.092	29.1
VI	25	0.0069	0.069	13.4
	50	0.072	0.108	12.4
	90	0.150	0.111	23.8
	108	0.192	0.130	19.3

Sample Calculations

The sample calculations for this experiment are presented in the following section.

Physical Properties of the Deposit. Linear weight, weight, and density calculations were employed on all deposits.

Weight of Deposit. The deposit weight as tabulated in Table 5, page 50 was calculated as follows:

$$W = W_f - W_a$$

where:

W = deposit weight, gm

W_f = weight of anode and deposit after drying, gm

W_a = weight of copper anode, gm

For the test on emulsion I at 25 volts, the deposit weight was determined as follows:

$$W = 1.811 \text{ gm} - 1.332 \text{ gm}$$

$$= 0.479 \text{ gm}$$

Linear Weight of Deposit. The linear weight of each deposit as tabulated in Table 15, page 50 was determined from the total weight and deposit

length as follows:

$$W_L = \frac{W}{L}$$

where:

W_L = linear weight, gm/in

W = deposit weight, gm

L = deposit length, in

For the test on the deposit of emulsion I obtained at 25 volts, the linear weight was determined as follows:

$$W_L = \frac{0.479 \text{ gm}}{1.658 \text{ in}}$$

$$= 0.263 \text{ gm/in}$$

Total Current Passed. The quantity of current passed into each emulsion as tabulated in Table 3, page 30 from the anode was determined as follows:

$$Q = \int_0^T i \, dT$$

where:

Q = charge passed into cell, coulombs

i = instantaneous cell current, amp

T = time, sec

For emulsion I at 25 volts, the total quantity of current through the cell was calculated by graphical integration of the time-current graph from zero time to the end of the test.

$$Q = \int_0^{400} i \, dT \quad \text{amp-sec}$$

$$= 12.09 \text{ coulombs}$$

Gram Equivalent Weight. Table 3, page 30 lists the gram equivalent weight of all deposits. These values were computed as follows:

$$E = \left(\frac{W}{Q} \right) \times F \quad \text{gm/Faraday}$$

where:

E = gram equivalent weight, gm/Faraday

W = total weight of deposit, gm

Q = total charge passed through the electroplating cell, coulombs

F = Faraday's equivalent, 96,494 coulombs/Faraday

For the deposit obtained at 25 volts from emulsion I, the gram equivalent weight was calculated as follows:

$$E = \left(\frac{0.479 \text{ gm}}{12.09 \text{ coulombs}} \right) (96,494 \text{ coulombs/Faraday})$$

$$= 3,480 \text{ gm/Faraday}$$

IV DISCUSSION

Recommendations for future work, limitations of the experiment, and an analysis of the procedure and observation are the concern of this section.

Discussion of Results

A general discussion of the procedure employed and observations made during the emulsion production, electrochemical, and film evaluation segments of the experiment is presented in this section.

Emulsion Composition. Isolation of as many variables as possible was the primary goal when the homopolymer of methyl acrylate, a single surface active agent, an aqueous emulsion enviroment, and a single catalyst were selected and used in the emulsion preparation portion of the experiment. The formulation of five emulsions involved a common anionic surface active agent, Tergitol; a common suspension medium, water; a common monomer, methyl acrylate; a common catalyst, ammonium persulfate; and common reaction temperatures and agitation rates. Formulation

of a sixth emulsion only involved a change in the sur-
face active agent so that nonionic colloidal particles
could be studied under electrochemical conditions
similas to those of anionic ones, and thus allow com-
parision of their behavior with that of the anionic
particles.

Activation of Surface Active Agents. Preliminary
tests were made with Tergitol and Igepal CO-890 to de-
termine their solution ability on a 50-50 volumetric
mixture of methyl acrylate and water. Twelve samples
of the mixture were prepared and Tergitol added in
integrals of 5 volume per cent of the original mixture
to six samples, and Igepal CO-890 added, in the same
integral proportions, to the remaining samples.

Each sample was shaken vigorously by hand for 30
seconds at a room temperature of 20 to 25°C and allowed
to settle. In all cases, solution of the organic phase
never exceeded 10 to 20 per cent of its original volume.

