

THE EFFECT OF CERTAIN ORGANIC
ADDITIVES ON THE MORPHOLOGY
OF ELECTRODEPOSITED ZINC

THE STATE
UNIVERSITY OF MINNESOTA
DULUTH

by

R. C. VILLAS BÔAS

ProQuest Number: 10781707

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10781707


Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346


A Thesis respectfully submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering .

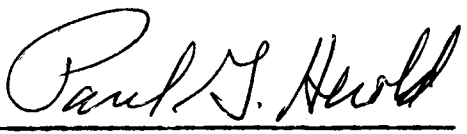
Signed : 
R. C. Villas Bôas

Golden, Colorado

Date: JAN 29 , 1971

ARTHUR LAKES LIBRARY
COLORADO SCHOOL OF MINES
GOLDEN, COLORADO

Approved: 
T. Balberyszski
Advisor


P. G. Herold
Head of Department
Metallurgical Engineering

Golden, Colorado

Date: Feb 10 , 1971

ARTHUR LAKES LIBRARY
COLORADO SCHOOL OF MINES
GOLDEN, COLORADO

ABSTRACT

A study was made of the physical structure of electrodeposited zinc under the influence of seven factors, namely, the acidity of solution, the salt concentration, the current density, the bath temperature, the rate of agitation, the time of electrodeposition, and the concentration of organic additives . The behaviour of electrodeposited zinc was determined for the three classes of organic additives: cationic, anionic and non-ionic .

Preliminary tests were carried out to choose the representative additives for the three classes .

The quality of the deposit was defined as a function of the cathode efficiency and the physical appearance of the cathodic surface .

The effectiveness of the surfactants was determined from a statistical model, according to a two level factorial design analysis . The consistency and significance of the experimental results were obtained and the experimental data discussed .

An electrocapillary study was carried out to establish the behaviour of the various organic additives .

TABLE OF CONTENTS

ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF FIGURESviii
LIST OF TABLES	x
ACKNOWLEDGEMENTSxiii
INTRODUCTION	1
Statement of the Problem	1
Importance of the Study	3
Scope of Research	3
SURVEY OF THE LITERATURE	5
Factors Influencing the Physical Structure of the Deposit	5
The Purity of the Electrolyte	5
The Salt Concentration	6
The Structure of the Substrate Metal	6
The Bath Temperature	6
Acidity of the Solution	7
Current Density	7
Ohmic Factor of the Electrolyte	8
Rate of Agitation	8

Length of Deposition	8
The Presence of Organic and Inorganic Matter	9
Surface Active Substances	9
Classification of Surface Active Agents	11
Mechanism of Adsorption	11
Electrode Processes	13
Reactions at Solid Surfaces	13
Hydrogen Polarization and Depolarization.	16
Hydrogen Overvoltage	17
Hydrogen Depolarization	18
Electrocapillary Phenomena	20
The Electrical Double Layer	21
The Electrocapillary Curve	22
Influence of Surface Active Substances on the Electrocapillary Curve	23
Thermodynamics of the Electrocapillary Curve	24
THE FACTORIAL DESIGN OF THE EXPERIMENTS	28
Two Level Factorial Design	30
The Eighth Replicate	31
EXPERIMENTAL EQUIPMENT AND PROCEDURE	37
Equipment	37
Procedure	42
Choice of the Representative Additive	42
The Study of the Seven Factors	43

Electrode Preparation	43
Solutions Preparation	43
Data Acquisition	44
The Electrocapillary Curve	44
EXPERIMENTAL RESULTS	46
Choice of the Representative Surface Active Agent	46
The Factorial Design of the Experiments.	48
The Electrocapillary Curves.	53
DISCUSSION OF RESULTS	56
Choice of the Representative Surface Active Agent	56
Properties of the Chosen Additives	62
The Factorial Design of the Experiments	65
The Electrocapillary Curves.	95
CONCLUSIONS	100
FURTHER RESEARCH	103
APPENDICES	105
Appendix 1: A list of various surface-active agents according to their physicochemical properties	106
Appendix 2: A list of the 128 treatments required in a full factorial design of seven factors, each at two levels	112
Appendix 3: A listing of the computer program used to calculate the statistical consistency and significance of the experimental results	115

Appendix 4: A listing of the computer program used to calculate the F - Ratios of the trans - formed results	124
Appendix 5: Yates' analysis for the significant inter- actions	129
BIBLIOGRAPHY	135

LIST OF FIGURES

Figure	Page
1. Design of the electrolytic cell	38
2. Design of the electrode holders	39
3. The electrolytic cell and thermostat bath	40
4. Side view of the thermostat bath	40
5. View of the control panel for the electrodeposition	41
6. View of the Polarograph used for determining the electrocapillary curves	41
7. The surfaces obtained with various cationic additives	59
8. The surfaces obtained with various anionic additives	60
9. The surfaces obtained with various non-ionic add- itives	61
10. Effect of the chosen additives on the surface-tension of water	63
11. Effect of the chosen additives on the surface-tension of H_2SO_4	64
12. Effect of additive concentration on the morphology of electrodeposited zinc	85

Figure	Page
13. Effect of an increase in all factor levels . . .	87
14. Interaction effect of acidity, current-efficiency rate of agitation, electrodeposition time, and salt concentration on the morphology of the deposit	89
15. Interaction effect of salt concentration, current density and additive concentration on the morpho- logy of the deposit	91
16. Comparison between treatments 1 and 25	92
17. Comparison between treatments 24 and 25	94
18. The electrocapillary curves	98

LIST OF TABLES

Table	Page
1. The chosen levels	31
2. Randomized Order of the treatments	35
3. Levels of the process parameters for the choice of representative surface-active agent	46
4. Choice of surface active agent - Summary of the results	47
5. Treatments with the additive concentration at its * lower level	49
6. Cationic additive treatments	50
7. Anionic additive treatments	51
8. Non-ionic additive treatments	52
9. Drop time of Hg drops against the applied potential.	54
10. Summary of the chosen representative additives . .	57
11. The sixteen treatments in the standard order . . .	66
12. Consistency analysis - The F-ratio	67
13. Probability points of the variance ratio	68
14. Factors which significantly alter the statistical consistency of the results	69

Table	Page
15. Statistical significance of the results	71
16. Percentage points of the t - distribution	72
17. Influence of the main effects	73
18. Effect of temperature and current density on the cathode efficiency - Cationic Additive	76
19. Effect of acidity and time of deposition on the cathode efficiency - Cationic Additive	77
20. Effect of acidity and salt concentration on the cathode efficiency - Cationic Additive	77
21. Effect of temperature and deposition time on the cathode efficiency - Cationic Additive	78
22. Effect of current density and deposition time on the cathode efficiency- Cationic Additive	78
23. Effect of acidity and temperature on the cathode efficiency - Cationic Additive	79
24. Effect of additive concentration and deposition time on the cathode efficiency - Cationic Additive	79
25. Effect of temperature and current density on the cathode efficiency - Anionic Additive	80
26. Effect of acidity and deposition time on the cathode efficiency - Anionic Additive	80
27. Effect of acidity and salt concentration on the cathode efficiency - Anionic Additive	81

Table	Page
28. Effect of the current density and deposition time on the cathode efficiency - Anionic Additive. . .	81
29. Effect of additive concentration and time of deposition on the cathode efficiency - Anionic Additive	82
30. Effect of temperature and current density on the cathode efficiency - Non-ionic Additive. . .	82
31. Standard error of the experiment	83

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Professor T. Balberyszski, Department of Metallurgical Engineering, Colorado School of Mines, for his invaluable guidance and assistance throughout this investigation .

The author's gratitude is also extended to his committee, Dr. F. G. Herold and Dr. W. R. Bull . Thanks also to J. C. Gathje , research assistant of the Department of Metallurgical Engineering for the design of the experimental apparatus used in electrowinning .

Thanks also are due to the author's wife, Irina, for her understanding during this period of study .

Finally, the author would like to thank the Colorado School of Mines for providing Graduate Research and Teaching Assistantships .

The author dedicates this Thesis to his father and mother .

INTRODUCTION

The electrowinning of zinc, from zinc sulphate solutions, accounts today for almost 50 % of the world's zinc production . It is, therefore, surprising how largely empirical is the knowledge of such electrodeposition, lacking not only an understanding of the fundamentals involved but also needing a systematic study of the process parameters and the establishment of optimum conditions for the electrodeposition .

Statement of the Problem

Electrodeposits, being solid metals, are fundamentally crystalline . From the atomic lattice, specific to the metal, crystals are aligned and joined together in various ways to give the physical structure of the deposit, i.e., the various characteristic shapes and patterns which can be observed visually .

The physical structure of the deposit is one of the critical parameters which depends upon such variables as the purity of the electrolyte, the salt concentration, the structure of the substrate, the temperature of the solution, the acidity of the electrolyte, the rate of agitation, the current density, the ohmic factor of the electrolyte, the electrodeposition time, and the presence of organic and/or inorganic matter in the bath .

Advances in the study of these process parameters have been developed to a large extent on a trial-and-error basis or by means of the classical approach in studying these factors, i.e., keeping everything else constant except for one factor, say the salt concentration, and exploring the effects of this on the structure of the deposit . Then, having chosen an optimum salt concentration, the experiments would be repeated, again keeping everything else constant except, perhaps, the bath temperature and this time, exploring a range of temperatures . Having chosen the optimum temperature everything else would be kept as before, and using the salt concentration and bath temperature constant, another factor would be explored, and so on .

The value to be gained from the establishment of a statistical model of process parameters is enormous since one is not restricted to keeping everything else constant while studying the effect of one factor on the whole process. At the same time mathematical analysis will indicate whether the results are significant . Actually, the researcher can vary all the variables and get the influence of a particular variable, as well as some significant interactions of variables, on the process under study.

This investigation is part of a research program to establish the effect of process parameters and optimum conditions for the electro-deposition of metals, being carried out by the hydrometallurgical research group .

It is the purpose of this thesis to develop a statistical method for studying the physical structure of the deposit as a function of three classes of organic additives - cationic, anionic, and non-ionic,

as well as to investigate the fundamentals involved in the electrical nature of the additive being used .

Importance of the Study

The structure of an electrodeposit affects its properties and, therefore, its uses . For instance, brittle deposits cannot be used in mechanical applications; the harder and less ductile electrodeposits are the results of the generally finer grain size and the presence of inclusions in the deposit .

The changes in electroplating conditions affect largely the grain size of the electrodeposit which, in turn, affects the mechanical properties of the metal . Depending on those changes even a worthless deposit can be obtained, one that is burnt and powdery .

Scope of Research

Of the various factors which influence the nature of the electrodeposit, seven were considered in this research . These are :

1. the acidity of the solution
2. the salt concentration of the electrolyte
3. the additive concentration
4. the bath temperature
5. the current-density
6. the rate of agitation
7. the electrodeposition time

A two-level factorial design of the experiments was planned .

A plexiglass electrolytic cell, described in a later section,

was connected to a power supply unit and the electrowinning tests were carried out keeping the various factors of interest at the desired levels. The cathodes were weighed before and after each test giving, therefore, the cathode-efficiencies for the various treatments .

These cathode-efficiencies were considered the quantitative measure of the physical structure and were analysed within the criteria of the two-level factorial design developed in order to get the statistical consistency and significance of the various factors involved in the experimentation, as well as their effects and interactions, for each class of organic additive used .

Finally, an electrocapillary study of the organic additives and their responses in an acid medium was carried out .

SURVEY OF THE LITERATURE

No statistical model on the study of organic additives in electrowinning has been reported so far in the literature .

This survey covers four sections, namely, the factors influencing the physical structure of an electrodeposit, surface-active agents, the electrode processes and the electrocapillary phenomena .

The Factors Influencing the Physical Structure of the Electrodeposit

As reported in the Introduction, the physical structure of the deposit is a function of various factors . They are :

The Purity of the Electrolyte: The foreign matter present in the solution will behave in two ways:

a) it will be deposited on the cathode, causing the formation of a solid solution with the metal being deposited or, the formation of inclusions, i.e., discrete foreign particles present in the electro-deposited metal .

b) it will be precipitated in the solution . For example, hydroxides and other basic compounds formed very near the cathode surface where the hydrogen being evolved reduces the acidity^(1) .

The hydrogen, however, is not always evolved and frequently enters the deposit as an impurity^(2) .

The Salt Concentration: Increasing the supply of ions available for discharge at the cathode favors large grain size^(3,4). If, however, the degree of ionization is decreased by adding an other salt giving the common ion effect, then the grain size is reduced^(3).

Depending on the nature of the salt, more particularly the anion, a change in its concentration can influence the rate of dissolution of the electrodeposited metal^(5). If the salt is not a neutral salt, but an acid or basic salt, it leads to an increase in the acidity or alkalinity of the solution, contributing, therefore, to a decrease or an increase of the pH.

The Structure of the Substrate Metal: A phenomenon known as "continuity" appears some times in the structure of the deposit. This phenomenon is the growth of an electrodeposited metal crystal, with the same habit and orientation of those of the substrate metal crystal. HOTHERSALL^(6) showed that the continuity between metals belonging to the same crystallographic system was possible only when the ratio between their lattice parameters obeyed certain ranges. He developed a theory relating continuity with adhesion between substrate metal and electrodeposit. Confirmed by X-ray and electron diffraction analysis, some degree of continuity always exists, although it is seldom visible in a microscopic examination.

The Bath Temperature: Once the bath temperature is raised, the ionic mobility is increased, the ions arriving faster at the cathode surface causing a very marked increase in grain size. On the other hand, the rate of electrochemical dissolution of the metal species usually in-

creases with a rise in temperature^(5). However, the dependence of the rate of dissolution on temperature is not as simple as it would appear at a first glance, because it is physicochemical and sometimes a chemical and physical phenomenon, with different kinetic properties and different temperature dependences, i.e., different activation energies .

Acidity of the Solution: Deposits from acid baths are normally large-grained, columnar and are frequently twinned .

Hydrogen ion concentration has an important effect on the electrode process . Increasing the acidity of a solution means that more hydrogen ions are available at the cathode surface, increasing the cathodic process of hydrogen depolarization^(7). This subject will be extensively described in a later section . This effect will decrease the rate of deposition, allow the dissolution of the metal species, and will result in the production of a rough deposit^(8).

The Current-Density: Grain size is reduced as the current-density is increased, for a high current-density favors an increasing rate of deposition depleting the metal ion concentration in the vicinity of the cathode . Occasional exceptions to this occur, for example, in the case of nickel plating solutions in a certain acidity range^(3).

As the current-density is increased the deposited metal has a tendency to sprout out in needle shaped form, inhibiting the formation of thick deposits^(9). The current-density plays a very important role in determining the nature of the deposit . Under some conditions it will result in a spongy, dark, porous form; changing those conditions may give a very hard, adherent deposit .

Ohmic Factor of the Electrolyte: In an electrolyte with low specific electrical conductivity, i.e., a high specific resistivity, the voltage drop across the cell will be higher, for a given current-density, than if the electrolyte had a lower specific resistivity. Thus, for a given potential, the cathode-efficiency will decrease with an increase in the ohmic resistance (5).

Rate of Agitation: Agitation favors an increase in the grain size (3,9), for it helps to bring fresh metal ions to the cathode layer. These changes in grain size are accompanied by considerable changes in hardness (3).

A well known effect of agitation on the solution is to eliminate the phenomenon of concentration polarization, i.e., the polarization due to the ion concentration in the vicinity of the electrode.

NAYBOUR (11) points out that a successful method for preventing dendritic growth must inhibit the formation of the diffusion depleted layer in the vicinity of the electrode surface. Since the diffusion controlled processes in liquids depend very much upon the hydrodynamic conditions (12), the velocity of the medium has a very accentuated effect upon it. The literature shows the current-density being studied over a range of Reynold's Numbers (11).

The Electrodeposition Time: Time is a very important factor in electrodeposition. From Faraday's law, the amount of material being deposited on the cathode is directly proportional to the time allowed for the electrodeposition.

Time has a decisive influence on the acidity of some baths,

on the performance of the additives and on the salt concentration . For example, a long electrodeposition time, without periodic addition of organic reagent will cause a very burned deposit (1) . In zinc electro-winning, a long deposition time will allow the formation of enormous trees on the edges .

The Presence of Inorganic and Organic Additives: These substances are added to the solution in relatively small amounts in order to smoothen or brighten the electrodeposited surface and to prevent excessive dendritic growth, which would cause short-circuiting of the electrodes, a very high local current-density, and a pitted electrode surface .

The presence of organic matter will be discussed in more detail in the next section .

Surface-Active Agents

Certain substances are strongly adsorbed at surfaces or interfaces in the form of an oriented mono-molecular layer . These substances are called surface-active agents .

The adsorption phenomena occurring under the influence of these substances are a dynamic process, leading to an equilibrium between the tendency to adsorb and the tendency to mix completely due to the thermal motion of the molecules .

The surfactants are polar, containing a hydrocarbon chain of variable length and a solubilizing group . The hydrocarbon chain is hydrophobic, i.e., water repellent, and the solubilizing group is hydrophilic, i.e., water attracted . These two groups, constituting a molecule, impart to it a property of being active at interfaces by reducing the surface-

tension of the solution .

The orientation of molecule at interfaces depends on the components of the interface . At the interface between two immiscible substances, the hydrocarbon chain is oriented towards the hydrophobic phase and the solubilizing group is oriented towards the hydrophilic substance .

The presence of organic matter in electrolytes has been studied and is known to affect the electrodeposit . One of the first reported papers on the subject was that of CLASSEN^(13), who in 1906 took out a patent claiming that the deposit of zinc is much improved if certain organic compounds of the glucoside class are added to the electrolyte . The substance he suggested to use was licorice root or extract.

Other experiments using addition of small amounts of licorice to the electrolyte are reported in literature^(14). The conclusions always are that this substance has a very marked effect on the zinc deposits obtained . It was observed that a very small amount of licorice is occluded in the deposit .

Other additives reported in literature are beta-naphthol, starch and glue, all improving the bath conditions for plating^(30).

According to ANTROPOV^(15), the effects caused by organic compounds are not only a function of their chemical properties and structure, but depend also on the nature of the metal being plated or dissolved, on the composition of the medium and on the conditions under which the overall process occurs . Organic compounds show a selectivity of action which has not been explained satisfactorily . Under certain

conditions they can protect a given metal from dissolution and prevent dendritic growth. At same time, they can loose this ability under other conditions, such as change in concentration, or with other metals .

Classification of Surface-Active Agents: Surface-active agents are grouped into three classes, according to their physicochemical properties^(16). They are :

- a) cation-active compounds
- b) anion-active compounds
- c) non-ionic compounds

The properties of the surface-active molecules can be varied at will^(17), by changing the length of the hydrocarbon chain and/or modifying the nature of the solubilizing group .

Appendix 1 lists the various surface-active additives according to their charges^(16).

Mechanism of Adsorption

The rate of diffusion of the surface-active molecules through the solution toward the interface determines the formation of the adsorbed layer .

Most of the electrochemical processes are greatly influenced by the adsorption of organic substances . Unusual physical properties are observed in solutions of highly surface-active substances . Although they act as normal electrolytes in dilute solutions, at defined concentrations several physical properties change abnormally . For instance, the increase in osmotic pressure with concentration is asymptotic, suggesting

that molecular association is taking place . However, with the electrical conductivity remaining high, ionic dissociation still exists .

This behaviour is explained (18) by the existence of organized aggregates, called micelles, of the surface-active ions, in which the lipophilic hydrocarbon chains are oriented toward the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. These micelles could also be formed by non-ionic surfactants at small concentrations .

Beyond the critical micelle concentration, i.e., the concentration at which there exists a large number of micelles, the surface-tension of the solution does not change appreciably, since the micelles themselves are not surface-active .

Adsorbed layers can have a very great influence upon the kinetics of electrochemical processes . FRUMKIN (19) gives examples of this nature, i.e., when in the presence of adsorbed layers, a limiting current nearly independent of the potential is observed, indicating that the rate determining step is the penetration of the dissolved reacting particles in the adsorbed layer .

In some reactions, although the adsorption influences the rate, the mechanism apparently remains the same . This is, for instance, as reported by FRUMKIN - after ERSHLER, RANGLES, and GERISHER -, the case of the exchange of zinc between Zn-amalgam and $ZnSO_4$ solution .

It is a well known fact that some inorganic ions retard the hydrogen evolution, e.g., on a Hg-electrode from a dilute HCl solution, because of the change in the distribution of the potential within the

double layer at the metal/solution interface (19) .

This electrostatic picture, although perfectly valid for inorganic ions, is not so easily structured for organic compounds . FRUMKIN suggests that, at least in the case of organic cations it is partly possible because of the strong dependence of those cations on coulombic forces since the potential at a distance of closest approach of the reacting particle to the electrode surface is reversed .

The action of adsorbed neutral molecules and, to some extent, the action of large organic cations is related to the coverage of the surface by adsorbed particles .

An adsorbed layer can act in two ways :

a) it can create unfavorable conditions at the electrode/solution interface for the process of discharge . These unfavorable conditions can be set on certain areas of the electrode surface, for instance, on the surface peaks, contributing, therefore, to the development of a homogeneous deposit .

b) by hindering the approach of the reacting particles to the surface .

Electrode Processes

In order to better understand what is happening on an electrode , it is useful to review some important facts about the reactions at solid surfaces, and about hydrogen polarization and depolarization .

Reactions at Solid Surfaces: The surface of a solid can be thought of chemically as an array of dangling bonds⁽²⁰⁾ . Since the solid

surfaces are non-homogeneous we observe great variations in reactivity, depending on the face of the crystal. Atomically rough surfaces show the greatest reactivity, while the close packed surfaces are the least reactive. On the other hand, as stated by VERMILYEA^(20), on close packed surfaces the atoms at steps and kinks are more reactive than atoms in normal position in the plane .

Great variations in the surface structure of a crystal, whose qualitative evidence comes from observations of crystal growth^(21), are observed with adsorption and reaction at solid/electrolyte interface .

VERMILYEA, after BUCKLEY, points out the principal aspects of those qualitative observations^(20);

a) the adsorption takes place preferentially on established faces of growing crystals .

b) the addition of small amounts of impurities changes the shape of growing or dissolving crystals .

Crystals ranging from large polyhedra through whiskers to the extremely fine polycrystals of bright deposits can be grown by changing the solution .

The interpretations of the specific interactions are not satisfactory at the present time . All those interpretations, involving changes in the relative surface energy of various faces, changes in the kinetic processes involved in atom deposition or dissolution at surfaces, are feasible^(20,21) .

The important point, however, is that the interactions of solutions with solid surfaces are highly specific and vary markedly with

the structure of the surface . The reactivities of the various crystal faces are heavily dependent upon the variations from face to face of a crystal, in the surface electrical double layer .

FRUMKIN has demonstrated the effects of the structure of the double layer at the metal surface on the electrode processes . Those effects are of three kinds:

- a) the effect of the double layer field in altering the distribution of ions in the solution near the electrode .
- b) the field in the double layer may modify the adsorption of a charged or uncharged substance on the surface .
- c) the field in the double layer may change the rate of coupled reactions occurring in the solution near the surface .

A different thermionic work function arises in each face of a crystal placed in a solution, although it is at an uniform potential .

A general correlation between the thermionic work function, i.e., the energy gradient required to separate an electron in the ionization of a metal atom and remove it to a distance where electrostatic interaction between the ion and electron becomes infinitely small, and the point of maximum electrocapillary potential of the metal in solution, i.e., the value of the potential when the other measured variable in an electrocapillary curve is at its maximum value, does exist, hence a different solution double layer is expected at each face of a crystal (20) .

The concentration of ions in the solution near each face will therefore differ . As a result, the adsorption of species from the solution may differ on each face, and different reactions may occur in

the solution near each face .

As stated by VERMILLYEA^(20), such effects decide the type of overall reactions which can occur in various regions of a metal surface at any instant .

For instance, with the repulsion of the ion involved from the double layer, the cationic reaction may be inhibited throughout large regions of the surface . On the other hand, the anodic reaction could be confined to certain regions of the surface because of the exclusion of acceptor ions from the surface elsewhere . As a result, pitting can occur in those areas .

Hydrogen Polarization and Depolarization: The decrease in the initial potential difference between two electrodes in a galvanic cell is called polarization . Hence polarization is a measure of the deviation of the actual electrode potentials from the initial static potentials ,

Two types of polarization phenomena can be present in an electrolytic cell . Those are the anodic and cathodic polarization .

a) anodic polarization is defined by the displacement of the anode potential toward a more positive potential .

b) cathodic polarization is defined by the displacement of the cathode potential toward a more negative potential .

Depolarization is an electrode process that decreases the polarization on the surface of an electrode . By the very same reason that anodic and cathodic polarization occur, anodic and cathodic depolarization exist .

The displacement of electrons^(5) in a polarization pheno-

menon is achieved faster than the process of depolarization or such secondary process as diffusion .

TOMASHOV^(5) suggested the following steps for both cathodic and anodic polarization :

a) chemical polarization, i.e., any retardation of the electrode process by interfering with the electrode reaction .

b) concentration polarization, i.e., any cumulative concentration of the metal ions at the vicinity of the electrode surface, due to a loss in the ability of the ions to diffuse into the solution .

Hydrogen Overvoltage: Hydrogen overvoltage is a cathodic polarization phenomenon at a given current density, caused by hydrogen evolution at a potential more negative than that of the hydrogen electrode in the same solution, without passing current . Any potential in excess of the reversible potential of an electrode is defined as overpotential or overvoltage^(10) .

Hydrogen overvoltage has a tremendous importance in electrochemistry and it has been established^(5) that it is highly dependent on the material, impurities, the state of the cathode surface, the nature of the solvent, the presence of surface-active agents, presence of polyvalent cations and those cations capable of being discharged on the cathode in the presence of oxidizing agents, particularly oxygen . Following is a summary of the effects of the various factors on hydrogen overvoltage^(10) :

a) condition of the electrode surface: the rougher the electrode surface, the lower the overvoltage .

b) purity of the electrode metal: impurities, even at very

small concentrations may alter the overvoltage .

c) length of electrolysis: a certain length of time is required to reach the maximum overvoltage .

d) temperature variation: this is a controversial point . Some researchers found that increasing temperature lowers the overvoltage, others that it raises it, and still others that it does not change at all.

e) exposure of the reaction to light: the electroevolution of hydrogen and oxygen is accelerated by exposure of the electrodes to light of short wave length .

f) alternating current: the superimposition of alternating current lowers the overvoltage .

g) time: overvoltage may increase or decrease with time .

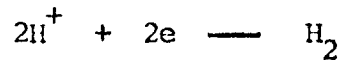
h) surface tension: no definite relation

i) pressure and acidity: hydrogen overvoltage is independent of external pressure and practically independent of the acidity .

Hydrogen overvoltage is of great importance in electrochemical reactions since without it the electrochemical dissolution of metals would occur at very high rates . Some of the known electrolytic processes, such as the deposition of Zn in an acid media, would not take place because hydrogen would evolve preferentially .

Hydrogen Depolarization: Hydrogen evolution on a cathode is called hydrogen depolarization .

The hydrogen ion discharge at the cathode is given by the following general reaction:



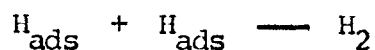
TOMASHOV (5), after FRUMKIN, gives the consecutive steps for such a discharge in acid media:

a) diffusion of hydrated hydrogen ions - hydronium ions - H_3O^+ (or $\text{H}^+ \cdot \text{H}_2\text{O}$) to the cathode .

b) discharge of the hydronium ions with the formation of adsorbed hydrogen atoms



c) recombination of the hydrogen atoms



d) diffusion of the hydrogen molecules or atoms from the cathode or the formation and detachment of hydrogen bubbles .

Dissolution of the electrodeposited metal, or broadly speaking corrosion of metals, with hydrogen evolution at the cathode may be characterized by (5):

a) if dissolution takes place in concentrated alkali or concentrated acid there is little dependence of the dissolution process on concentration polarization .

b) with the initial cathode potential being dependent on the acidity - or pH -, the dissolution process is greatly dependent on acidity - or pH - .

c) with the hydrogen overvoltage being dependent upon the

composition and state of the cathode surface, the dissolution process is greatly dependent on the cathode material .

One of the dissolution processes where the cathodic process is constituted almost entirely by the discharge and evolution of hydrogen is the dissolution of Zn in H_2SO_4 or HCl . Dissolution will be greatly accelerated by the presence of cathodic impurities that lower appreciably the hydrogen overvoltage .

Electrocapillary Phenomena

The relations between interfacial potential, surface tension, and adsorption are called electrocapillary phenomena .

In order to explain these relations, specially when the system being investigated contains surface-active molecules, it is necessary to understand the electrocapillary phenomena .

When charged colloidal matter is dispersed in a given medium, they constitute an electrolyte system . Being so, this system must contain equivalent amounts of oppositely charged ions in order to maintain the condition of electroneutrality of the system . However, the charged colloidal species having, of course, colloidal dimensions may have a net charge many times greater than that of simple monovalent ions .

Since the electrolytic system containing colloidal matter may have other ions, both of opposite and similar charge to that of the colloidal species, an excess of opposite charged ions must be present in the electrolyte, in the locality of each colloidal particle, according to DEBYE-HUCKEL theory, in order to assure electroneutrality of the

system .

As a matter of definition, those ions with opposite charge to that of the colloidal species are called counter-ions; those with similar charge are called co-ions .

The electrical Double Layer: (18) The distribution of the counter-ions and co-ions in the locality of a charged surface immersed in a polar medium, and consequently the electric potential that arose in this region, is interpreted and explained by the electrical double layer theory.

Three different views of the electrical double layer were proposed, one almost complementing the other .

The first, proposed by HELMHOLTZ, assumes only electrostatic forces being active in the double layer .

The second, proposed by GOUY and CHAPMAN, assumes that thermal motion and electrostatic forces have a decisive influence upon the ions located in the liquid side of the double layer . The thermal motion and electrostatic forces together create a diffuse double layer . This theory has been developed mathematically using the MAXWELL-BOLTZMANN distribution law and the POISSON equation .

The third, proposed by STERN, includes adsorption as one of the decisive forces acting on the ions in the liquid side of the double layer . Thus, the STERN's picture of the double layer includes adsorption, thermal motion and electrostatic forces .

Actually, the STERN's model of the double layer introduces a correction for the finite size of the ions in the first atomic layer adjacent to the charged surface . Although, still a crude picture, the

STERN theory gives the best model of the double layer to date . However, a possible deformation of the adsorbed ions was not considered by STERN^(10) .

The Electrocapillary Curve: This curve expresses the relation between the potential of a metal surface and the surface-tension at a metal/electrolyte solution interface .

The technique used to obtain an electrocapillary curve for a metal other than Hg is very sophisticated and complex .

According to ANTROPOV^(15) the electrocapillary behaviour of solutions at other metal interface can be deduced from the behaviour on mercury, if his concept of a scale of potentials is used . This concept will be discussed later .

LIPPMANN^(22) , studying the interaction between surface-tension and the drop of potential at a mercury/electrolyte interface, found that the surface-tension of cathodically polarized mercury first increases, and then decreases again with increasing negative potentials, giving a parabolic shaped curve .

In order to understand this relationship one must know that the total surface-tension depends on two effects^(22) :

- a) attractive van der Waals forces on the surface atoms or molecules which act collectively to decrease the surface-area .
- b) an electrical contribution to the surface energy, due to the repulsive coulomb force between fixed charges, which acts to increase the surface-area, hence counteracts the van der Waals forces .

If we are going to cathodically polarize the Hg surface, its

initially positive charge, no potential being applied, will decrease, increasing, therefore, the surface-tension to a maximum point, where the surface is uncharged . This maximum is called electrocapillary maximum, isoelectric point, electrocapillary zero, or point of zero-charge .

At this point it is worthwhile to observe that, although, at the maximum of the electrocapillary curve the charge of the mercury surface is zero, the potential difference between the mercury and the aqueous solution is not . This fact, as explained by FRUMKIN, is due to the presence of water dipoles oriented at the surface, for capillary-in-active substances .

An almost identical curve is obtained^(15,22,23) when we plot the lifetime of the mercury drop against the potential of the dropping - Hg electrode, since the drop time is proportional to the surface tension.

The Influence of Surface-Active Ions on the Electrocapillary Curve: Several organic and inorganic ions are adsorbed on the surface of mercury and, as a result, lower the interfacial-tension between the metal surface and the solution . Therefore, the shape of the electrocapillary curve is altered, and the point of zero-charge is shifted .

The new location of the electrocapillary maximum will depend on the nature of the substance present . Thus, inorganic cations do not change the original position at all, while several anions shift markedly this isoelectric point . Anions such as bromide, thiocyanate, cyanide, iodine, and sulfide are increasingly capillary-active in this order . However, anions such as nitrate, perchlorate, sulfate, carbonate, hydroxide, and phosphate have no influence on the electrocapillary curve^(22) .

The shift due to inorganic anions is toward higher negative values of the electrocapillary maximum .

Organic compounds may shift the maximum depending on their charges . For instance, organic cations will shift the maximum to less negative values than organic anions . Organic non-electrolytes may be capillary-active, shifting or not the maximum but always lowering the surface-tension . As a matter of fact^(22), all organic compounds lower the surface-tension at the maximum, while inorganic compounds may decrease or even slightly increase the surface-tension at this point .

Thermodynamics of the Electrocapillary Curve: As explained by DOLE^(10), the energy of an interface is a function of the performance of mechanical work, gain or loss of heat, and change in interfacial concentration .

The mathematical expression for this function is :

$$dU = TdS + \gamma d\Omega + \sum_{i=1}^p \mu_i d\eta_i + \sum_{j=1}^p \mu_j d\eta_j \quad (1)$$

where:

U = the energy of the interfacial layer

S = the entropy of the interfacial layer

Ω = the surface area of the interfacial layer

μ_i = the electrochemical potential of an ionic constituent per mole, as defined below

μ_j = the chemical potential of a neutral constituent per mole

$d\eta_i$ = the change in the number of moles of an ionic

$d\mu_j$ = the change in the number of moles of a neutral constituent in the interfacial layer

p = represents the ionic constituents of the system

r = represents the neutral constituents of the system

The electrochemical potential is defined by:

$$\bar{\mu}_i = \bar{\mu}_i + z_i F \psi \quad (2)$$

where:

z_i = the algebraic valence of the i_{th} ion

F = the Faraday constant

ψ = the potential at the double layer

At equilibrium $\bar{\mu}_i$ and $\bar{\mu}_j$ are the same on both sides of the interface .

$$\bar{\mu}_i = \bar{\mu}_j \quad (3)$$

From equation (1) it is possible to derive:

$$d\gamma = -\frac{S}{\Omega} dT - \sum_i^p \Gamma_i d\bar{\mu}_i - \sum_j^r \Gamma_j d\mu_j \quad (4)$$

where:

Γ = the surface concentration, i.e., moles divided by surface area

The term $\sum_i^p \Gamma_i d\bar{\mu}_i$ is composed of:

$$\sum_i^p \Gamma_i d\bar{\mu}_i = \sum_i^p \Gamma_i d\bar{\mu}_i' + \sum_i^p \Gamma_i d\bar{\mu}_i'' \quad (5)$$

where the subscripts (') and (") represent the metallic and aqueous phase,

respectively .

Using the relations (2) and (5), equation (4) becomes:

$$\begin{aligned}
 d\gamma = & -\frac{S}{\Omega} dT - \frac{p'_i}{\sum \Gamma_i} d\mu'_i - \frac{p'_i}{\sum z_i F \Gamma_i} d\psi' - \frac{p''_i}{\sum \Gamma_i} d\mu''_i - \\
 & - \frac{p''_i}{\sum z_i F \Gamma_i} d\psi'' - \sum_j^r \Gamma_j d\mu_j \quad (6)
 \end{aligned}$$

Assuming that:

a) the boundary line between the two phases coincides with that dividing the positive and negative charges in the HELMHOLTZ double layer .

b) the double layer is completely polarized, acting as a perfect condenser, i.e., no current flow .

Then:

$$d(\psi' - \psi'') = -dE \quad (7)$$

where:

E = the externally applied e.m.f.

ψ = the potential within the double layer

Defining the charge density as:

$$\sigma = zF\Gamma \quad (8)$$

we must have:

$$\sigma' = \sigma'' \quad (9)$$

for the electroneutrality of the system, and the double layer acting as a condenser . So equation (6) becomes:

$$d\gamma = -\frac{S}{\Omega} dT - \sum_1^i \Gamma_i' d\bar{\mu}_i' - \sum_1^i \Gamma_i'' d\bar{\mu}_i'' - \sum_1^r \Gamma_j d\mu_j + \sigma dE \quad (10)$$

If the system under study is at constant temperature, pressure and composition of both phases, equation (10) becomes:

$$\frac{d\gamma}{dE} = \sigma' \quad (11)$$

which is the LIPPMANN-HELMHOLTZ equation . From this equation it is clear why the charge on the metal side of the double layer must be positive on the anodic branch of the electrocapillary curve, zero at the maximum and negative on the cathodic branch .

THE FACTORIAL DESIGN OF EXPERIMENTS

Numbers are of fundamental importance to any research . However, far more important than the numbers themselves is the question of how significant are these numbers, or what confidence can the researcher, or those who follow him, have in his work . The answer to these inquiries lie in Statistics .

A statistical model in planning and evaluating research is a valuable tool, for it provides the researcher with a mathematical explanation and accuracy of the phenomena being investigated .

In order to develop a statistical model for the study of the factors under investigation in this thesis, a factorial design was chosen for it fits very well the purpose of this study . Main effects as well as interaction effects could be investigated and explained by means of this model .

First of all, it is necessary to establish the factors of interest .

From previous sections, we saw that the physical structure of the deposit is a function of several factors . In this research, zinc was deposited on aluminum, in a cell containing a sulfuric acid solution of zinc sulphate, the anode being a platinum electrode. Surface-active

substances were added to the electrolyte, and their effect on the morphology of the cathode observed .

Of the factors listed in a previous section, one, the ohmic factor of the electrolyte will not be considered because of the very high conductivity of an acid solution of zinc sulphate; two of them, the purity of the electrolyte and the structure of the substrate metal will be implicitly taken into account, since they are constant throughout the experimental procedures . Therefore, we can express the dependence of the physical structure of the electrodeposited zinc by means of an implicit mathematical function:

$$PS = f(H , Z , A , T , I , V , R)$$

where:

PS = the physical structure of the electrodeposit

H = the acidity of the solution

Z = the salt concentration of the electrolyte

A = the additive concentration

T = the bath temperature

I = the current-density

V = the amount of agitation

R = the electrodeposition time

In order to study on a systematic and statistical basis the physical structure of the electrodeposit, it is convenient to subdivide these process parameters into two parts . First, is that concerning the

amount of material actually being deposited ; the other is that concerning the physical appearance of the deposit. The former is a measurable quantity, the latter is a qualitative expression .

In developing a statistical model, however, we must consider the factor which has a measurable value . So, in studying the physical structure of the electrodeposited zinc, we measured the mass actually deposited on the cathode, and observed the physical appearance of the deposit, as a function of the seven factors already discussed . The mass values enables us to perform the mathematical model, and the observed physical appearance gives us a way to compare the surface deposits coming from baths of different compositions .

The Two Level Factorial Design

The study of the seven factors is made between two significant levels, and the observations resulting from this variation are recorded . These levels come from the technical data available in the field under investigation . The chosen levels are given in Table 1 .

If a full factorial design of the experiments, with seven factors each at two level, were carried out, we should have performed $2^7 = 128$ treatments , for each class of organic additive used . With duplication to determine the experimental error involved the total number of treatments would be doubled . This, of course , was not feasible .

However, since many of the treatments were concerned with interactions higher than second order - which have little physical significance -, a fractional-replication of the experiments is possible with-

out the loss of any useful information . Thus, an eighth-replicate of the original factorial design with seven factors was planned to be used as a model .

TABLE 1 - The chosen levels

Factor	Lower level	Higher Level	Units
H	23.00	46.00	gpl
Z	35.91	71.89	gpl
A	0.00	0.01	% by weight
T	20	40	° C
I	30	150	A/sq.ft.
V	50	70	% powerstat output
R	60	120	minutes

The Eighth-Replicate

With the eighth-replicate (25) the original 128 treatments are reduced to 16 . With replication, to allow experimental error 32 treatments for each class of organic additive were carried out .

Since this eighth-replicate is equivalent to a full factorial of four factors, the confounded interactions must be combinations of the first three letters HZA with the last four letters TIVR giving no combination of any three letters .

The following selection is optimum in this respect since, after rejecting the squared letters obtained by multiplication of the various letters and group of letters, we do not get any combination of three letters:

H	TVR
Z	TIR
A	TIV

After multiplication and rejection of the squared terms, the seven confounded interactions are:

HTVR, ZTIR, HZIV, ATIV, HAIR, ZAVR, HZAT

The alias configuration, discharging interactions higher than second order are:

a) main effect:

H	=	TVR	=	ZIV	=	AIR	=	ZAT
Z	=	TIR	=	HIV	=	AVR	=	HAT
A	=	TIV	=	HIR	=	ZVR	=	HZT
T	=	HVR	=	ZIR	=	AIV	=	HZA
I	=	ZTR	=	HZV	=	ATV	=	HAR
V	=	HTR	=	HZI	=	ATI	=	ZAR
R	=	HTV	=	ZTI	=	HAI	=	ZAV

b) first order:

HZ	=	AT	=	IV
HA	=	ZT	=	IR
HT	=	ZA	=	VR
HI	=	ZV	=	AR
HV	=	ZI	=	TR
HR	=	AI	=	TV

$$ZR = AV = TI$$

c) second order

$$HAV = ZAI = IVR = ZTV = ATR = HTI = HZR$$

Finally, the sixteen treatments are derived from a full factorial in TIVR . They are obtained from the multipliers (1), t, i, v, and r.