Subsequent emulsion preparation proved that 93 per
cent solution of 800 grams of methyl acrylate could be
obtained with 6 grams of Tergitol and 1250 grams of
water in which this anionic surface active agent had
been activated. Activation of the surfactant was accom-
plished by heating the water-surfactant solution to

60°C where agitation of 350 revolutions per minute was employed for ten minutes.

Emulsion Preparation Procedure. Celenese Corporation's recommendation (3) for preparation of a paint emulsion was used as a guide to prepare all emulsions. As this procedure was listed for a vinyl acetate-ethyl acrylate co-polymer in which five surface active agents were employed, it required modification of the suggested quantity of monomer and surface active agent. The solids content of Celenese's emulsion was listed to be 55.95 per cent, the solids content of those emulsions prepared for this experiment ranged from 30.5 to 39.1 per cent.

Emulsion Stability. The first emulsion, when removed from the reaction kettle, was saturated with colloidal particles, for 58 grams of coagulated polymethacrylate was collected immediately from the emulsion. An elastic film formed at the surface of the emulsion immediately after its removal from the reaction kettle. The emulsion temperature at that time was 90°C. Additives were tested on the first three emulsions to locate a suspension aid.

Glycerine, hydrochloric acid, and sodium hydroxide were added to freshly prepared emulsion samples and the

emulsion stability observed at various times. Table 2,
page 28 shows that both hydrochloric acid and glycerine
exert coagulant forces, while small amounts of sodium
hydroxide tended to stabilize the product. There is,
however, a bascisity, above which the base acted as a
coagulant. No pH measurements were made on these
emulsions.

Film Forming Properties. The polymer of all emul-
sions formed an elastic translucent film. A film pre-
pared by dipping from the second emulsion was estimated
to have a Young's modulus of 500 to 600 pounds per
square inch. Films could be formed in variable thick-
ness by consecutive dipping of random solid objects
such as wood, steel, glass etc. directly into the
emulsion. Films formed in this manner were believed
to have greater water solubility.

Solids Content. The solids content of emulsion I
to V was 30.3, 35.4, 35.8, and 39.1 weight per cent for
Tergitol quantities of 6, 12, 20, and 25 grams. The
increase in solids content was the result of increasing
quantity of anionic surfactant. In all emulsions, a
couglomerate formed during preparation of each emulsion
and decreased in quantity with increasing amounts of
Tergitol. No reason can be given for the decrease to

36.1 weight per cent for the fifth emulsion where 30 grams of Tergitol was present.

Emulsion Storage. Each emulsion was poured at 85°C to 90°C directly from the reaction kettle into a 1000 ml flask which was then sealed with a rubber stopper. The flask was stored at room temperature for periods of two to three weeks until the electroplating tests were made. In all cases, coagulation in the flasks was not noticeable.

Electrical Circuit. The anode and cathodes were connected in series with a 811 ohm resistance and a 95 ampere, 25 to 108 volt DC generator.

Electroplating Cell. No gas evolved from the anode, but hydrogen gas was liberated from the carbon cathode. The aqueous 0.5 normal solution of sodium chloride acted as a bridge between the anode and cathode compartments.

Coagulation of Polymethacrylate within the Diaphragm. Migration of aqueous sodium chloride solution from the cathode chamber into the diaphragm and of the colloidal particles from the anode chamber also into the battery cup resulted in the coagulation of polymethacrylate within the pores of the cup. The quantity of this plastic increased with subsequent plating

tests, and may have caused an increase in the electrical potential across the cup walls. There was no way of estimating the error introduced from one test to another by this gradual clogging.

Effects of Increasing Generator Voltages. For each anionic emulsion tested, an increase in the generator voltage resulted in a decrease in the thickness and linear weight of the deposit, an increase in the initial current density, and a decrease in the time of the cell operation. For the nonionic emulsion, the linear weight and the deposit thickness increased with increasing generator voltages and each film appeared more permeable than any anionic films since greater quantities of current were passed through the cell and current reduction was at a rate far less than those of the anionic emulsion. This fact was observed from a comparision of Figure VI, page 49, with Figures I - V, pages 44 to 48.