At this point, it is worthwhile to explain that in factorial design, as a matter of nomenclature, the treatments are coded in the following way:

- a) the letter which represents the factor appears in its lower case when the factor is at its higher level .
- b) it does not appear at all when the factor is at its lower level .
- c) when all the factors are in their lower level, then the code is (1) .

In the selection of the confounded interactions H was associated with TV and R, Z with TI and R, and A with TI and V . Therefore, from the two level factorial theory, the full set of multipliers to use for the fractional factorial treatments is (1), hzat, zai, hti and hzr .

The full sixteen treatments in standard order are given in the following page :

The treatments in a standard order are:

(1)

hzat

zai

hti

hav

ztv

hziv

ativ

hzt

atr

hair

ztir

zavr

htvr

ivr

hzativr

Now, since we need to have the experimental error involved, we made a replication of the sixteen treatments .

In order to avoid the systematic errors, i.e., those due to an existing trend in some parameter throughout the sequence of trials, e.g., operator's skill, rising temperature, deterioration of any used solution or equipment, a randomization of the treatments must be done . This operation is carried out by using a table of Random Numbers^(25,26) .

Thus at the randomized order, we have, with duplication, the order in which the treatments must be done . Table 2 lists the order and the respective experiments .

TABLE 2 - Randomized order of the treatments

Order	Treatment
1	zai
2	hav
3	h zr
4	ativ
5	hzat
6	ativ
7	(1)
* 8	hav
9	zai
10	z tv
11	z tir
12	z tir
13	h tvr
14	i vr
15	(1)
16	h tvr
17	i vr
18	z tv
19	h zat i vr

continuation		
	20	hziv
	21	atr
	22	hziv
	23	hzat
	24	atr
	25	hair
	26	hti
	27	hti
	28	hair
	29	hxr
	30	zavr
	31	zavr
	32	hzativr

The original 128 treatments are listed in Appendix 2 .

EXPERIMENTAL EQUIPMENT AND PROCEDURE

This section describes the design of the equipment and the procedures used in carrying out this research .

Equipment

A plexyglass cell containing two plexyglass electrode holders, shown in Figures 1 and 2 , was placed in a constant temperature bath . The electrolyte was agitated with a magnetic stirrer . The surface of the constant temperature bath was covered by a layer of isopor pieces, in order to avoid excessive evaporation of the bath water . This assembly is shown in Figure 3 .

The cell electrodes were connected to a power supply unit (Harrison 6201B DC , Hewlett and Packard) which once adjusted to a given value of current, maintained a constant current-density . The voltage drop across the cell, measured from the cathode to the anode by means of a digital voltmeter (3430 A , Hewlett and Packard) , was recorded on a recorder (Speedomax Type G, Leeds and Northrup Co.) .

The experimental assembly is shown in Figures 4, 5, and 6 .

To obtain the electrocapillary curves a polarograph (Model XV, Sargent & Co) was used - Figure 6 - . The drop lifes of the mercury drops were measured with a stop-watch .

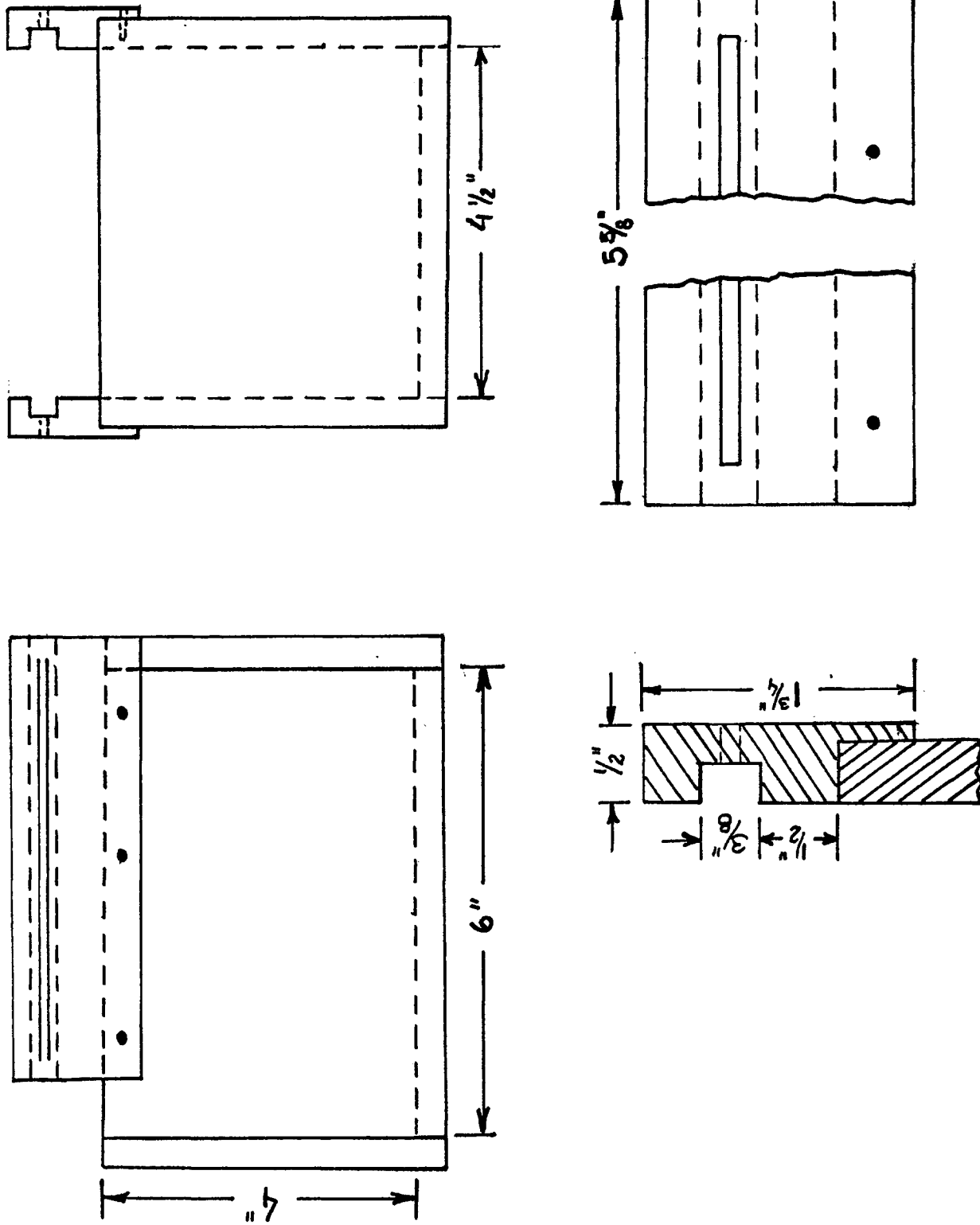


Figure 1 - Design of the electrolytic cell

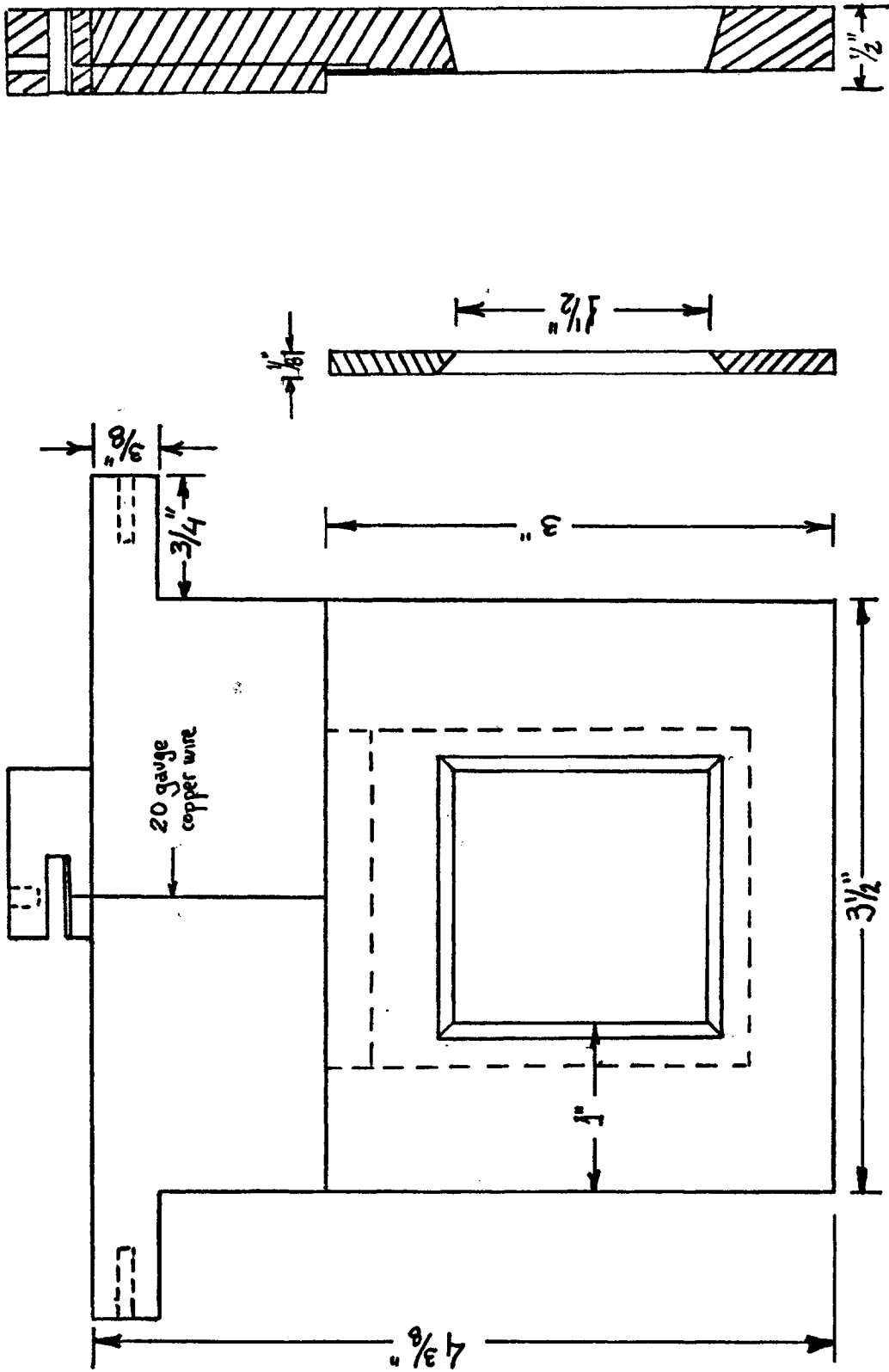


Figure 2 - Plexiglass electrode-holders

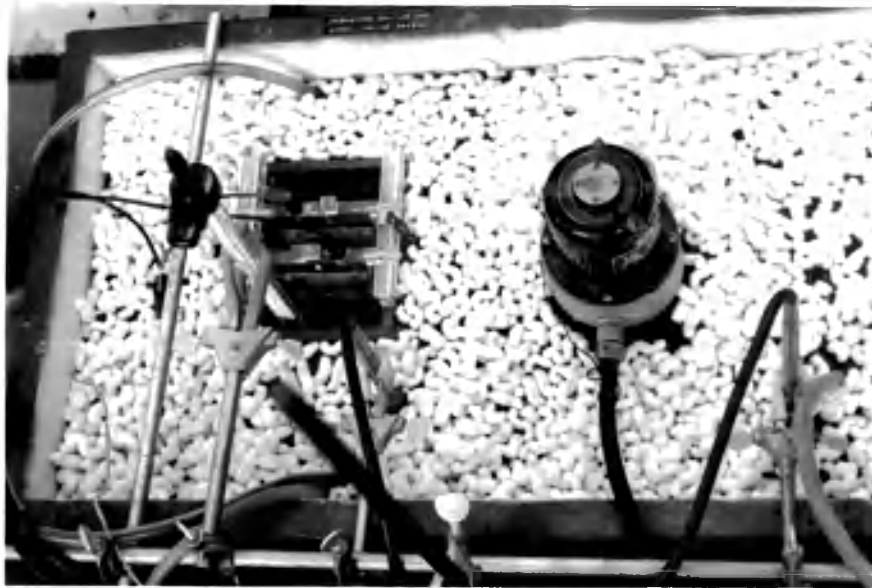


Figure 3 - The electrolytic cell and thermostatic bath

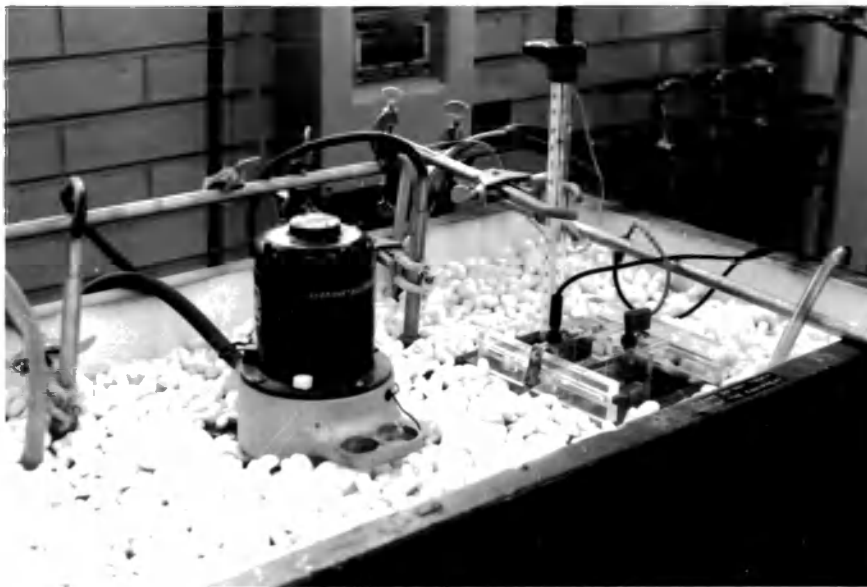


Figure 4 - Side view of the thermostatic bath



Figure 5 - View of the control panel for electrolysis



Figure 6 - View of the polarograph used for the determination of the electrocapillary curves

Procedure

In the first part of this work a study of various commercially available surface-active agents was carried out, in order to choose those additives that resulted in a deposit possessing best morphological properties . In the second part, a study of the effects of acidity, salt concentration, additive concentration, temperature of the solution, current-density, rate of agitation, and length of electrodeposition, for the three classes of organic additives was carried out .

Finally, a study of the relationship between the adsorption behaviour of the organic on the electrode surface, the variation of surface-tension of the metal/electrolyte interface, and the electrical potential drop of the metallic surface was conducted for each selected organic additive dissolved in a 1 N H_2SO_4 solution .

Choice of Additives

Twenty five commercial surface-active agents were chosen, at random, and tested in the previously described electrolytic cell . These substances are listed in Table 4 .

All the factors influencing the physical structure of the deposit were kept at their lower level, except the additive concentration which was at its higher level . After allowing one hour time for the electrodeposition, the cathodes were rinsed with distilled water and dried for 24 hours . They were then reweighted and the cathode-efficiencies were recorded as a function of the particular additive used .

The cathode-efficiencies together with the physical appearances of the cathode surfaces were the criteria used in choosing the

representative surfactant for each group .

Procedure for the Study of the Seven Factors: According to the statistical model described in a previous section, the different treatments were conducted in three successive stages .

Electrode Preparation: A 2 1/2 " by 1 3/4 " starting sheet of high purity aluminum foil was degreased with isopropilic alcohol and covered on both sides with an electrolytic tape . A square opening of 1/100 sq.ft. area was cut on one side of the tape providing an exposed electrode surface . The size of the opening was kept constant in all experiments giving a constant area of deposition . The exposed aluminum area was washed with acetone, after which the electrode was immersed in cold, dilute sulfuric acid, dipped in hot 1N H_2SO_4 solution and, finally, rinsed with distilled water .

The cathodes were dried and weighted .

After electrodeposition, a 24-hour drying period was allowed for each cathode before weighing .

Platinum was used as an anode . The degreasing and cleaning operations described above were performed on the platinum anode as well .

Anodes and cathodes were placed in the electrode holders, shown in Figure 2, and sealed to the plexyglass surface by means of a stopcock grease .

Solution Preparation: Reagent grade seven-hydrated-zinc sulphate and sulfuric acid were used to make up solutions of 0.5 - 1.0N, and 1.0 - 2.0N, respectively . These solutions were stored for no more

than four days, in order to assure their freshness .

Data Acquisition: After all the treatments were completed, their cathode-efficiencies, i.e., the amount of zinc actually deposited divided by the amount of zinc theoretically predicted from Faraday's law, were obtained and a digital computer program was designed to calculate the statistical consistency and significance of the obtained results . A listing of the program in Basic language is given in Appendix 3 . The data were processed by a General-Electric Time-Sharing computer .

The input data were:

a) the square difference between results of each treatment, for computing the statistical consistency .

b) the sum of the results obtained of each treatment, the degrees of freedom of the experiment and the variance of the experiment for computing the statistical significance .

The output were:

a) the ratio of two variances, i.e., the F-ratio, for the statistical consistency .

b) the standardized deviate, i.e., the t-values, for the statistical significance .

Procedures for the Electrocapillary Study: For this study, high-purity, triple-distilled mercury was placed in a reservoir and connected to a glass capillary by means of a rubber tube . All the air was drained from the rubber-tube, assuring that just mercury filled both the tube and the capillary .

The solutions studied were:

- a) a 1 N H_2SO_4 solution
- b) a 1 N H_2SO_4 solution plus a cationic surfactant
- c) a 1 N H_2SO_4 solution plus a anionic surfactant
- d) a 1 N H_2SO_4 solution plus a non-ionic surfactant

They were placed, one at a time, in a polarographic cell .

The tip of the capillary tube was immersed in the solution and a potential was applied to the mercury surface .

The drop lifes were obtained by means of a stop-watch for each applied potential .

With the obtained drop life time and applied potential, the electrocapillary curves were obtained and analysed, using ANTIPOV's approach, to explain the behaviour of the organic additives on the zinc surface .

EXPERIMENTAL RESULTS

The experimental results of this research are divided into three categories, namely, choice of the representative surface-active agent, the factorial design of the organic additive experiments, and the electrocapillary curves .

Choice of the Representative Surface-Active Agent

This study was carried out keeping all the influencing factors at their lower levels, except the additive concentration .

Table 3 gives the used levels for each factor .

TABLE 3 - Levels of the process parameters for the choice of representative surface-active reagents .

Factor	H	Z	A	T	I	V	R
Level	23.00	35.91	0.01	20	30	50	60
Units	gpl	gpl	%	°C	A/Sq.ft.	%	min.

Table 4 summarizes the results obtained

TABLE 4 - Choice of Surface Active Agent - Summary of the Results

Commercial Name	Cathode % Efficiency	Additive Class	Initial Voltage
None used	96.50	-	4.10
Ethoquad C/12	12.41	cationic	4.20
Ethoquad C/25	1.74	cationic	4.09
Ethoduomeen T/25	0.65	cationic	4.07
Ethoduomeen T/13	4.35	cationic	4.02
Ethomeen S/15	8.00	cationic	4.03
Arquad T/50	8.25	cationic	4.02
Armac T	56.32	cationic	4.00
Armac C	22.78	cationic	4.04
Aerosol C-61	1.00	cationic	3.97
FC - 134	49.83	cationic	4.10
FC - 128	75.95	anionic	3.88
FC - 95	71.00	anionic	3.82
FC - 98	69.90	anionic	3.86
Separan AF-30	73.80	anionic	3.78
Neo Fat 8	75.70	anionic	3.85
Neo Fat 18	74.00	anionic	3.90
Superfloc 16	57.00	non-ionic	3.83
Superfloc 127	48.60	non-ionic	3.83
Ethofat O/20	42.60	non-ionic	3.84

TABLE 4 - (Continued)

Commercial Name	Cathode % Efficiency	Additive Class	Initial Voltage
Separan MGL	47.00	non-ionic	3.85
Separan NF-20	41.00	non-ionic	3.82
Separan NF-10	41.50	non-ionic	3.77
Armeen Z	41.30	amphoteric	3.88

The chosen additives were EC-134, EC-95, and SUPERFLOC 127 as representatives of the cationic, anionic, and non-ionic class, respectively . The reasons for choosing the above additives are given in next section .

The Factorial Design of the Experiments

Following the two level factorial design developed for this research, the results listed in Tables 5, 6, 7, and 8 were obtained .

The results obtained at the lower level of the additive concentration are given in Table 5 . Table 6 gives the treatments for the cationic additive . Table 7 the treatments for the anionic additive and, finally, Table 8 for the non-ionic additive .

All the treatments are listed in the randomized order in which they were carried out .

TABLE 5 - Treatments with the additive concentration at its lower level .

Treatment Number	Zn Deposited gm	Cathode Efficiency %	Factorial Code	Voltage Readings
3	0.59480	81.76	h zr	Vo= 3.48V Vf= 3.35V
7	0.28350	77.90	(1)	Vo= 3.81V Vf= 3.63V
10	0.33705	92.66	z tv	Vo= 3.48V Vf= 3.47V
11	3.13675	90.36	z tir	Vo= 6.56V Vf= 5.05V
12	3.09395	90.24	z tir	Vo= 6.32V Vf= 5.03V
13	0.33150	45.55	h tvr	Vo= 3.22V Vf= 3.18V
14	2.53500	69.69	i vr	Vo= 7.70V Vf= 6.00V
15	0.25415	67.15	(1)	Vo= 3.91V Vf= 3.64V
16	0.35520	48.82	h tvr	Vo= 3.45V Vf= 3.14V
17	2.82310	77.61	i vr	Vo= 6.90V Vf= 5.13V
18	0.31600	86.87	z tv	Vo= 3.43V Vf= 3.35V
20	1.50465	82.73	h ziv	Vo= 5.47V Vf= 4.98V
22	1.52375	83.78	h ziv	Vo= 5.31V Vf= 4.99V
26	1.12275	61.73	h ti	Vo= 5.37V Vf= 5.45V
27	1.07210	58.95	h ti	Vo= 4.91V Vf= 4.54V
29	0.60532	83.21	h zr	Vo= 3.59V Vf= 3.92V

TABLE 6 - Cationic-Additive Treatments

Treatment Number	Zn Deposited gm	Cathode Efficiency %	Factorial Code	Voltage Readings
1	0.17940	9.86	zai	V _o = 7.30V V _f = 7.20V
2	0.17600	48.33	hav	V _o = 3.65V V _f = 3.73V
4	0.79200	43.54	ativ	V _o = 6.42V V _f = 5.75V
5	0.25935	71.30	hzat	V _o = 3.31V V _f = 3.33V
6	0.70405	38.71	ativ	V _o = 6.53V V _f = 6.19V
8	0.15420	42.39	hav	V _o = 3.53V V _f = 3.53V
9	0.16550	9.10	zai	V _o = 7.40V V _f = 6.40V
19	2.07350	57.00	hzativr	V _o = 5.04V V _f = 5.15V
21	0.37700	51.83	atr	V _o = 3.65V V _f = 3.55V
23	0.21340	63.26	hzat	V _o = 3.47V V _f = 3.34V
24	0.41015	56.51	atr	V _o = 3.61V V _f = 3.52V
25	1.08775	29.91	hair	V _o = 5.40V V _f = 5.10V
28	1.26005	34.64	hair	V _o = 5.45V V _f = 5.10V
30	0.52990	72.84	zavr	V _o = 3.97V V _f = 4.09V
31	0.51385	70.63	zavr	V _o = 3.80V V _f = 3.96V
32	2.06365	56.76	hzativr	V _o = 5.08V V _f = 4.86V

TABLE 7 - Anionic-Active Treatments

Treatment Number	Zn Deposited gm	Cathode Efficiency %	Factorial Code	Voltage Readings
1	1.46490	80.60	zai	V _o = 6.80V V _f = 5.52V
2	0.27950	76.84	hav	V _o = 3.45V V _f = 3.25V
4	1.09970	60.46	ativ	V _o = 6.20V V _f = 5.24V
5	0.32650	89.95	hzat	V _o = 3.21V V _f = 3.18V
6	1.20655	66.34	ativ	V _o = 6.57V V _f = 5.15V
8	0.24330	66.88	hav	V _o = 3.49V V _f = 3.34V
9	1.30455	71.73	zai	V _o = 7.00V V _f = 5.62V
19	2.80030	79.73	hzativr	V _o = 4.92V V _f = 4.39V
21	0.49060	67.44	atr	V _o = 3.57V V _f = 3.36V
23	0.29445	80.95	hzat	V _o = 3.24V V _f = 3.19V
24	0.47810	65.72	atr	V _o = 3.56V V _f = 3.36V
25	1.77640	48.86	hair	V _o = 5.22V V _f = 4.72V
28	1.88840	58.35	hair	V _o = 5.25V V _f = 4.83V
30	0.62372	85.73	zavr	V _o = 3.78V V _f = 3.54V
31	0.63960	87.92	zavr	V _o = 3.70V V _f = 3.53V
32	2.69605	74.12	hzativr	V _o = 4.78V V _f = 4.38V

TABLE 8 - Non-Ionic Additive Treatments

Treatment Number	Zn Deposited gm	Cathode Efficiency %	Factorial Code	Voltage Readings
1	1.25885	69.22	zai	Vo= 7.10V Vf= 6.25V
2	0.12000	32.99	hav	Vo= 3.45V Vf= 3.38V
4	0.90870	49.96	ativ	Vo= 6.25V Vf= 5.57V
5	0.13620	37.44	hzat	Vo= 3.29V Vf= 3.25V
6	0.91165	50.12	ativ	Vo= 6.47V Vf= 5.63V
8	0.12000	32.99	hav	Vo= 3.53V Vf= 3.54V
9	1.21635	66.88	zai	Vo= 7.20V Vf= 6.29V
19	1.96414	54.01	hzativr	Vo= 4.96V Vf= 4.80V
21	0.31280	42.93	atr	Vo= 3.52V Vf= 3.47V
23	0.15235	41.88	hzat	Vo= 3.28V Vf= 3.30V
24	0.38505	52.94	atr	Vo= 3.57V Vf= 3.53V
25	1.20555	33.14	hair	Vo= 5.35V Vf= 5.11V
28	1.12425	30.91	hair	Vo= 5.43V Vf= 5.21V
30	0.51550	70.86	zavr	Vo= 3.76V Vf= 3.63V
31	0.49730	68.36	zavr	Vo= 3.76V Vf= 3.66V
32	2.29150	63.00	hzativr	Vo= 5.03V Vf= 4.71V

ELECTROCAPILLARY CURVES

Using the polarograph described in a previous section, the drop times of mercury against the applied electrical potential on the mercury surface were recorded .

The range of applied potential was from 0 to -2 volts, measured against an internal standard cell of the polarograph . The drop times were measured three times for each particular applied potential and the average of the three readings was taken as the most probable value .

The mercury head was 89 cm, measured from the laboratory table to the mercury surface in the reservoir .

Table 9 summarizes the results obtained .

TABLE 9 - Drop Time of Hg-drop Against the Applied Potential

Applied Voltage	Time in seconds for the solutions			
	H ₂ SO ₄ 1N	H ₂ SO ₄ 1N + cationic add.	H ₂ SO ₄ 1N + anionic add.	H ₂ SO ₄ 1N + nonionic add.
0	6.00	6.00	5.90	6.00
0.10	6.62	6.62	6.30	6.62
0.20	7.16	7.16	6.85	7.16
0.30	7.64	7.64	7.30	7.54
0.40	8.00	7.90	7.69	7.80
0.50	8.31	8.11	7.91	8.10
0.60	8.46	8.20	8.11	8.10
0.64	8.50	8.22	8.14	8.10
0.68	8.55	8.25	8.20	8.10
0.70	8.57	8.26	8.25	8.10
0.72	8.60	8.27	8.26	8.10
0.76	8.61	8.25	8.29	8.10
0.80	8.65	8.22	8.30	8.10
0.90	8.55	8.15	8.31	8.10
1.00	8.41	8.10	8.29	8.10
1.10	8.29	7.94	8.25	8.10

TABLE 9 - (continued)

Applied Voltage	Time in seconds for the solutions			
	H ₂ SO ₄ 1M	H ₂ SO ₄ 1M + cationic add.	H ₂ SO ₄ 1M + anionic add.	H ₂ SO ₄ 1M + nonionic add.
1.20	8.11	7.62	8.11	8.09
1.30	7.90	7.16	7.90	7.90
1.40	7.70	6.80	7.70	7.70
1.50	7.40	5.70	7.40	7.40
1.60	6.80	5.90	6.80	6.80
1.70	6.00	5.50	6.00	6.00

DISCUSSION OF RESULTS

The results obtained will be discussed under the following three headings:

- a) choice of additive
- b) factorial design of experiments
- c) electrocapillary curves

The Choice of Representative Additive

From the experimental results shown in Table 4, it can be seen that some of the additives inhibit to a certain extent the electro-deposition of zinc. Although all the treatments lower the cathode-efficiency, treatments using the FC - 134, FC - 95, and SUPERFLOC - 127 additives gave reasonable cathode-efficiencies within their own groups, and the best physical structure of the deposited surfaces.

The structures of some surfaces are shown in Figures 7, 8, and 9. The current-efficiencies obtained with the chosen surfactants are given in Table 10, as well as the chemical group to which they belong and their foam heights.

It can be seen from the figures that the surface obtained with additives FC - 134, FC - 95, and SUPERFLOC 127 (Figures 7f, 8f,

and 9f) have a smoother and more dense surface deposit than those obtained with the other additives . Their current-efficiencies are given in Table 10, and if compared to those given in Table 4, we see that these current-efficiencies are not necessarily the highest in their respective groups . However, these additives, namely, FC - 134, FC - 95, and SUPER-FLOC 127 , were chosen as representative of the cationic, anionic, and non-ionic group, respectively, because of the effect they have on the morphology of the deposit, as discussed below .

TABLE 10 - Summary of the chosen representative additives

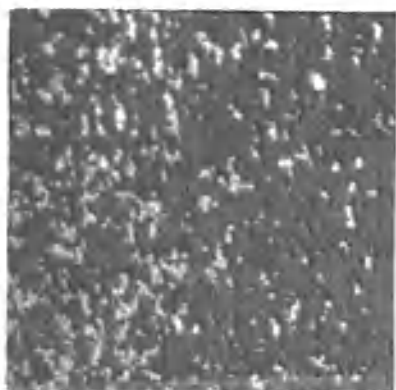
Additive Class	Brand Name	Cathode Efficiency %	Chemical Group	Foam Height 0.01% conc.
Cationic	FC-134	49.83	Fluorocarbon	62 mm
Anionic	FC- 95	71.00	Fluorocarbon	23/5 mm
Non-Ionic	SUPERFLOC 127	48.60	Plyacrylamine	none

Figure 7a shows the surface obtained using ARQUAD T as the additive; the cathode-efficiency is low - see Table 4 -, and the deposition of zinc is hindered . The same conclusions can be drawn from figures 7b, 7c, and 7d which show surfaces coming from a bath using ETHOQUAD C/25, ETHODUQUATEEN T/15, and ETHOQUAD C/25 as additive, respectively . Figure 7e shows the cathodic surface of a bath using ARMAC T . The cathode-efficiency was fairly good - see Table 4 - and the surface obtained was dense, although somewhat rougher than the surface shown in Figure 7f, which

was obtained with FC-134, the representative additive for the cationic group .

The surface shown in Figure 8a was obtained with SEPARAN AP-30 . The cathode surface is smooth, although somewhat porous and presents no brightness . Figure 8b shows a brittle cathode surface ; it was obtained using FC-98 as the additive . Figure 8c is a surface obtained using NEOFAT 8 ; it is brittle and shows signs of shrinkage . The surface shown in Figure 8d is very thin coated and was produced using NEOFAT 18 . Figure 8e shows a brittle and shrinking surface obtained using FC-128 as the additive . Finally, for the anionic group, the surface shown in Figure 8f, obtained with the representative additive, FC-95, is bright, smooth and dense .

Figure 9a shows a cathode obtained with FC-170 as the additive; it is a burnt and brittle deposit and the cathode-efficiency is low . Figure 9b shows a deposit obtained with SEPARAN MGL . This deposit is smooth and dense, less bright than any of the surfaces obtained with the non-ionic additives . Figure 9c shows a cathode obtained from a bath using SEPARAN NP-20; it is a brittle and slightly burnt surface . Figure 9d shows a metallic bright surface obtained with SUPERFLOC 16 which, however, is very brittle . Figure 9e, SEPARAN NP-10, shows a very bright surface . However, it has the disadvantage of being brittle and having a tendency to shrink and fall off the starting sheet . Finally, Figure 9f shows the surface obtained with the chosen representative additive for the non-ionic class, SUPERFLOC 127 . It is a bright metallic, smooth and dense deposit .



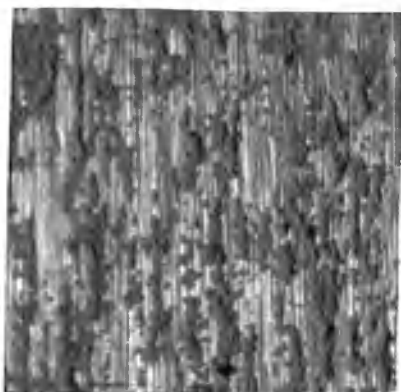
a) ARQUAD T



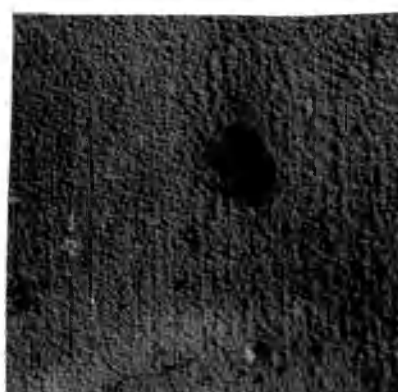
b) ETHOQUAD C/15



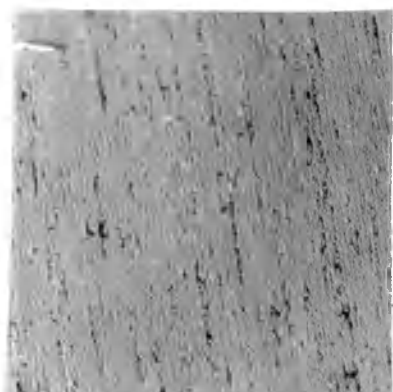
c) ETHODUOMEEEN T/15



d) ETHOQUAD C/25



e) ARIAC T



f) FC-134

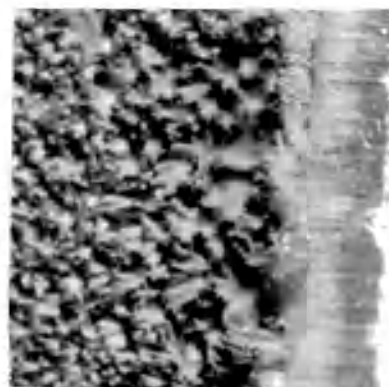
Figure 7 - The Surfaces Obtained Using Various Cationic Additives (15X)



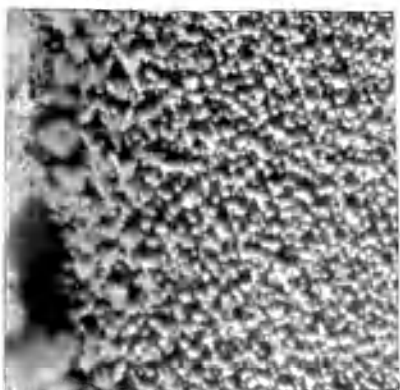
a) SEPARAN AP-30



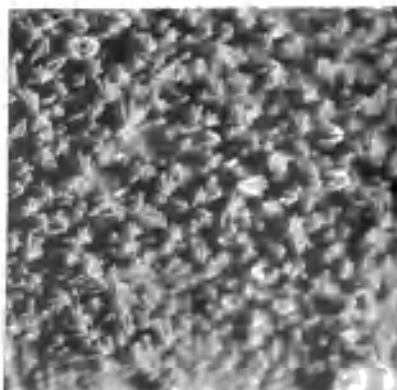
b) FC-98



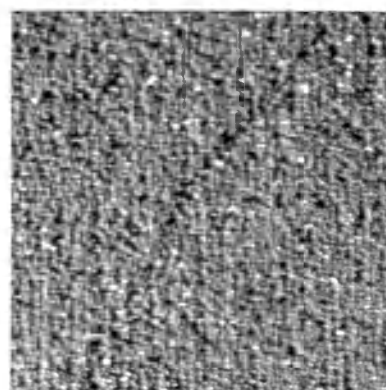
c) NEOFAT 8



a) NEOFAT 18

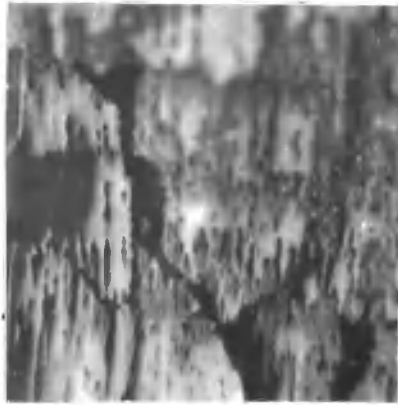


e) FC - 128



f) FC - 95

Figure 8 - The Various Surfaces Obtained Using Different Anionic Additives (15X)



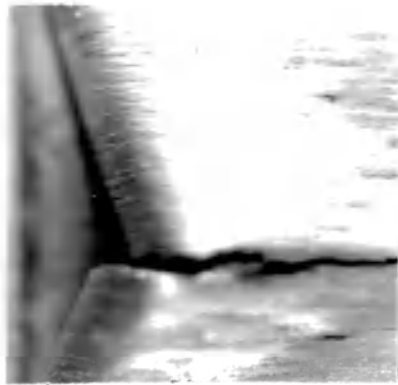
a) FC - 170



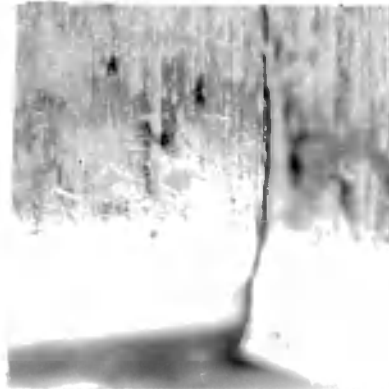
b) SEPARAN MGL



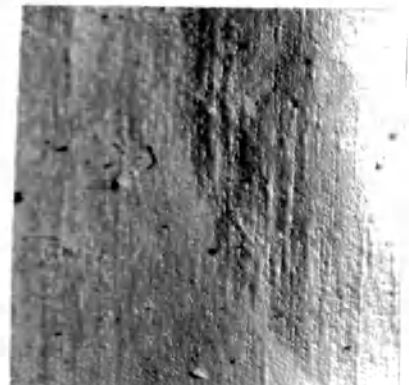
c) SEPARAN NP - 20



d) SUPERFLOC 16



e) SEPARAN NP - 10



f) SUPERFLOC 127

Figure 9 - The Surfaces Obtained Using Various Non-Ionic Additives (15X)

From the photographs shown in Figures 7f, 8f, and 9f, we can see that all the three surfaces are built up of fine grain sizes . On the "cationic" surface we observe some pitting and cracks probably due to the hydrogen evolution . The "anionic" surface is the roughest of the three, showing grain size bigger than the other two surfaces . The "non-ionic" surface is the smoothest of the three .

Properties of the Chosen Additives: The chemical structure of the FLUORAD surfactants, the FC - 134 and FC - 95, is characterized by a stable fluorocarbon tail and a solubilizing group Z . The nature of Z is not disclosed^(27,28), although it can be an anionic, cationic or non-ionic group . The fluorocarbon tail brings to these surfactants very good resistance to thermal, chemical, electrical and biological attack with good resistance to radiation . This tail possesses a very low solubility in both aqueous and organic systems, as well as an extremely low surface-energy .

The SUPERFLOC 127 flocculant⁽²⁹⁾ is the highest molecular weight polyacrylamine of the SUPERFLOC series . It is essentially non-ionic in nature, giving micelles formation at low concentrations .

Figures 10 and 11 show the effect of those additives on the surface-tension of distilled water and an H_2SO_4 solution .

It can be seen from these figures that in all cases an increase in the concentration of additive will decrease the surface - tension .