No conclusion can be drawn from the variations in density of the deposits. The curing or drying procedure used on the deposits probably stimulated random orientation of the polymer. The density determinations on the cured deposits as seen from Table 15, page 50 were extremely random.

Gram equivalent weight had a slight tendency to increase with increasing voltages.

Effect of Surface Active Agent. Table 3, page 30 lists the gram equivalent weight of all deposits. The value for the first emulsion is 50 to 60 per cent lower than would be normally be expected for the 6 grams of Tergitol present. The equivalent weight of deposits from emulsion II - V generally showed a slight tendency to increase with increasing voltage. From this, the mechanism of deposition is seen not to depend solely on charge transference, but also on the electrode voltages. It appeared that there was a minimium charge distribution below which the colloidal particles could not be effectively attracted to the anode and thus deposited on it. This minimium charge distribution lay between that of emulsions I and II.

Deposits from emulsions II, III, IV, and V showed a general decrease in equivalent weight which is properly associated with an increasing ionic charge where the mechanism is solely transference of charge directly from the electrode to the ionic surface. The charge density of these four emulsions surpassed the minimium requirments allowing the current to more effectively deposit polymethacrylate on the anode.

This theory is further strengthened from tests on emulsion VI. If charge neutralization was the paramount variable, no deposit should be obtained; however, one resulted, and was deposited in increasing thickness and gram equivalent weight with increasing voltages. The cell voltages attracted colloids to the anode where the concentration of the polymethacrylate increased to cause retention of copper ions which emanated from the anode as the deposition product.

Emulsion V under 25 volts, did not yield a deposit, because the voltage of the cell was not great enough to overbalance the stabilizing effect of so large a surface active agent concentration. At 35 volts these repulsive forces were subdued and a deposit obtained.

Mechanism of Deposition. From the three distinct portions of the curves of Figures I to VI, pages 44 to 49, and from the equivalent weight data of Table 3, page 30, the author positively feels that the plating of a plastic from an emulsion occured in two steps: (1) attraction of the particles to the deposition electrode, during which time the anode deposition product, in the case of this experiment, copper ions, was passed freely into the emulsion; and (2) deposition of the polymer when its concentration had reached the

minimium level so as to effectively contain the anode
deposition product within the concentrated layer where
the ionic clouds associated with each colloid were
efficiently neutralized. As coagulation proceeded a
layer formed and the electrical resistance of the cell
increased to the point where the current was reduced,
in most cases of this experiment, to 90 per cent be-
low that of the initial value. The flow of current
was finally halted as ions from the anode could no
longer migrated from the anode surface through the
polymer layer into the emulsion. The electrical neu-
trality of the cell was thus ended and the flow of
current was reduced to zero.

Contradiction of Szegavri's Proposed Mechanism.
The proposed mechanism is in contradiction with the
conclusions drawn by A. Szegavri (11) that migration
effects of the colloidal particle, in the case of
rubber, has little influence on the deposition of gum
rubber. I feel that his tests were at high voltages
which affecting a high concentration of latex glo-
bules surrounding the anode. This concentration was
beyond that minimium amount for which a lesser cell
efficiency would have been realized. Naturally, the
power requirment for these high voltages was greater

than necessary. A fact which may have solely caused
the electrochemical application of rubber coatings
to have been replaced by a chemical means of surface
deposition. A positive ion releasing chemical sub-
stance is presently employed to plate rubber on va-
rious surfaces.

Recommendations

The following recommendations are made for future
investigation into the mechanism and application of
electrochemically deposited polymer films.

Electrical Resistance of Deposited Layer. Deter-
mination of the resistance of the deposited layer as a
function of either the linear weight or deposit thick-
ness would supply a balance between layer thickness
and power requirment. As the nature of a deposit is
dependent on the cell voltage, it is recommended that
generator voltages of 35, 50, and 90 be tested on va-
rious emulsions to balance the voltage and power and
plating efficiencies for a single emulsion.