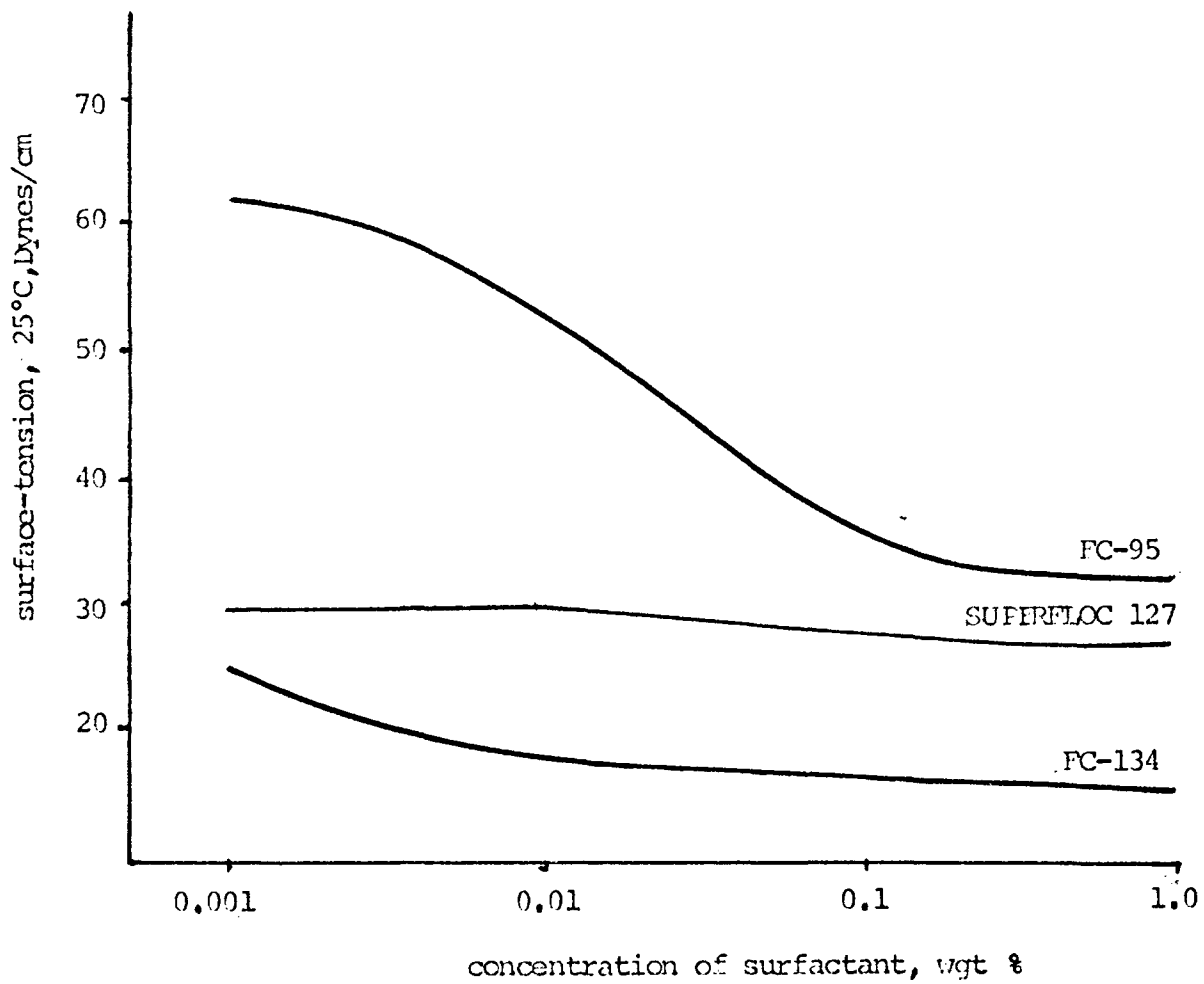


Figure 10 - Effect of the Chosen Additives on the Surface-Tension of Distilled Water

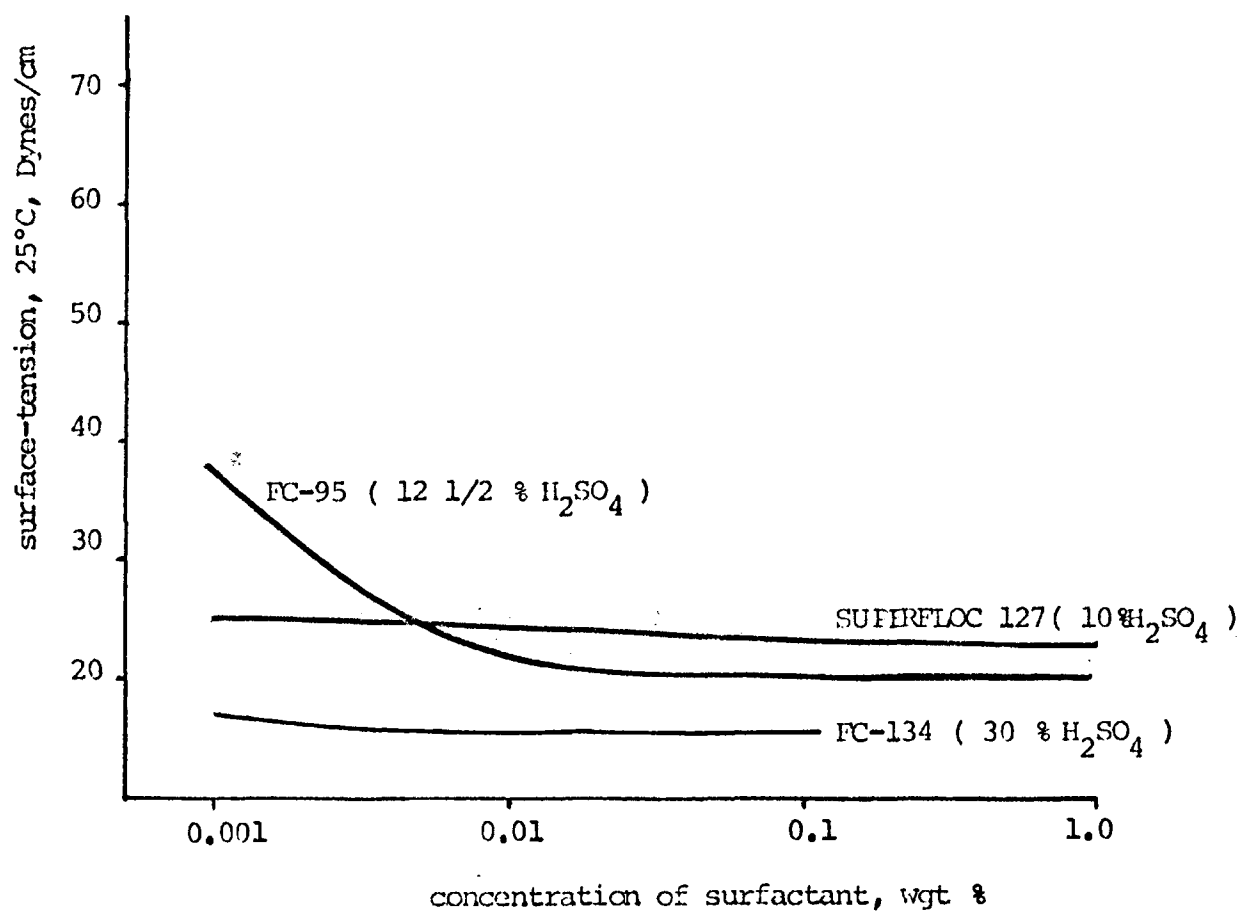


Figure 11 - Effect of the Chosen Additives on the Surface-Tension of a solution of H₂SO₄

Factorial Design of Experiments

With the cathode-efficiencies given in Tables 5, 6, 7, and 8, Table 11 summarises these results in the standard order required by the analysis of consistency and significance of the results .

The analysis of statistical consistency and significance of an experiment is of paramount importance, since one can assess the reproducibility of the experimental results . One must know if the individual variation around the mean value is not large enough to invalidate the conclusions coming from the results obtained .

This knowledge is given by the analysis of consistency of the experiment . Statistical consistency is measured by calculating the standard deviations of the results about their mean .

Significant differences in standard deviations are detected by means of the F-ratio . Table 12 shows the F-ratios obtained from the analysis of consistency for the cationic, anionic, and non-ionic additive experiments, as they come from the computer calculations shown in Appendix 3 .

TABLE 11 - The Sixteen Treatments in the Standard Order

Treat. Number	Code	Factor Levels				Cathode-Efficiencies for Various Agents								
		h	z	a	t	r	Cationic	Anionic	Non-Ionic					
1	(1)	23	35.91	0	20	30	50	60	77.90	67.15	77.90	67.15	77.90	67.15
2	hzat	46	71.89	0.01	40	30	50	60	71.30	63.26	89.95	80.95	37.44	41.88
3	zai	23	71.89	0.01	20	150	50	60	9.86	9.10	80.60	71.73	69.22	66.88
4	hti	46	35.91	0	40	150	50	60	61.73	58.95	61.73	58.95	61.73	58.95
5	hav	46	35.91	0.01	20	30	70	60	48.38	42.39	76.84	66.88	32.99	32.99
6	ztv	23	71.89	0	40	30	70	60	92.66	86.87	92.66	86.87	92.66	86.87
7	hziv	46	71.89	0	20	150	70	60	82.73	83.78	82.73	83.78	82.73	83.78
8	ativ	23	35.91	0.01	40	150	70	60	43.54	38.71	60.46	66.34	49.96	50.12
9	h zr	46	71.89	0	20	30	50	120	81.76	83.21	81.76	83.21	81.76	83.21
10	atr	23	35.91	0.01	40	30	50	120	56.51	51.83	67.44	65.72	42.94	52.94
11	hair	46	35.91	0.01	20	150	50	120	29.91	34.64	48.86	58.35	33.14	30.91
12	ztir	23	71.89	0	40	150	50	120	90.36	90.24	90.36	90.24	90.36	90.24
13	zavr	23	71.89	0.01	20	30	70	120	72.84	70.63	85.73	87.92	70.86	68.36
14	htvr	46	35.91	0	40	30	70	120	45.55	48.82	45.55	48.82	45.55	48.82
15	ivr	23	35.91	0	20	150	70	120	69.69	77.61	69.69	77.61	69.69	77.61
16	hzativr	46	71.89	0.01	40	150	70	120	57.00	56.76	79.73	74.12	61.00	63.00

TABLE 12 - Consistency Analysis - The F - ratios

Treatment Number	Code	Main Effect	F-ratios		
			Cationic	Anionic	Non-Ionic
1	(1)				
2	hzat	T	1.52	2.22	1.26
3	zai	I	2.46	1.12	1.77
4	hti	TI	1.14	1.25	1.12
5	hav	V	1.37	1.40	1.31
6	ztv	HR	1.05	1.58	1.30
7	hziv	HZ	2.52	1.05	5.65
8	ativ	A	1.34	1.78	1.07
9	h zr	R	2.27	2.17	1.46
10	atr	TR	1.18	1.05	2.30
11	hair	IR	4.64	3.57	2.40
12	ztir	Z	2.51	1.79	2.02
13	zavr	HT	1.91	1.53	2.19
14	htvr	H	1.82	1.06	2.57
15	ivr	HZR	1.48	1.09	1.84
16	hzativr	AR	1.04	1.26	3.49

From the F-ratios given in Table 12 and since each of the eight individual contributions to each estimate is based upon two observations, hence one degree of freedom, there are eight degrees of freedom for the experiment .

Using a Table of probability points of the variance ratio, i.e., the F-ratio, with eight degrees of freedom, we get ^(25,26) :

TABLE 13 - Probability Points of the Variance Ratio

Probability points	F-ratios
0.100	2.50
0.050	3.44
0.025	4.43
0.010	6.18

The analysis of consistency is carried out comparing the values obtained in Table 12 with those listed in Table 13 . The F - ratios for the probability points higher than 10 % are not significant; therefore, estimates of the same variance .

On the other hand, if the variance estimates obtained at one level of some factor are significantly higher than those obtained at the lower level, the F-ratio will be significant, i.e., the increase or decrease of this factor level will significantly affect the consistency of the cathode-efficiency value obtained and, therefore, its probability of occurring by chance is very small .

Examining Table 12 and 13, we can see that the F-ratios lying within the range of probability points of Table 13 are:

TABLE 14 - Factors which Significantly Alter the Statistical Consistency of the Results

Type of Additive			
Cationic	Anionic	Non - Ionic	
IR	IR	HZ	AR
2.5%	5.0%	2.5%	5.0%

These results show that the variance does vary within the levels of the factors listed in Table 14 . However, as explained in statistical theory (25,26) , the F test is very "robust", i.e., it is not seriously invalidated by moderate amounts of variance inhomogeneity .

One way of solving such a problem is to transform all the experimental results into their logarithms and again carry out the consistency analysis . If the new obtained values of the F-ratios are not significant, the variances are homogeneous and the analysis is valid .

Appendix 4 show such a calculation for the three sets of organic additives . From these calculations we can consider Table 14 as meaningless and, therefore, the variances within the treatments

are homogeneous, for a given additive .

Having determined the effects of the factor levels on the homogeneity of variance, we can analyse the statistical significance of the results . This analysis is based on the homogeneity of the variance, already discussed, and can be done once this homogeneity is assured .

As stated earlier, 32 treatments were performed in order to provide us with an independent estimate of error .

Actually, sixteen treatments with two observations in each having one degree of freedom were compared . The total number of degrees of freedom is, therefore, 16 .

Table 15 show the value of the mean difference and \underline{t} - the standardized deviate - for the three sets of experiments performed, i.e, using cationic, anionic, and non - ionic organic compounds .

This table indicates the probability of the data being meaningless . If this probability is small, we accept the data as being significant .

TABLE 15 - Statistical Significance of the Experimental Results

Main Effect	Mean Difference			t		
	Cationic	Anionic	Non-Ionic	Cationic	Anionic	Non-Ionic
	122.23	147.53	124.79			
T	4.53	-2.56	-3.86	3.60	1.61	2.92
I	-10.40	-3.12	4.25	8.25	2.12	3.20
TI	7.96	3.63	4.41	6.30	2.28	3.32
V	5.02	0.68	1.46	3.80	0.42	1.10
HR	-14.30	-7.02	0.35	11.25	4.41	0.26
HZ	10.61	3.52	2.22	8.45	2.21	1.67
A	-27.65	-2.34	-25.00	22.00	1.47	18.80
R	4.94	-3.14	0.63	3.92	1.97	0.47
TR	-7.43	-1.33	0.40	5.90	0.84	0.30
IR	9.79	5.97	-2.44	7.75	3.75	1.83
Z	15.57	20.24	20.62	12.35	12.70	15.50
HT	-7.46	-2.78	-2.41	5.92	1.75	1.81
H	-3.46	-7.27	-15.68	2.75	4.55	11.18
HZR	-4.19	1.91	3.64	3.32	1.19	2.74
AR	8.00	-7.81	3.70	6.35	7.81	2.78

Using 16 degrees of freedom, as explained before, with the t-distribution (double-sided) the percentage points of the t-distribution are given by Table 16 (25,26) :

TABLE 16 - Percentage Points of the t-distribution

16 Degrees of Freedom	Probability						
	50	25	10	5	2.5	1	0.5
t	0.690	1.19	1.75	2.12	2.47	2.92	3.29

Thus, from Table 16, the value for 95 % significance is $t = 2.12$. Therefore, only effects with \underline{t} greater than 2.12 are significant at 5 % level . Comparing this value of \underline{t} with the values of \underline{t} obtained in Table 15, we find that all treatments for the cationic group are significant, while for the anionic and non-ionic groups some of the treatments are and some are not significant at this level .

Therefore, in discussing the effects of the various factors upon the electrodeposit - as a function of the particular additive used - we must take into account just those effects which are significant, i.e., those whose occurrence by chance is improbable .

Studying Table 15 we can draw the following conclusions about the main effects:

TABLE 17 - Influence of the Main Effects

Main Effect	Additive Groups		
	Cationic	Anionic	Non-Ionic
T	$\uparrow T = \uparrow CE$	NS	$\downarrow T = \uparrow CE$
I	$\downarrow I = \uparrow CE$	$\downarrow I = \uparrow CE$	$\uparrow I = \uparrow CE$
V	$\uparrow V = \uparrow CE$	NS	NS
A	$\downarrow A = \uparrow CE$	NS	$\downarrow A = \uparrow CE$
R	$\uparrow R = \uparrow CE$	NS	NS
Z	$\uparrow Z = \uparrow CE$	$\uparrow Z = \uparrow CE$	$\uparrow Z = \uparrow CE$
H	$\downarrow H = \uparrow CE$	$\downarrow H = \uparrow CE$	$\downarrow H = \uparrow CE$

where:

\uparrow = increases

\downarrow = decreases

CE = cathode-efficiency

NS = not significant

Looking at the above table it can be seen that for all three additive groups increasing the salt concentration and decreasing the acid concentration will increase the cathode-efficiency .

The fact that the increasing salt concentration will increase

the cathode-efficiency is related to the discharge of zinc ions in the vicinity of the electrode surface . With a greater salt concentration more Zn ions will be available at the cathode surface . On the other hand, decreasing the hydrogen concentration, the phenomenon of hydrogen depolarization tends to be less sensitive, giving a more favourable condition for the deposition of the zinc species .

An interesting fact coming from Table 16 is that increasing the current-density will actually increase the cathode-efficiency with the addition of the non-ionic compound . A possible explanation for this fact is that since hydrogen overvoltage strongly depends on the nature of the solvent and, thus, on the presence of organic agents, the non-ionic compound in being adsorbed on the cathode surface will alter the effective cathode potential to more negative value, increasing, therefore, the hydrogen overvoltage and creating a better condition for the Zn ions to deposit .

Although for the anionic treatments the additive concentration was not significant at all, for the cationic and non-ionic species it showed a very high significance . Thus, concentrations less than 0.01 % by weight are recommended, as they increase the cathode-efficiencies . This fact will be discussed later .

The effect of temperature is quite controversial . An increasing temperature increases the cathode-efficiency for the cationic additive, decreases the cathode-efficiency for the non-ionic additive and has no effect at all for the anionic species . It is known from literature that

an increase in temperature increases the ionic mobility of the species, causing a very marked increase in grain size, and decreases the surface-tension of the electrolyte / electrode interface . Using the Le Chatelier principle, the organic species must be desorbed from the cathode surface in order to balance this decrease in the surface-tension . On the other hand, large grain size means a rough cathode surface and, therefore, the creation of a favourable condition for the dissolution of the deposited metal species . Thus, due to the effect of temperature on the grain size of the deposit, the organic species would tend to be adsorbed on the cathode in order to prevent excessive dendritic growth and dissolution of the electrodeposited metal species and, at same time, due to the effect that temperature has on the surface-tension would tend to be desorbed from the cathodic surface .

However, as pointed out in the electrocapillary studies section, when there exists a tendency to dissolution of the deposited metal species occurs the cationic additive will be adsorbed to a less extent than the non-ionic compound . Having, therefore, less tendency to be adsorbed and because of the effect of temperature on surface-tension, being forced to desorb from the cathode, an increase in temperature in a bath using cationic additive helps to raise the cathode-efficiency for it gives more available places for the deposition of Zn than the non-ionic additive .

An increase in the rate of agitation helps to increase the cathode-efficiency for the cationic additive treatments . It is not sign-

ificant, however, for the other two organic additives used .

Since the process of electrodeposition depends on time, it would be expected that an increase in electrodeposition time would allow more zinc species to deposit . However, one must keep in mind some deleterious effects of a long length of deposition such as additive deterioration, growth of long crystals on the electrode surface, increasing acidity, reduction in the salt concentration, and so on . The length of electrodeposition was significant for the cationic compound and not significant at all for the other two organics .

Some of the interactions shown in Table 15 are significant, as we can conclude comparing the values of t with those given in Table 16 .

The following tables show the interactions between the various factors . The calculations for the listed values were obtained by means of a reversed Yates analysis and are given in Appendix 5 .

TABLE 18 - Effect of Temperature and Current-density on the Cathode-efficiency - Cationic Additive

Current-Density	Temperature	
	20°C	40°C
30 A/sq.ft.	68.03%	61.45%
150 A/sq.ft	49.67%	62.16%

This interaction shows that at low temperature a raise in current-density has a much significant effect on the cathode-efficiency .

At 40°C practically no variation is observed when the current-density is increased from 30 A/sq.ft. to 150 A/sq.ft. . However, if the electro - deposition is being carried out at high current-density, an increase in the cell temperature would help to obtain a high cathode-efficiency .

TABLE 19 - Effect of the Acidity and Length of Deposition on Cathode-Efficiency - Cationic Additive

Time	Acidity	
	23 gpl	46 gpl
60 min	53.22%	63.56%
120 min	72.46%	54.20%

The above table shows the negative effect of the high acidity with increasing electrodeposition time .

TABLE 20 - Effect of Acidity and Salt Concentration on Cathode-efficiency - Cationic Additive

Salt Concentration	Acidity	
	23 gpl	46 gpl
35.91 gpl	60.36%	46.29%
71.89 gpl	65.32%	72.47%

Here, an increase in the cathode-efficiency with high acidity is obtained when the salt concentration is increased . At low salt concentrations, the efficiency decreases as the acidity is increased .

TABLE 21 - Effect of Temperature and Deposition Time on Cathode-efficiency - Cationic Additive

Time	Temperature	
	20°C	40°C
60 min	52.66%	64.62%
120 min	65.03%	62.13%

This interaction shows that an increase in the cathode - efficiency with time is only obtained when the temperature is lowered, decreasing slightly when the temperature is raised .

TABLE 22 - Effect of Current-density and Deposition Time on Cathode-efficiency - Cationic Additive

Time	Current-density	
	30 A/sq.ft.	150 A/sq.ft.
60 min	68.74%	48.55%
120 min	63.89%	63.28%

This table shows that with a high current-density and a low deposition time, the cathode-efficiency is reduced nearly by 70 %, while with a long deposition time and high current-density the cathode-efficiency is almost the same as that with low current-density and long electro - deposition time . This shows that it is preferable to lower the current-density of electrodeposition .

TABLE 23 - Effect of Acidity and Temperature on the Cathode-efficiency - Cationic Additive

Temperature	Acidity	
	23 gpl	46 gpl
20°C	56.85 %	60.85 %
40°C	68.84 %	57.92 %

Here, a raise in temperature decreases the cathode-efficiency in a bath with a high acid content, while in a bath with low acid concentration, an increase in temperature results in an increase in the cathode - efficiency .

TABLE 24 - Effect of Additive Concentration and Deposition Time on the Cathode-efficiency - Cationic Additive

Time	Additive Concentration	
	0 %	0.01 %
60 min	76.47 %	40.82 %
120 min	73.41 %	53.76 %

This shows that the lowering of the cathode-efficiency with a high concentration of additive is more marked when the time is at its lower level .

The interactions likely to be significant for the anionic treatments are given in Tables 25, 26,27, 28, and 29 .

TABLE 25 - Effect of Temperature and Current-density on the Cathode Efficiency - Anionic Additive

Current Density	Temperature	
	20°C	40°C
30 A/sq.ft.	78.42%	72.73%
150 A/sq.ft.	71.67%	72.74%

This table shows that a rise in current-density has a negative effect on the cathode-efficiency at low temperature, and no effect at all at 40°C .

TABLE 26 - Effect of Acidity and Deposition Time on the Cathode-efficiency - Anionic Additive

Time	Acidity	
	23 gpl	46 gpl
60 min	75.43 %	75.21 %
120 min	79.36 %	65.05 %

The above table shows that a rise in the acid concentration has a negative effect on the cathode- efficiency if the electrowinning time is at the high level .

TABLE 27 - Effect of Acidity and Salt Concentration on
Cathode-efficiency - Anionic Additive

Salt Concentration	Acidity	
	23 gpl	46 gpl
35.91 gpl	69.04 %	58.25 %
71.89 gpl	85.76 %	82.01 %

This table shows that increasing the acidity of the solution decreases the cathode-efficiency whatever is the salt concentration .

TABLE 28 - Effect of Current-density and Electrodeposition
Time on Cathode-efficiency - Anionic Additive

Time	Current-density	
	30 A/sq.ft.	150 A/sq.ft.
60 min	79.88 %	70.79 %
120 min	70.77 %	73.62 %

This interaction shows that increasing the current-density and allowing a short deposition time the cathode-efficiency is lowered . However, if a long electrodeposition time is allowed, the cathode - efficiency will increase .

TABLE 29 - Effect of Additive Concentration and Time on
Cathode-efficiency - Anionic Additive

Time	Additive Concentration	
	0 %	0.01 %
60 min	72.60 %	78.07 %
120 min	77.27 %	67.12 %

This interaction shows the deleterious effect of a long electro-winning time on the cathode-efficiency when the anionic additive is present in the electrolyte .

The other interactions are not likely to be significant for the anionic additive treatments, for at least one of the factors in those interactions is not significant .

Finally, the only interaction for the non-ionic group, at the 95 % level, is given in the following table .

TABLE 30 - Effect of Temperature and Current-density on
Cathode-efficiency - Non-Ionic Additive

Current Density	Temperature	
	20°C	40°C
30 A/sq.ft.	64.40%	56.13%
150 A/sq.ft.	64.24%	64.79%

This interaction shows the deleterious effect of a rise in the bath temperature at low current-density, but practically no effect at all at high current-density .

The remaining interactions are not significant for this group at 95 % level .

The standard error of the experimental results is given in Table 31 .

TABLE 31 - Standard Error of the Experimental Results

Standard Error	Cationic	Anionic	Non-Ionic
σ	1.26%	1.59%	1.33%

Having discussed all the factors and interactions between these factors which are significant for the three groups of additives, Figures 12, 13, 14, 15, 16, and 17 show the various surfaces obtained and present some comparison of the effects due to the various factors on the morphology of electrodeposited zinc .

Figure 12 shows:

12a - shows the surface obtained with the cationic additive, already discussed in Figure 7f .

12b - shows the surface obtained with the anionic additive, already discussed in Figure 8f .

12c - shows the surface obtained with the non-ionic additive, already discussed in Figure 9f .

All the surfaces were obtained with the factors at their lower level, except the additive concentration .

12d - shows the surface obtained with all the factors at their lower level, including the additive concentration; it shows a fine-grained, smooth, and dense deposit surface .

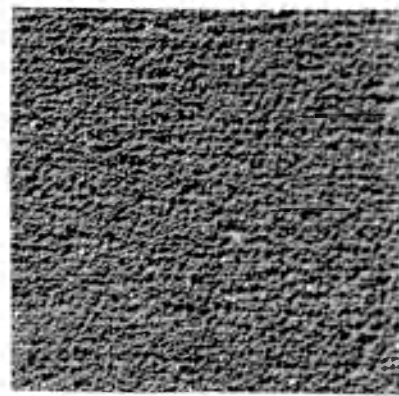
Comparing the pictures shown in Figure 12, we can conclude that the "cationic" surface (12a) has a finer grain size and shows cracks due to hydrogen evolution, and a less dense surface than that shown in Figure 13d . The "anionic" surface (12b) has a coarser grain size and shows a tendency to grow faster on the edges . The "non-ionic" surface (12c) shows a finer grain size and a better physical appearance, with metallic bright, than the surface of Figure 12d . Thus, in this case the non-ionic additive helped to obtain a better surface appearance than the other two .

Figure 13 shows:

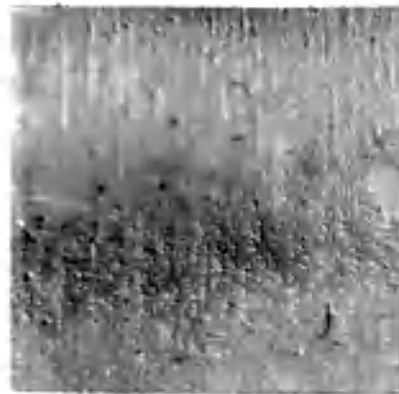
13a - shows the surface obtained with the cationic additive; it is a medium-grained surface showing a smooth, eventually cracked - due to hydrogen evolution - surface, and presenting "trees" on the edges and corners .

13b - shows the surface obtained with the anionic additive; it is a coarse-grained, bright surface, showing the growth of "trees" on the edges and corners .

13c - surface obtained with the non-ionic additive; it is a very hard, medium-grained surface, showing signals of burning on the



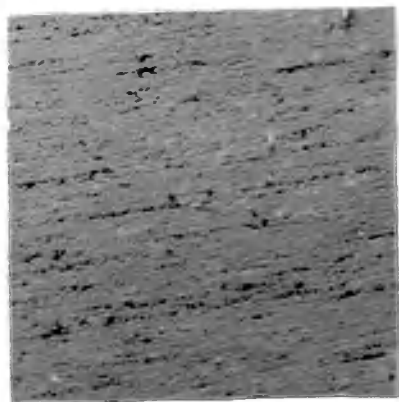
d) without additive



c) non-ionic



b) anionic



a) cationic

Figure 12 - Effect of Additive Concentration on the Morphology of electro-deposited zinc (15X)

corners and surface-depressions caused by the adsorption of gels formed by the non-ionic additive species . Very few "trees" are visible on the edges and corners .

All the above surfaces were obtained using treatment 19, i.e., with all the factors at their higher level .

13d - is the same picture already described in Figure 12d, with all the factors at their lower level .

Comparing the pictures shown in Figure 13, we can see that the altering the factor levels cause a very marked influence on the deposited surface .

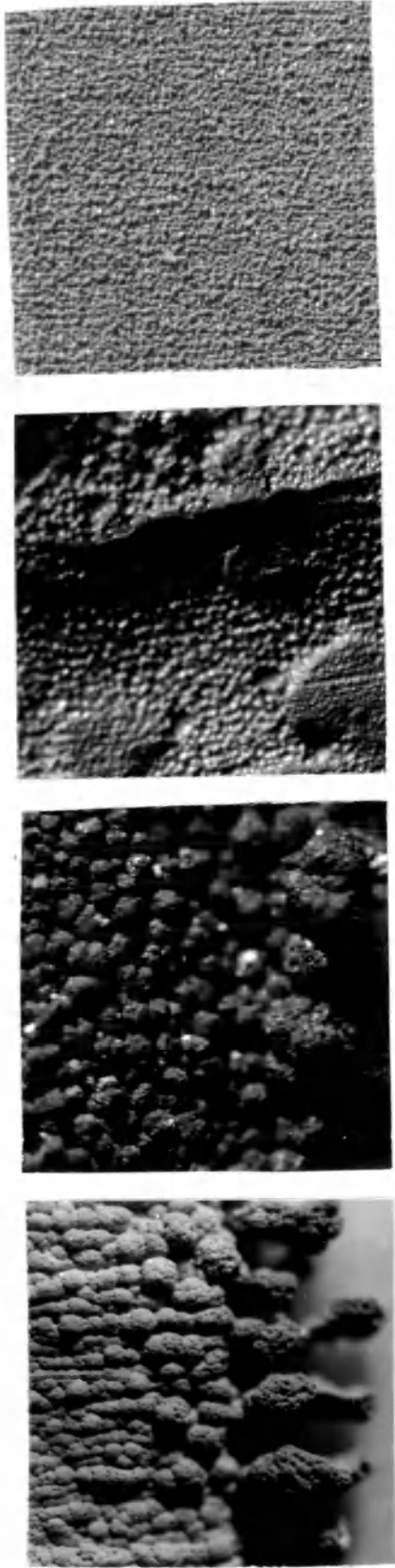
Figure 14 shows:

14a - picture already discussed in Figure 13d - all the factors at their lower level .

14b - shows the surface obtained with all the factors at their lower level, except the current-density, rate of agitation and length of deposition; it is a very rough surface, showing cracks due to hydrogen evolution and the growth of "trees" all over the cathode surface, growing faster on the edges .

14c - shows a "tree" grew on the edge of the cathode surface coming from treatment 11, i.e., high salt concentration, temperature, current-efficiency, and time of electrodeposition .

Comparing the three pictures shown in Figure 14, we see that agitation and electrodeposition time increase the grain size, and that the current-density, if increased, promotes a tendency of the deposited



d) without additive 7

c) non-ionic 19

b) anionic 19

a) cationic 19

Figure 13 - Effect of an increase in all factor levels (15X)

metal to sprout out in form of "trees". It is visible, also, that an increase in salt concentration and temperature, decreasing the rate of agitation (Figure 14b and c) favor the growth of long "trees", keeping the same values for the current-density and length of deposition .

Figure 15 shows:

15a - already discussed . Corresponds to Figure 12a .

15b - already discussed . Corresponds to Figure 12b .

15c - already discussed . Corresponds to Figure 12c .

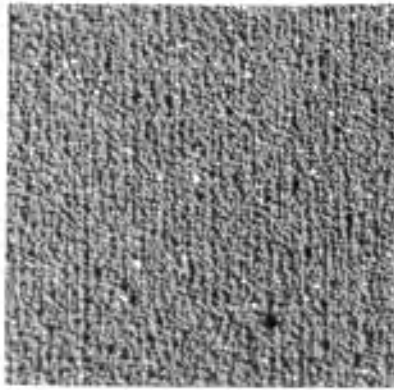
15d - shows a surface obtained with the cationic additive; it is fine-grained, eventually cracked, and shows the growth of small dendrites .

15e - obtained with the anionic additive; it is coarse-grained, showing the perpendicular growth of "trees" to the cathode surface . The shape of the "trees" were not modified by the additive .

15f - surface obtained with the non-ionic additive; it is fine-grained, smooth surface showing the growth of few "trees" on the edges .

All the surfaces shown in Figures 15d, 15e, and 15f were obtained using treatment 1, i.e., high salt concentration, current-density, and additive concentration .

Comparing the six pictures shown in Figure 15, we can see that increasing the salt concentration, current-density, and additive concentration cause a very marked effect upon the quality of the surface, producing the growth of "trees" and a coarser grain size - compare Figures 15d-15a,



a) without additive 7 (15X)



b) without additive 17 (15X)



c) without additive 11 (mm)

Figure 14 - Interaction Effects of Acidity, Current-density, Rate of Agitation, Time of Electrodeposition, and Salt Concentration on the Morphology of Electrodeposited Zinc .

15b-15c, and 15c-15f .

• Figure 16 shows:

16a - described in Figure 15d .

16b - described in Figure 15e .

16c - described in Figure 16f .

16d - surface obtained with cationic additive; it is a fine-grained surface, showing pits due to hydrogen evolution, and few crystals growing faster on the edges .

16e - surface obtained with anionic additive; it is a coarse-grained surface showing a perpendicular growth of the crystals on the cathode surface and preferentially on the edges .

16f - surface obtained with non-ionic additive; it is very fine-grained, showing some brightness and cracks .

The surfaces shown in Figures 16d, 16e, and 16f were obtained using treatment 25, i.e., high acidity, additive concentration, current-density and electrodeposition time .

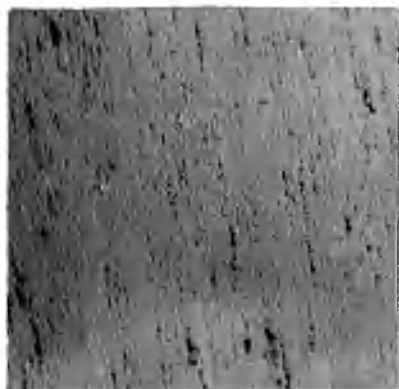
Comparing the pictures shown in Figure 16, we are comparing treatments 1 and 25 . Thus, we can conclude that if the salt concentration is decreased and increase the acidity and electrodeposition time, the surfaces obtained show less "tree" growth .

Finally, Figure 17 shows:

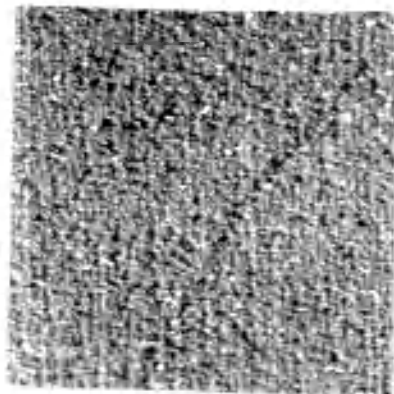
17a - described in Figure 16d .

17b - described in Figure 16e .

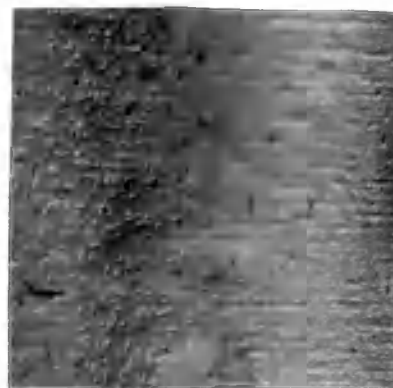
17c - described in Figure 16f .



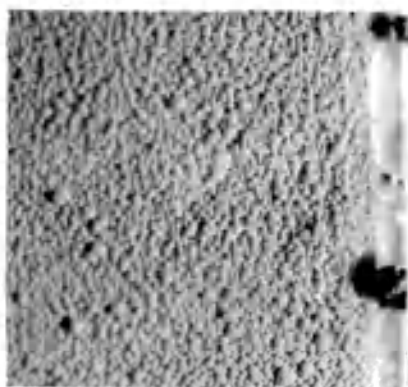
a) cationic



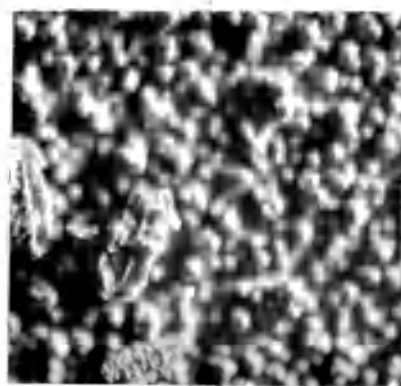
b) anionic



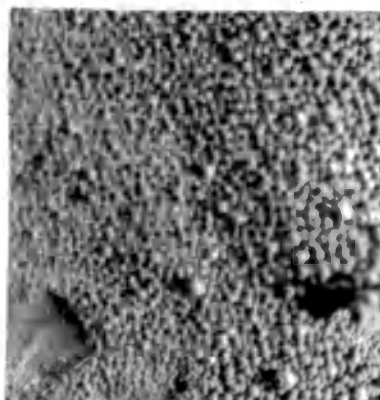
c) non-ionic



d) cationic 1



e) anionic 1



f) non-ionic 1

Figure 15 - Interaction Effects between Salt Concentration, Current-density and Additive Concentration on the Morphology of Electrodeposited Zinc (15X)

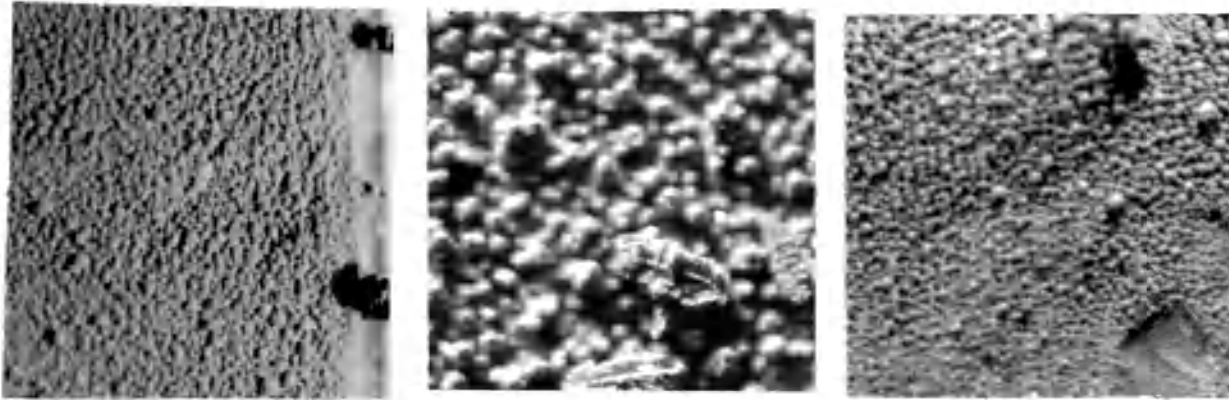
17d - shows the surface obtained with the cationic additive; it is a very fine-grained surface, showing some pits .

17e - surface obtained with the anionic additive; it is fine-grained, showing some brightness .

17f - surface obtained with the non-ionic additive; it is a very homogeneous surface, dense and with metallic bright .

The surfaces of Figures 17d, 17e, and 17f were obtained using treatment 24, i.e., high additive concentration, temperature and length of deposition .

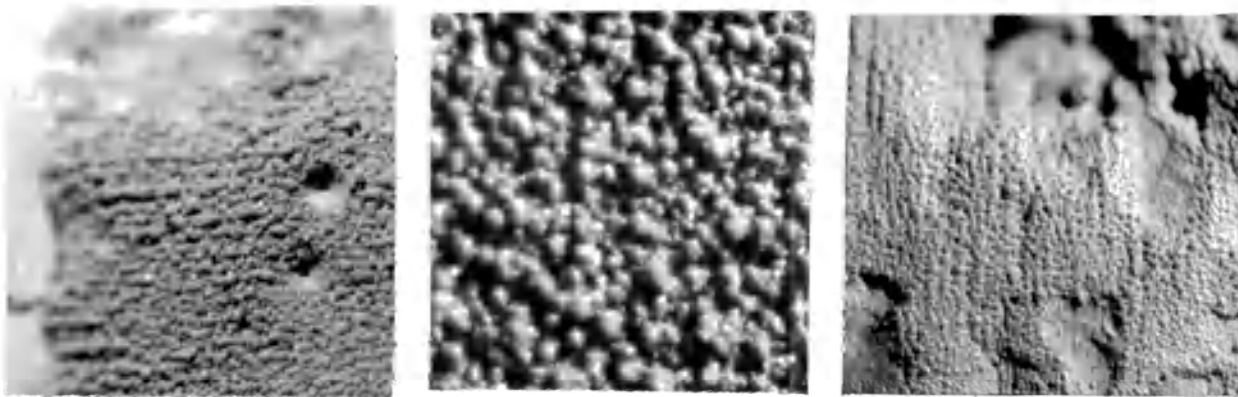
Comparing the pictures of Figure 17, we are comparing treatments 25 and 24 . We can see that if the acidity is decreased, as well as the current-density, and increase the temperature, for the same electrodeposition time and additive concentration, the surface obtained will be smoother and more appealing .



a) cationic 1

b) anionic 1

c) non-ionic 1

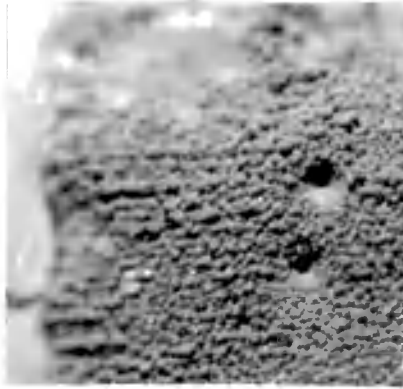


d) cationic 25

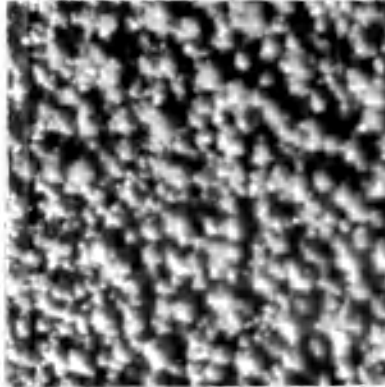
e) anionic 25

f) non-ionic 25

Figure 16 - Comparison between treatments 1 and 25 (15X)



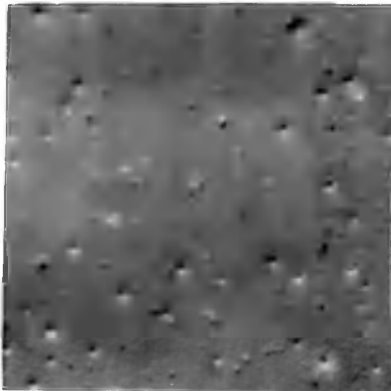
a) cationic 25



b) anionic 25



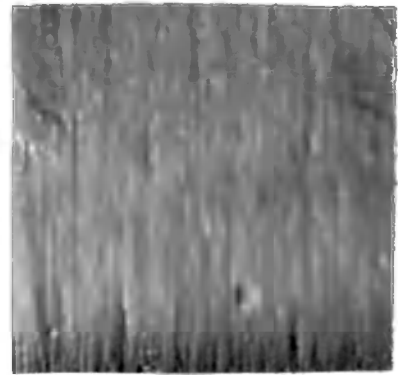
c) non-ionic 25



a) cationic 24



b) anionic 24



c) non-ionic 24

Figure 17 - Comparison between Treatments 25 and 24 (15X)

THE ELECTROCAPILLARY PHENOMENA

As shown in the literature review section, the ability of a metal/solution interface to adsorb ions or molecules can be explained in terms of the electrocapillary phenomena occurring at this interface .