Verification of Mechanism. To verify the mecha-
nism, it may be possible to enter a tracer with the

monomer before polymerization and observe the migra-
tion of the colloidal particles, the resulting con-
centration of particles around the plating electrode,
and the rate of deposition. A weighing device must
be connected to the plating electrode and two of
three time-weight, time-current, or time-concentra-
tion recorders employed. The simultaneous measure-
ment of current, time, concentration, and weight
would be beyond human ability.

Magnetized Plating Electrode. Plating may be
made more efficient by eliminating the attraction
period deemed necessary by adding an electrostatic
field around the plating electrode to attract the
particles. Tracer substances must be employed to
study the time concentration relationship and conse-
quently determine the time of entrance of neutrali-
zing electrodeposition product ions into the colloid-
al layer.

It may be possible to directly coagulate the film
solely from the magnetic effect, however the deposit
will have a lower water resistance depending on the
quantity of unneutralized surface charge. The densi-
ty of the magnetically coagulated films may show va-
riations from those of electrochemical coagulated
films.

Film Properties. Preparation of various films under the same conditions as those of this experiment with subsequent chemical resistance and physical strength measurements will determine the chemical and physical characteristics of the electrodeposited product.

Influence of Solids Content. Solids content may affect current efficiency. This topic is of primary interest in application investigations.

Limitations

The limitations of the experimental investigation follow in this section.

One Polymer. Only a single polymer, polymethacrylate, was studied.

Rate of Monomer Addition. Rate of methyl acrylate addition to the reaction kettle could not be maintained at a constant value.

Reaction Temperature. A one to two degree centigrade temperature fluctuation was inherent in the polymerization apparatus.

Anode Surface Area. The exposed surface area of the copper anode fluctuated from one test to another.

Minimium Generator Voltage. The minimium generator voltage was 24 volts.

Plating Temperature. At all times, the polymer was plated at room temperature ($20^{\circ}C$ to $25^{\circ}C$).

V. CONCLUSIONS

The following section lists those conclusions drawn from both the electroplating and emulsion preparation segments of this investigation which empolyed emulsions prepared from 800 grams of methyl acrylate, 1250 grams of water, 3.2 grams of ammonium persulfate, and 6, 12, 20, 25, or 50 grams of the anionic surfactant, Tergitol, or 20 grams of the nonionic surfactant, Igepal CO-890.

1. Of all the factors in an electroplating operation, cell voltage was estimated to have the largest influence, colloidal charge density next, emulsion solids content next, and cell plating current density next.

2. For all anionic emulsions, maximum deposit thickness was 0.0375, 0.0350, 0.022, 0.017, and 0.0145 inches for generator voltages of 25, 35, 50, 75, and 90 volts.

3. Contrary to the mechanism proposed by Szegavre for electrodeposition of rubber from latex, it was found that the mechanism for the electrodeposition of emulsified polymethacrylate apparently consisted of two distinct steps. The colloids first migrated to the anode and then were rapidly neutralized by the copper ions emanating from the anode when the colloid concen-

tration had reached a critical value required for coagulation.

VI. <u>SUMMARY</u>

To the date of this thesis, little technical knowledge was known of the electrochemical behavior of an emulsified plastic other than that electrodeposition had been effected by Fink and Feinleib (6) from three commercial emulsions of unknown surface active agent nature and concentration.

Analogy was drawn between a more widely understood phenomenon and that of the unknown action of a plastic. Rubber had been coagulated from latex and from commercial butadiene emulsions by an electrical current, and consequently was studied in the literature to enable the experimenter to gain knowledge of variable factors such as latex solids content, stability, and composition in the plating operation.

Electrodeposition conditions as determined by Fink and Feinleib were then integrated with knowledge of the behavior and component quantities of latex to give a slight insight into the problem of the surface deposition action of an electric current on an emulsified plastic.

Polymethacrylate was arbitrarily selected as the plastic which was to be prepared in an emulsion polymerization reaction and then electrodeposited from emulsion in an electrochemical cell. A single anionic surfactant was chosen for the preparation of all five anionic emulsions, and also a single nonionic surfactant chosen for production of the one nonionic emulsion. Tergitol, the anionic surfactant, was added in quantities of 6, 12, 20, 25, and 30 grams per batch which contained 800 grams of methyl acrylate, 1250 grams of water, and 3.2 grams of ammonium persulfate. 30 grams of Igepal CO-890, the nonionic agent, was employed in a single emulsion of identical compositions as those of the Tergitol additions.