Capillary-active anions are preferentially adsorbed at potentials positive to the isoelectric point, hence depressing the corresponding limb of the electrocapillary curve, the isoelectric point being shifted to a slightly more negative values .

Capillary-active cations are adsorbed at potentials corresponding to the negative branch of the electrocapillary curve, hence depressing this limb and shifting the isoelectric point to a more positive value .

The neutral molecules are adsorbed at potentials around that of the isoelectric point , causing just a depression of the maximum of the electrocapillary curve .

This behaviour applies to all metallic surfaces in contact with a solution . However, as pointed out earlier, the electrocapillary curves of metals other than mercury are extremely difficult to obtain experimentally .

Adsorption of the additive on the metallic surface results in

surface homogeneity and, sometimes, inhibit dissolution of the metallic species . Therefore, the potential of the electrode relative to its isoelectric point is of importance in determining whether adsorption is possible .

ANTROPOV showed that if the electrocapillary properties of a substance are found for one metal, than it is possible to estimate adsorption of the same substance on another metal surface, once the potential of the metal being investigated is the same for both the metal of interest and mercury on the zero point scale . The zero point scale is not a function of the nature of the reference electrode chosen and, consequently the conditions of adsorption are similar for any metal, within the same zero point scale range of potentials . This scale is defined as the difference between the working potential E and the relevant null potential $E_{q=0}$. Thus,

$$\sigma = E - E_{q=0}$$

The above relation, therefore, determines the charge of the metal with respect to the medium in which it is placed .

The results obtained by means of the polarographic technique described in an earlier section, given in Table 9, were converted into the zero point scale by subtracting the voltage readings from the relevant null potential, obtained in plotting the electrocapillary curve .

Keeping in mind that the drop-life times are proportional to

the surface-tensions for a given applied potential, the graph shown in Figure 18 was drawn .

On the basis of this graph it is possible to interpret the behaviour of various additives at the surface of a zinc cathode immersed in an acid solution . It should be remembered that in the process of dissolution, Zn will attain negative potentials of the order of -0.75 V . In the process of deposition the cathode potential will decrease from this value . Thus, knowing the relevant null potential of Zn ($E_{q=0} = -0.63$ V) and introducing it in the given mathematical expression for the zero point potential, we can see that the region of interest lies on the negative side of the electrocapillary curve . This branch of the curve is called cathodic .

From Figure 18 we can see that the behaviour of the surface-active molecules agrees with the expected theoretical results, i.e., the parabolic shaped curve for the acid solution is altered as differently charged additives are added . The electrocapillary maximum for the cationic and anionic additives is shifted and for the non-ionic additive is depressed .

Therefore, we have a range of zero point potentials within which the surface-tension of the electrolyte/electrode interface is decreasing with the applied potentials, due to the adsorption of the organic additive species . The most adsorption of an additive is, therefore, a function of the zero point potential . Within the $0 - -0.2$ V range, the order of preferential adsorption will be:

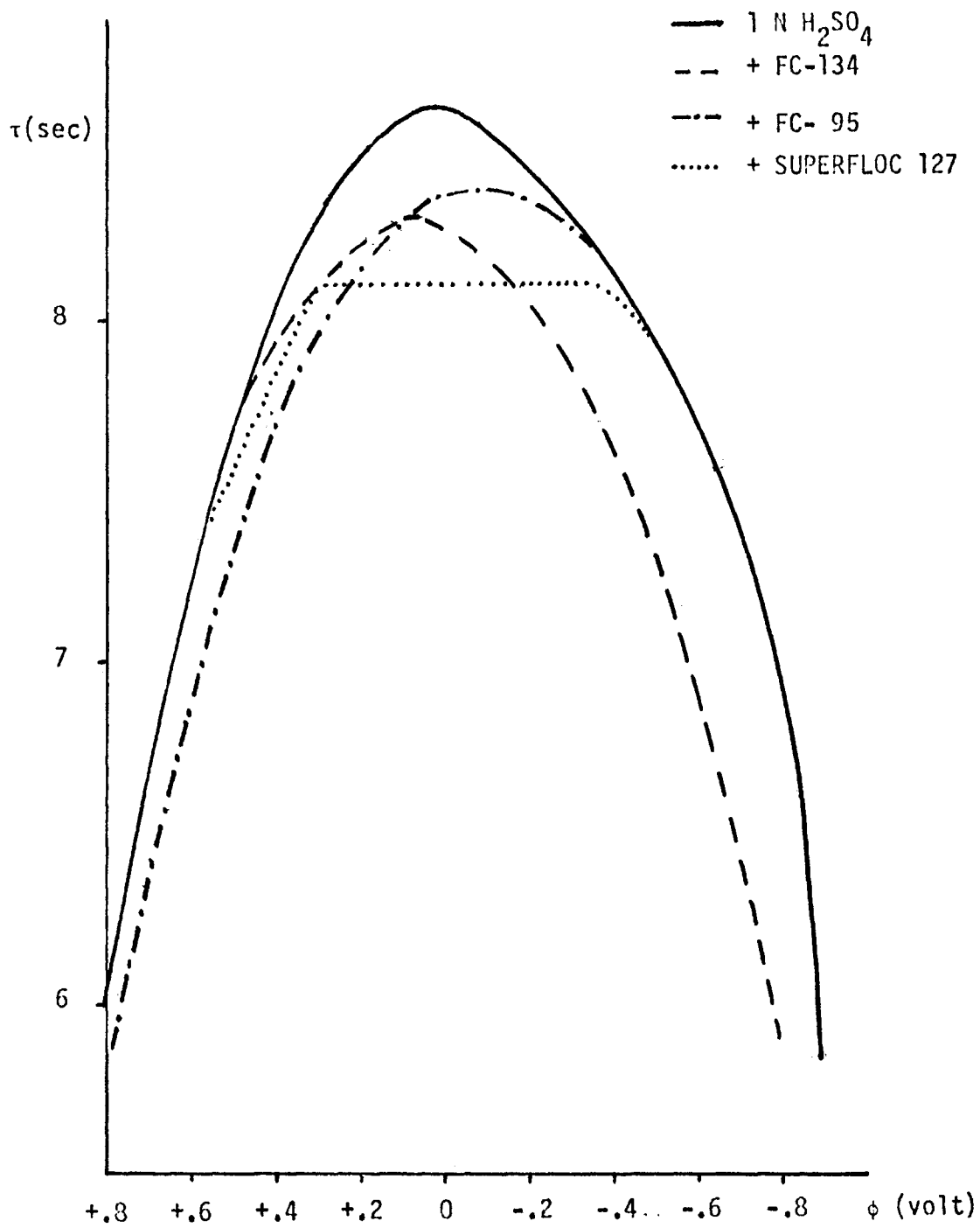


Figure 18 - The electrocapillary curves

non-ionic → cationic → anionic

Since the corrosion zero-point-potential of zinc ($-0.12V$) is in that range, it is apparent that most effective inhibition of corrosion can be achieved with a non-ionic additive . The cationic and anionic additives will be less effective .

At zero point potentials greater than $-0.12V$, in the negative direction, the cationic additive adsorbs preferentially and can be used to produce a smooth and dense surface .

Therefore, if the system is at more negative potentials the cathodic adsorption is predominant, i.e., cations will be adsorbed on the metal surface . Now, if the system goes towards more positive potentials the cationic Gibbs adsorption ceases and the replacement of organic compound by water molecules is verified . At those potentials anionic adsorption is favoured, with the anions being desorbed at increasingly negative potentials - see Figure 18 - .

The non-ionic molecules are adsorbed in a much narrower range of potentials, depressing the electrocapillary maximum, due to perhaps their orientation on the metal surface, searching for the state of minimum free energy of the metal/electrolyte system, lowering, therefore, the surface-tension .

CONCLUSIONS

On the basis of the results obtained, we can conclude:

1. Cationic and non-ionic species are preferentially adsorbed on the metal surface, resulting in a reasonably homogeneous cathode surface . The degree of homogeneity depends on the nature of the adsorbing species .

2. When deposition and corrosion of zinc are taking place simultaneously, the non-ionic additive will be adsorbed preferentially and will result in a fine-grained, smooth and somewhat bright deposit .

3. In the deposition/dissolution region, the adsorption of a cationic additive will be less effective and the cathode surface produced will be rougher and the grain size coarser than the non-ionic surfaces .

4. For the same region, the anionic additive is less effective and the cathode surfaces obtained exhibit poor morphological properties .

5. The addition of organic lower the cathode efficiency of the deposition process . This may be due to some or all of the following phenomena :

- a) lowering of hydrogen overvoltage
- b) decrease in the effective surface area
- c) electrochemical reactions at the interface

6. An increase in temperature results in a coarser grain size and a higher rate of dissolution . The non-ionic species are more effective than either the cationic or anionic additives in smoothening the electrodeposited surface, as temperature is increased .

7. An increase in current-density results in a finer grain size . However, it promotes growth and formation of "trees" .

8. In the presence of non-ionic and anionic additives , increasing the rate of agitation will not have a significant effect on the morphology of the deposit . However, with cationic additive a coarser grain size is obtained at high rates of agitation .

9. Within the range of additive concentrations studied, decreasing concentration is recommended for the non-ionic and cationic additives, and increasing for the anionic, for better morphological properties .

10. An increase in the time of deposition promotes the formation of dendrites, increases the acid concentration in the electrolyte, and decreases the salt concentration, affecting, therefore, the physical aspect of the surface . Time was a statistically significant variable for cationic additive only .

11. An increase in the concentration of zinc sulphate results in a higher current-efficiency and coarser grain size .

12. An increase in the hydrogen ion concentration favors a coarse-grained and columnar structure . It also lowers the current - efficiency . Non-ionic additive was more effective at high acidities than either the cationic or anionic additives .

FURTHER RESEARCH

Emphasis must be given to the statistical model developed in this Thesis .

It seems to the author that this model offers a wider field for investigation of the effects of the various factors upon the process parameter being studied, than the classical approach .

The advantages of assessing the statistical consistency and significance of the results give to the reader a ready check of the validity of the experimental data, as well as of the discussion and conclusions coming from the experiment .

Although this study restricted itself to the evaluation of the effects of various process parameters on the morphology of the deposit, a similar approach can be used in the investigation of other variables .

As suggestion for further work, similar models should be developed and investigated for other process parameters . Then, a statistical correlation of the various process parameters studied could be established giving, therefore, those in which care must be exercised in order to avoid any serious plating problem, and those in which a larger degree of tolerance can be given for the process operator without changing the

quality of the electrodeposit in a significant way .

It is believed that this Thesis is a valuable contribution to the understanding of electrodeposition of zinc and should form the basis for further work on a systematic study of the process parameters for the electrodeposition .

APPENDIX 1

A list of the surface active agents
according to their physicochemical
group .

I. ANIONIC COMPOUNDS

I/A - Products obtained by saponification of fats

I/A₁ - Industrial soaps

I/A₂ - Soaps derived from fatty acids obtained by oxidation
of paraffin

I/A₃ - Naphthenic soaps

I/A₄ - Soap substitutes or special soaps

I/B - Products obtained by direct sulfonation of fatty matters without
previous treatment

I/B₁ - Products obtained by normal sulfonation of glycerides
or their fatty acids

I/B₁₁ - Alkaline sulforicinate

I/B₁₂ - Sulfoleates and sulfonated oils of this type

I/B₁₃ - Sulfonated tallow

I/B₁₄ - Sulfonated coconut oil

I/B₁₅ - Sulfonated marine animal oils

I/B₂ - Products obtained by normal sulfonation of glycerides
or their fatty acids followed by intramolecular
condensation

I/B₂₁ - Monopole oil

I/B₂₂ - Monopole soap

I/B₃ - Products obtained by high sulfonation of glycerides or
their fatty acids

I/C - Products obtained by sulfonation of fatty acids esters

I/C₁ - Sulfonated derivates of esters of monovalent alcohols

I/C₂ - Sulfonated derivates of esters of polyvalent alcohols

I/C₂₁ - From saturated oils or fatty acids

I/C₂₂ - From unsaturated oils or fatty acids

I/D - Products obtained by esterification of fatty acids with sulfonated monovalent alcohols

I/E - Sulfonated derivates of fatty esters of low molecular weight

I/F - Products obtained by sulfonation of fatty amides

I/F₁ - Sulfonated derivates of aliphatic amides, ammonia or amines

I/F₂ - Sulfonated derivates of cyclic amides

I/F₃ - Sulfonated derivates of cyclic amides

I/F₄ - Sulfonated heterocyclic compounds derived from aromatic diamines (benzimidazol)

I/F₅ - Sulfonated derivates of amides of amino alcohols

I/G - Condensation products of fatty acid chlorides with amines

I/G₁ - Amides derived from aminosulfonic acids

I/G₂ - Amides derived from amino acids

I/G₃ - Amides derived from polypeptide amino acids

I/H - Sulfonation products of fatty nitriles

I/I - Sulfonation products of fatty aldehydes

I/J - Sulfonation products of fatty ketones

I/K - Products obtained by sulfonation of natural and synthetic alcohols

having six or more carbon atoms, with a view to obtaining sodium salts of sulfuric acid esters, R_2OSO_3Na or true alkali sulfonates.

I/K₁ - Sodium salts of sulfuric acid esters of alcohols having eight or less carbon atoms

I/K₂ - Sodium salts of sulfuric acid esters of alcohols having more than eight carbon atoms

I/K₂₁ - from lauryl alcohol or alcohols derived from coconut palm oil

I/K₂₂ - from cetyl alcohol

I/K₂₃ - from stearyl alcohol

I/K₂₄ - from oleyl-cetyl alcohol (alcohols derived from Spermaceti)

I/K₂₅ - from various fatty alcohols

I/K₃ - Sodium salt of a sulfuric acid ester of an unsaturated fatty alcohol

I/K₃₁ - from oleyl alcohol

I/K₄ - Special sulfonates of fatty alcohols

I/K₄₁ - Oleyl alcohol sulfonate

I/K₄₂ - Oleyl alcohol disulfonate

I/K₄₃ - PERSulfuric esters of fatty alcohols

I/L - Sulfonation products of secondary alcohols

I/M - Products obtained by use of mineral esterification agents other than sulfuric acid

I/A₁ - Phosphoric esters of fatty alcohols

- I/M₂ - Pyrophosphoric esters of fatty alcohols
- I/M₃ - Peroxides of pyrophosphoric esters of fatty alcohols
- I/N - Aminocarboxylic acids containing several COOH groups
- I/O - Sulfonated aromatic hydrocarbons
 - I/O₁ - Sulfonated derivatives of benzene, its homologs and its derivatives
 - I/O₁₁ - Sodium benzylsulfanilate
 - I/O₁₂ - Sodium dimethyl metanilate
 - I/O₂ - Sulfonation products of naphthalene and its derivatives
 - I/O₂₁ - Naphthalene monosulfonate
 - I/O₂₂ - Sodium naphthalene trisulfonate 1-3-6
 - I/O₂₃ - Sodium tetrahydronaphthalene sulfonate
 - I/O₂₄ - Condensation products of naphthalene sulfonic acids with formaldehyde
 - I/O₃ - Sulfonation products of anthracene and its derivatives
 - I/O₄ - Alkylaryl sulfonates
 - I/O₄₁ - Alkylaryl sulfonates with one or more alkyl groups having eight or less carbon atoms
 - I/O₄₂ - Alkylaryl sulfonates with an alkyl group containing ten or more carbon atoms
 - I/O₅ - Alkyl naphthalene persulfonic acids
 - I/O₆ - Sulfonation products of phthalic anhydride and their derivatives
 - I/O₇ - Sulfonation products of rosin and its derivatives

- I/O₇₁ - Sulfonated derivatives of rosin
- I/O₇₂ - Sulfonated derivatives of abietene
- I/O₇₃ - Sulfonated derivatives of abietenic alcohol
- I/O₈ - Sulfonation products of terpenes or terpene alcohols
- I/O₉ - Sulfonation products of phenol or its homologs with
or without previous or simultaneous condensation
- I/O₉₁ - Sulfonated alkylphenols
- I/P - Sulfonated derivatives of nonionic compounds of class III/C
- I/Q - Products obtained from paraffinic hydrocarbons
 - I/Q₁ - Products obtained by sulfonation of the ingredients of
mineral oils
 - I/Q₂ - Products obtained by chlorosulfonation of paraffinic
hydrocarbons
 - I/Q₃ - Sulfamides derived from paraffinic hydrocarbons
 - I/Q₄ - Sulfinides derived from paraffinic hydrocarbons
- I/R - Products obtained from waste sulfite liquors

II. CATIONIC

- II/A - Aliphatic (fatty) amines and their derivatives
- II/B - Homologs of aromatic amines having fatty chains
- II/C - Fatty amides derived from disubstituted diamines
- II/D - Fatty amides derived from aliphatic diamines
- II/E - Quaternary ammonium compounds
- II/F - Amides derived from amino alcohols and their quaternary ammonium

derivatives

- II/G - Quaternary ammonium bases of the benzimidazolines
- II/H - Basic compounds of pyridine and its derivatives
- II/I - Quaternary ammonium bases derived from fatty amides of disubstituted diamines
- II/J - Basic compounds of sulfonium, phosphonium and antimony
- II/K - Quaternary ammonium compounds of betaine
- II/L - Dimethylphenylbenzyl ammonium chloride
- II/M - Urethanes or basic salts of ethylene diamine
- II/N - Polyethylene diamines and their quaternary ammonium derivatives
- II/O - Polypropanol polyethanolamines
- II/P - Miscellaneous cation-active compounds

III. NON-IONIC

- III/A - Natural products
- III/B - Condensation products of fatty substances and their derivatives with ethylene oxide
- III/C - Products obtained by condensation of phenolic compounds having side chains with ethylene oxide
- III/D - Miscellaneous non-ionic compounds

APPENDIX 2

The original 128 treatments of the factorial
design

1) (1)	2) h	3) z	5) a	17) i	33) v
		4) hz	6) ha	18) hi	34) hv
			7) za	19) zi	35) zv
			8) hza	20) hzi	36) hzv
				21) ai	37) av
				22) hai	38) hav
				23) zai	39) zav
				24) hzai	40) hzav
				25) ti	41) tv
				26) hti	42) thv
				27) zti	43) ztv
				28) hzti	44) hztv
				29) tai	45) tav
				30) hati	46) hatv
				31) zati	47) zatv
				32) hzati	48) hzatv
					49) vi
					50) hiv
					51) ziv
					52) hziv
					53) aiv
					54) haiv
					55) zaiv
					56) hzaiv
					57) tiv
					58) htiv
					59) ztiv
					60) hztiv
					61) taiv
					62) hativ
					63) zativ
					64) hzativ

- continue next page -

- continued -

65) r	116) hzivr
66) hr	117) aivr
67) zr	118) haivr
68) hzr	119) zaivr
69) ar	120) hzaivr
70) har	121) tivr
71) zar	122) htivr
72) hzar	123) ztivr
73) tr	124) hzitr
74) thr	125) taivr
75) ztr	126) hativr
76) hztr	127) zativr
77) tar	128) hzativr
78) hatr	
79) zatr	
80) hzatr	
81) ir	
82) hir	
83) zir	
84) hzir	
85) air	
86) hair	
87) zair	
88) hzair	
89) tir	
90) htir	
91) ztir	
92) hztir	
93) tair	
94) hatir	
95) zatir	
96) hzatir	
97) vr	
98) hvr	
99) zvr	
100) hzvr	
101) avr	
102) havr	
103) zavr	
104) hzavr	
105) tvr	
106) thvr	
107) ztvr	
108) hztvr	
109) tavr	
110) hatvr	
111) zatvr	
112) hzatvr	
113) vir	
114) hivr	
115) zivr	

APPENDIX 3

A listing of the computer programs used to calculate the statistical consistency and the statistical significance of the experimental results

PROGRAM TO COMPUTE THE STATISTICAL CONSISTENCY OF THE RESULTS

```
LISTNH
10 DIM A(16),E(16)
20 DATA 116.52,81.00,78.68,7.31,92.20,33.52,1.10,34.57,2.10
3 DATA 2.96,90.06,0.01,4.80,10.69,62.73,31.47
40 FOR I=1 TO 16
50 READ A(I)
60 NEXT I
70 LET M=1
80 LET J=0
90 FOR I=1 TO 16 STEP 2
100 LET J=J+1
110 LET B=A(I)+A(I+1)
120 LET C=A(I+1)-A(I)
130 PRINT B, C
140 LET E(J)=B
150 LET E(J+8)=C
160 NEXT I
170 FOR I=1 TO 16
180 LET A(I)=E(I)
190 NEXT I
200 PRINT
210 PRINT
220 LET M=M+1
230 IF M<=4 GO TO 80
240 FOR I=2 TO 16
250 LET F=(ABS(A(1))+ABS(A(I)))/(ABS(A(1))-ABS(A(I)))
260 PRINT F
270 NEXT I
280 END
```

READY

CATION IC

181.17	-51.87
8.31	7.15
69.4	-2.36
24.42	22.22
24.	19.8
22.38	-22.36
15.57	5.81
62.79	-62.67
/	
189.48	-172.86
93.82	-44.98
46.38	-1.62
78.36	47.22
-44.72	59.02
19.86	24.58
-2.56	-42.16
-56.86	-68.48
.	
283.3	-95.66
124.74	31.98
-24.86	64.58
-59.42	-54.3
-217.84	127.88
45.6	48.84
83.6	-34.44
-110.64	-26.32
.	
408.04	-158.56
-84.28	-34.56
-172.24	263.44
-27.04	-194.24
-63.68	127.64
10.28	-118.88
176.72	-79.04
-60.76	8.12
.	
1.52063	
2.4609	
1.14194	
1.36985	
1.05169	
2.52793	
1.34992	
2.27112	
1.18507	
4.64371	
2.81703	
1.91041	
1.82224	
1.48049	
1.04061	

TIME: 0.40 SECS.

197.52	-35.52
85.99	-71.37
125.72	-58.68
35.67	33.47
5.06	0.86
90.07	-90.05
15.49	5.89
94.2	-31.26

283.51	-111.53
161.39	-90.05
95.13	85.01
109.69	78.71
-106.89	-35.85
-25.21	92.15
-89.19	-90.91
-25.37	-37.15

444.9	-122.12
204.82	14.56
-132.1	81.68
-114.56	63.82
-201.58	21.48
163.72	-6.3
56.3	128
-128.06	53.76

649.72	-240.08
-246.66	17.54
-37.86	365.3
-71.76	-184.36
-107.56	136.68
145.5	-17.86
15.18	-27.78
181.76	-74.24

2.22394
 1.12375
 1.24832
 1.39678
 1.57713
 1.04785
 1.77682
 2.17215
 1.05549
 3.56874
 1.79233
 1.53282
 1.05653
 1.08933
 1.25801

NONIONIC

136.23	-96.81
12.79	1.83
33.52	33.52
1.13	-1.07
102.1	97.9
4.95	-4.93
16.5	4
143.73	18.27
149.02	-123.44
34.65	-32.39
107.05	-97.15
160.23	127.23
-94.98	98.64
32.45	-34.59
92.97	-102.83
22.27	14.27
183.67	-114.37
267.28	53.18
-62.53	127.43
115.24	-70.7
-155.83	91.05
30.08	224.38
64.05	-133.23
-88.56	117.1
450.95	83.61
52.71	177.77
-125.75	185.91
-24.51	-152.61
-61.19	167.55
56.73	-198.13
315.43	133.33
-16.13	250.33
1.26471	
1.77337	
1.11495	
1.31399	
1.28781	
5.65511	
1.07419	
1.45522	
2.30149	
2.40288	
2.02306	
2.18243	
2.56736	
1.83956	
3.49556	

PROGRAM TO COMPUTE THE STATISTICAL SIGNIFICANCE OF THE RESULTS

```
LISTNH
10 DIM A(16),E(16)
20 DATA 145.05,79.32,136.10,120.68,65.98,179.53,166.51,100.08
30 DATA 164.97,95.88,64.05,180.60,139.22,94.37,147.30,124.00
40 FOR I=1 TO 16
50 READ A(I)
60 NEXT I
70 LET M=1
80 LET J=0
90 FOR I=1 TO 16 STEP 2
100 LET J=J+1
110 LET B=A(I)+A(I+1)
120 LET C=A(I+1)-A(I)
130 PRINT B, C
140 LET E(J)=B
150 LET E(J+8)=C
160 NEXT I
170 FOR I=1 TO 16
180 LET A(I)=E(I)
190 NEXT I
200 PRINT
210 PRINT
220 LET M=M+1
230 IF M<=4 GO TO 80
240 FOR I=1 TO 16
250 LET F=A(I)/16
260 PRINT F
270 NEXT I
280 END
```

READY

CATIONIC

279.61	-10.49
139.64	101.72
270.3	88.76
248.76	-84.26
273.31	-56.63
245.15	116.05
237.84	-49.1
261.06	-33.54
419.25	-139.97
519.06	-21.54
518.46	-28.16
498.9	23.22
91.23	112.21
4.5	-173.02
59.42	172.68
-82.64	15.56
938.31	99.81
1017.36	-19.56
95.73	-86.73
-23.22	-142.06
-161.51	118.43
-4.94	51.38
-60.81	-285.23
188.24	-157.12
1955.67	79.05
72.51	-118.95
-166.45	156.57
127.43	249.05
80.25	-119.37
-228.79	-55.33
169.81	-67.05
-442.35	128.11
122.229	
4.53188	
-10.4031	
7.96437	
5.01563	
-14.2994	
10.6131	
-27.6469	
4.94062	
-7.43438	
9.78563	
15.5656	
-7.46062	
-3.45812	
-4.19062	
8.00688	

TIME: 0.50 SECS.

315.85	25.75
273.01	-31.65
323.25	35.81
293.31	-39.71
298.13	-31.81
287.81	73.39
268.02	-79.28
301.15	6.55

588.86	-42.84
616.56	-29.94
585.94	-10.32
569.17	33.13
-5.9	-57.4
-3.9	-75.52
41.58	105.2
-72.73	85.83

1205.42	27.7
1155.11	-16.77
-9.8	2
-31.15	-114.31
-72.78	12.9
22.81	43.45
-132.92	-18.12
191.03	-19.37

2360.53	-50.31
-40.95	-21.35
-49.97	95.59
58.11	323.95
10.93	-44.47
-112.31	-116.31
56.35	30.55
-37.49	-1.24999

147.533
-2.55937
-3.12312
3.63187
0.683125
-7.01937
3.52188
/ -2.34312
-3.14437
-1.33438
5.97437
20.2469
-2.77938
-7.26937
1.90938
-7.81246 E-2

TIME: 0.41 SECS.

224.37	-65.73
256.78	-15.42
245.51	113.55
266.59	-66.43
260.85	-69.09
244.65	116.55
233.59	-44.85
264.3	-30.3

481.15	32.41
512.1	21.08
505.5	-16.2
497.89	30.71
-81.15	50.31
47.12	-179.98
47.46	185.64
-75.15	14.55

993.25	30.95
1003.39	-7.61
-34.03	128.27
-27.69	-122.61
53.49	-11.33
14.51	46.91
-129.67	-230.29
200.19	-171.09

1996.64	10.14
-61.72	6.34
68.	-38.98
70.52	329.86
23.34	-38.56
5.66	-250.88
35.58	58.24
-401.38	59.2

124.79
-3.8575
4.25
4.4075
1.45875
0.35375
2.22375
-25.0863
0.633749
0.39625
-2.43625
20.6163
-2.41
-15.68
3.64
3.7

TIME: 0.40 SECS.

APPENDIX 4

A listing of the computer program used to calculate
the F - ratios of the transformed results

```
10 DIM A(16),E(16)
20 DATA0.0042,0.0037,0.0011,0.0005
21 DATA0.0032,0.0009,0.0000,0.0029
22 DATA0.0000,0.0014,0.0043,0.0000

23 DATA0.0002,0.0010,0.0021,0.0000
24 GO TO 40
40 FOR I = 1 TO 16
50 READ A(I)
60 NEXT I
70 LET M= 1
80 LET J = 0

90 FOR I = 1 TO 16 STEP 2
100 LET J= J + 1
110 LET B = A(I)+A(I+1)
120 LET C=A(I+1)-A(I)
130 PRINT B,C

140 LET E(J)=B
150 LET E(J+8)=C
160 NEXT I
170 FOR I= 1 TO 16
180 LET A(I)=E(I)
190 NEXT I
200 PRINT
210 PRINT
220 LET M=M+1
230 IF M<=4 GO TO 80
240 FOR I=2 TO 16
250 LET G=(ABS(A(1))+ABS(A(I)))
260 LET F=G/(ABS(A(1))-ABS(A(I)))
270 PRINT F
280 NEXT I
290 END
```

READY

CATIONIC

0.0079		-5.00000	E-4
0.0016		-6.00000	E-4
4.10000	E-3	-2.30000	E-3
2.90000	E-3	2.90000	E-3
0.0014		0.0014	
0.0043		-0.0043	
1.20000	E-3	0.0008	
0.0021		-0.0021	

9.50000	E-3	-6.30000	E-3
0.007		-1.20000	E-3
0.0057		0.0029	
0.0033		9.00000	E-4
-1.10000	E-3	-1.00000	E-4
6.00000	E-4	0.0052	
-0.0029		-0.0057	
-1.30000	E-3	-0.0029	

0.0165		-2.50000	E-3
0.009		-0.0024	
-5.00000	E-4	0.0017	
-0.0042		0.0016	
-7.50000	E-3	5.10000	E-3
0.0038		-0.002	
5.10000	E-3	0.0053	
-0.0086		0.0028	

2.55000	E-2	-7.50000	E-3
-4.70000	E-3	-3.70000	E-3
-3.70000	E-3	1.13000	E-2
-3.50000	E-3	-0.0137	
-4.90000	E-3	1.00000	E-4
0.0033		-1.00000	E-4
3.10000	E-3	-7.10000	E-3
0.0081		-0.0025	

1.45192
 1.33945
 1.31818
 1.47573
 1.2973
 1.27679
 1.93103
 1.83333
 1.33945
 2.59155
 3.32203
 1.00787
 1.00787
 1.77174
 1.21739

TIME: 0.56 SECS.

ANIONIC

6.20000	E-3	-2.20000	E-3
2.90000	E-3	-0.0019	
4.60000	E-3	-0.0028	
0.0017		0.0017	
0		0	
0.0057		-0.0057	
0.001		0.001	
0.003		-0.0012	

0.0091		-3.30000	E-3
0.0063		-2.90000	E-3
0.0057		0.0057	
0.004		2.00000	E-3
-4.10000	E-3	3.00000	E-4
-1.10000	E-3	0.0045	
-0.0057		-0.0057	
-2.00000	E-4	-2.20000	E-3

0.0154		-0.0028	
9.70000	E-3	-1.70000	E-3
-0.0052		0.003	
-0.0059		0.0055	
-6.20000	E-3	4.00000	E-4
7.70000	E-3	-0.0037	
0.0048		0.0042	
-0.0079		0.0035	

2.51000	E-2	-5.70000	E-3
-1.11000	E-2	-7.00000	E-4
0.0015		1.39000	E-2
-3.10000	E-3	-1.27000	E-2
-0.0045		1.10000	E-3
8.50000	E-3	0.0025	
-3.30000	E-3	-4.10000	E-3
7.70000	E-3	-0.0007	

2.58571
 1.12712
 1.28182
 1.43689
 2.0241
 1.30275
 1.88506
 1.58763
 1.05738
 3.48214
 3.04839
 1.09167
 1.22124
 1.39048
 1.05738

TIME: 0.55 SECS.

NONIONIC

6.30000	E-3	-0.0021	
0.0008		2.00000	E-4
0.0009		0.0009	
0		0	
0.0084		0.0084	
0.0009		-0.0009	
0.0013		0.0007	
0.0024		-1.80000	E-3

0.0071		-5.50000	E-3
0.0009		-0.0009	
9.30000	E-3	-7.50000	E-3
0.0037		1.10000	E-3
-0.0019		2.30000	E-3
0.0009		-0.0009	
7.50000	E-3	-9.30000	E-3
-1.10000	E-3	-2.50000	E-3

0.008		-6.20000	E-3
0.013		-0.0056	
-1.00000	E-3	0.0028	
0.0064		-0.0086	
-0.0064		4.60000	E-3
-0.0064		0.0086	
1.40000	E-3	-0.0032	
-1.18000	E-2	0.0068	

2.10000	E-2	0.005	
0.0054		7.40000	E-3
-1.28000	E-2	0	
-1.04000	E-2	-0.0132	
-1.18000	E-2	6.00000	E-4
-0.0058		-0.0114	
0.0132		4.00000	E-3
0.0036		1.00000	E-2

1.69231
4.12195
2.96226

3.56522
1.76316
4.38462
1.41379
1.625
2.08824
1
4.38462
1.05882
3.375
1.47059
2.81818

TIME: 0.51 SECS.

APPENDIX 5

Yates' analysis for the significant interaction

Yates' analysis - Cationic Interactions

1. Temperature and current density

				%
TI	7.96	-2.44	124.32	62.16
I	-10.40	126.76	99.34	49.67
T	4.53	-18.36	129.20	61.45
T*	122.23	117.70	136.06	68.03

2. Acidity of the solution and time of electrodeposition

				%
HR	-14.30	-9.36	108.41	54.20
R	4.94	117.77	144.93	72.46
H	-3.46	19.24	127.13	63.56
T*	122.23	125.69	106.45	53.22

3. Acidity of the solution and salt concentration

				%
HZ	10.61	26.18	144.95	72.47
Z	15.57	118.77	130.65	65.32
H	-3.46	4.96	92.59	46.29
T*	122.23	125.69	120.73	60.36

4. Temperature of the bath and time of electrodeposition

				%
TR	-7.43	-2.49	124.27	62.13
R	4.94	126.76	130.07	65.03
T	4.53	12.37	129.25	64.62
T*	122.23	117.70	105.33	52.66

5. Current density and time of electrodeposition

				%
IR	9.79	14.73	126.56	63.28
R	4.94	111.83	127.78	63.89
I	-10.40	-4.85	97.10	48.55
T*	122.23	132.63	137.48	68.74

6. Acidity and temperature

				%
HT	-7.46	-2.93	115.84	57.92
T	4.53	118.77	137.68	68.84
H	-3.46	11.99	121.70	60.85
T*	122.23	125.69	113.70	56.85

7. Additive concentration and electrodeposition time

7. Additive concentration and time of electrodeposition

				%
AR	8.00	12.94	107.52	53.76
R	4.94	94.58	146.82	73.41
A	-27.65	-3.06	81.64	40.82
T*	122.23	149.88	152.94	76.47

Anionic Additive

1. Temperature and current density

				%
TI	3.63	0.51	145.48	72.74
I	-3.12	144.97	143.	71.67
T	-2.56	-6.75	-6.75	72.23
T*	147.53	150.09	150.09	78.42

2. Acidity and time of electrodeposition

				%
HR	-7.02	-10.16	130.10	65.05
R	-3.14	140.26	158.73	79.36
H	-7.27	3.93	150.42	75.21
T*	147.53	154.80	150.87	75.43

3. Acidity and salt concentration

				%
HZ	3.52	23.76	164.02	82.01
Z	20.24	140.26	171.52	85.76
H	-7.27	16.72	116.50	58.25
T*	147.53	154.80	138.08	69.04

4. Current density and time of electrodeposition

				%
IR	5.97	2.83	147.24	73.62
R	-3.14	144.41	141.54	70.77
I	-3.12	-9.11	141.58	70.79
T*	147.53	150.65	159.76	79.88

5. Additive concentration and time of electrodeposition

				%
AR	-7.81	-10.95	134.24	67.12
R	-3.14	145.19	154.54	77.27
A	-2.34	4.67	156.14	78.07
T*	147.53	149.87	145.20	72.60

Non-ionic Additive

Temperature and current density

				%
TI	4.41	8.66	129.59	64.79
I	4.25	120.93	128.49	64.24
T	-3.86	-0.16	112.27	56.13
T*	124.79	128.65	128.81	64.40

BIBLIOGRAPHY

1. Mohler, J.B., and Sedusky, H.J., Electroplating, Chemical Publishing Co., N.Y. (1951)
2. Schlotter, M., Electrodeposition of metals, Trans. Faraday Soc., 31, 1177 (1935)
3. Dale, J.J., The structure of electrodeposits, Metal Finishing, vol. 52, n. 7 and 8 (1954)
4. Blum, W., and others, Paper presented to the Electrochem. Soc., Trans. Electrochem. Soc., 80,249 (1941)
5. Tomashov, N.D., Theory of corrosion and protection of metals , McMillan Co., N.Y., (1966)
6. Hothersall, A.W., Electrodeposition, Trans. Faraday Soc., 31, 1242 (1935)
7. Gmytryk, M., and Sedzimir, J., Corrosion of Zn in deae - rated sulphate solutions at different pH values, Corrosion Science, vol. 7, pp. 683 to 695 (1967)
8. Allmand, A.J., The principles of applied electrochemistry Logmans, Green and Co., N.Y. (1920)
9. Prinq, J.N., The electrodeposition of zinc at high current densities, J.Chem.Soc. v.105,pp.710-724 (1914)

10. Dole, M., Principles of experimental and theoretical electrochemistry, McGraw-Hill Co., N.Y. (1935)
11. Naybour, R.D., The effect of electrolytic flow on the morphology of zinc electrodeposited from aqueous alkaline solution containing zincate ions, Electrochemical Technology, (1969)
12. Balberyszski, T., and Anderson, A.K., Economics of copper electrowinning at high current densities, AIME, Cleveland, Ohio, (1968)
13. Classen, T., U.S. Patent No. 809,492 (1906)
14. Tucker, J.A., and Thomssen, E.G., Electrodeposition of lead and zinc as affected by the addition of certain organic additives, paper presented at the 15th General Meeting of the American Electrochemical Society, Niagara Falls, Canada (1909)
15. Antropov, L.I., Inhibition of metallic corrosion and the zero point scale of potentials, First International Congress on Metallic Corrosion, p. 147, London, (1961)
16. Sisley, J.P., and Wood, P.J., Encyclopedia of surface active agents, Chem. Publishing Co., N.Y. (1952)
17. Degering, Ed.F., Organic Chemistry , Barnes and Noble, N.Y. (1969)
18. Shaw, D.J., Introduction to colloid and surface chemistry,

Butterworths, London (1968)

19. Frumkin, A., Adsorption of organic substances at the metal / electrolyte solution interface and its influence on electrochemical processes, Electrical Phenomena and Solid / Liquid Interface, vol.3, p. 58, Proceedings of the 2nd International Congress of Surface Activity London, (1957)
20. Vermilya, D.A., What I'd like to know about corrosion, First International Congress on Metallic Corrosion p.62, London (1961)
21. Milone, M. and Cettini, G., The variation of surface activity and growth of modified crystals in aqueous solutions , Electrical Phenomena and Solid/Liquid Interface, Proceedings of the 2nd International Congress of Surface Activity, p.469 , London (1957)
22. Kolthoff, I.M., and Lingane, J.J., Polarography, vol. 1 , Interscience Publishers Inc., N.Y. (1955)
23. Meites, L., Polarographic Techniques, Interscience Publishers , N.Y., (1967)
24. Harkins, W.D., The physical chemistry of surface films, Reinhold Publishing Co., N.Y. (1957)
25. Duckworth, W.E., Statistical techniques in technological research, Methuen & Co. Ltd., London, (1968)

26. Oliva, O., Curso de estatística, Escola Politécnica da Universidade de São Paulo, Depto. de Engenharia de Produção, DLPGP, S.P., (1968)
27. Various, Chemistry and physics of interfaces, American Chemical Society Publications, Washington, D.C. (1965)
28. 3M Company, Technical informations, 3M Company, Chemical Division, Minn., (1964)
29. American Cyanamide, Mining catalog, American Cyanamide Co., (1969)
30. Wever, G.T., Effect and control of impurities in the electrowinning of zinc, Journal of Metals, v. 2 p. 130, (1959)