A copper anode and a carbon cathode were employed in the electrochemical cell. All emulsions were placed in a porous battery cup which was then placed in a 0.5 normal aqueous sodium hydroxide solution containing the cathode. A line resistance was added entirely for the purpose of reducing the cell current and increasing the plating time so that plating characteristics could be accurately studied. Direct current was supplied to the cell by a 95 ampere, 24-108 volt DC generator, and the cell current measured

during plating as a function of time. For the five
anionic emulsions, generator voltages of 25, 35, 50,
75, and 90 were employed while 25, 50, 90, and 108
volt tests were used on the nonionic emulsion.

Migration and concentration of colloidal parti-
cles immediately surrounding the anode affected the
plating efficiency noticeably when the balance be-
tween charge density on the globule and voltage a-
cross the cell was broken. Attraction of the globule
for the plating surface during the plating of emulsion
I was far below those tests of emulsions II, III, IV,
and V so that a gram equivalent weight of 40-50 per
cent of that expected was observed.

The experiment raised the question as to the fea-
sibility of plating an emulsion directly through the
action of an economical electrostatic field, but re-
alized that any deposit obtained from such a method
will feature decreased chemical resistance and film
protection qualities.

VII. BIBLIOGRAPHY

1. Celanese Chemical Company, "Celanese Acrylates",
   pp. 12. Celanese Chemical Corporation of America,
   New York, N. Y., 1959.

2. ibid. pp. 15-16.

3. ibid. pp. 16-20

4. ibid. p. 29.

5. Eberlin, L. W. and Sheppard, S. E., C. A., 20, 873[6].

6. Feinleib, M. and Fink, C. G., Electrodeposition and
   Electrochemistry of the Deposition of Synthetic
   Resins, Trans. of the Electrochem. Soc., 94,
   809-40 (1948).

7. Groggins, P. H.: "Unit Processes in Organic Synthe
   sis", pp. 859-61, McGraw Hill Book Co. Inc., New
   York, N. Y., 1958. 5 ed.

8. ibid. p. 895.

9. Mantell, C. L.: "Industrial Electrochemistry",
   McGraw Hill Book Co. Inc., New York, N. Y., 1931.
   1 ed.

10. Marlies, C. A. and Schmidt, A. X.: "Principles of
    High Polymer Theory and Practice", pp. 552-3,
    McGraw Hill Book Co. Inc., New York, N. Y., 1948.
    1 ed.

11. Szeqavri, A., Pattern for Progress, Ind. and Eng. Chem., <u>49</u>, sup 89A (1957).

12. Szeqavri, A., Stabilized Latex Compounds Used for Plating, Physical Review, <u>37</u>, 1718 (1931).

VIII. ACKNOWLEDGMENTS

IX. VITA
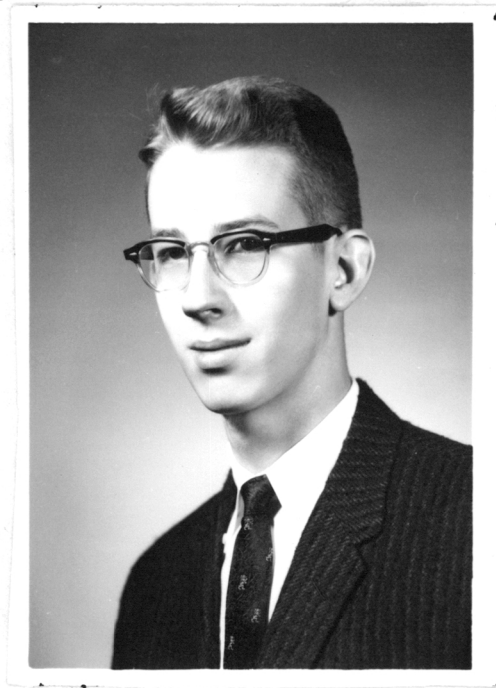
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