A STUDY OF THE CORROSION PROCESSES IN TIN-PLATED CONTAINERS USED FOR PACKAGING AQUEOUS "AEROSOLS"

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By

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ABSTRACT

The problem of corrosion in aerosols has been found by other investigators to be limited almost exclusively to aqueous formulations. The corrosion of the containers is characterized by removal of the interior tin plate and perforation of the container leading to failure of the unit. The problem was attacked on the basis of electrochemical action, and studies have shown that the corrosion is galvanic in nature.

The rate of corrosion by weight loss measurements, the reversible electrode potentials, and the polarization of both tin and mild steel specimens have been investigated. It has been shown that the tin suffers no destruction in a corrosive formulation unless it is in contact with mild steel. Electrochemical theory has been used to explain the behavior of the metals involved. It has been shown that it is feasible to use electrical measurements as a basis for determining the relative corrosiveness of a given formulation.

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The author wishes to dedicate this thesis to the memory of Dr. Dwight T. Ewing, under whose guidance and inspiration this investigation was carried out.

He also wishes to express his sincere thanks to Dr. James Dye, whose invaluable advice was freely offered during the final phases of this investigation and the writing of this thesis.

The writer deeply appreciates the financial support of the G. Barr Company of Chicago, Illinois, which made this investigation possible.

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INTRODUCTION

An aerosol is defined as a suspension of fine solid or liquid particles in air or other gas. In this paper, the term "aerosol" includes all those products which depend upon the pressure due to a compressed, liquefied gas to dispense them from their container. Thus, products ranging from insecticide sprays, which are of a type that most closely approaches a true aerosol, to pressure-dispensed shaving creams are included in the term.

The original aerosol insecticide, familiar as the type used by the Armed Forces during World War II, was based on the work done by L. D. Goodhue and W. N. Sullivan of the United States Department of Agriculture, and was covered by United States Patent Number 2,321,023, issued July 8, 1943, to the Secretary of Agriculture.[1] This type of package operated at a pressure of approximately seventy pounds per square inch, and necessitated the use of a container designed to withstand such pressures. The more common aerosol packages commercially available today operate at pressures in the range of thirty to fifty pounds per square inch, and are packaged

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[1] "Package for Profit," E. I. DuPont de Nemours and Co., Inc., Kinetic Chemicals Division, Wilmington, Delaware, p. 3.

in standard, mass-produced, tin-plated containers of typical "beer can" construction.

Another type of tin-plated container is used in packaging aerosols which has no side seam, as is present on the "beer can" type. This container is produced by deep-drawing a shallow cup of tin-plated mild steel into a cylindrical shape. A concave bottom is then crimped into place. This can has a more attractive appearance than the type with the side seam, and allows labeling designs to be lithographed completely around the container.

Containers of both types, which have been internally coated with various lacquers to offer further protection from corrosion than is offered by the layer of tin alone, are available. The lacquers utilized for this purpose are primarily phenolic resins, which exhibit a low solubility in halogenated hydrocarbons such as the various "Freon" compounds, which are used as the pressuring agents in the majority of commercial aerosol packages.

The compressed, liquefied gases most commonly used as the pressurizing agents in aerosol units are Freon-11, trichlorofluoromethane, and Freon-12, dichlorodifluoromethane. These compounds have been chosen as pressurizing agents, or propellents, because of their nonflammability, low toxicity, and favorable vapor pressures at temperatures approximating 25° centigrade. At this temperature, Freon-12 has a vapor pressure of approximately 4.75 atmospheres, while Freon-11 has a vapor pressure of approximately one atmosphere. These compounds are miscible in all proportions in the liquid state, and the vapor pressures of the mixtures follow generally Raoult's Law, the calculated pressures agreeing with the experimental values to within approximately 10 percent.

These propellents exhibit very slight corrosive effects toward most metals such as brass, copper, aluminum, steel, tin, and tin-plated steel. When in conjunction with water, these propellents hydrolyze to a small degree to produce halogen acids and the corresponding alcohols. Freon-11 hydrolyzes most rapidly, to the extent of 28 grams per liter of water per year, in the presence of steel. Freon-12 hydrolyzes to the extent of 10 grams per liter of water per year in the presence of steel, and in water alone, the hydrolysis rate is less than one milligram per liter per month. Both Freon-11 and Freon-12 are more susceptible to hydrolysis in alkaline media, with Freon-12, the most stable compound, hydrolyzing at the rate of five grams per liter per month in 10 percent NaOH at sixty degrees centigrade.[2] Elevated temperatures, far

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[2] Kinetic Technical Bulletin B-2, E. I. DuPont de Nemours and Co., Inc., Wilmington, Delaware (1952), p. 3.

above those to which the standard aerosol containers are subjected, cause relatively rapid decomposition of both Freon-11 and Freon-12, in the presence of metals. At such elevated temperatures, these Freon compounds exhibit corrosive properties toward most metals used in constructing containers.

The problem of corrosion in aerosol containers is one of economic significance. Since the original patent for self-contained, pressure-dispensed insecticides was issued, the number of products available in this form has increased tremendously, as has the total number of aerosol units packaged per annum. At the present time, such widely diversified products as insecticides, room deodorants, paints and lacquers, waxes, and various cosmetics, such as shaving creams, shampoos, and personal deodorants are available. All of these products have attracted favorable notice from the public, with the result that the packing of aerosols has become a rapidly expanding industry. As an example of this rapid growth, market surveys show that in 1951 the total number of aerosol units packaged, which were other than food products, was approximately 43,000,000 units. In 1952, this figure had increased to 96,600,000 units, representing approximately $110,000,000 worth of business. In 1953, the figure had increased still further to approximately 140,000,000 units.[3] These figures include all types of products, irrespective of the size of the container.

Since a wide variety of products are packaged in aerosol containers, the problem of corrosion has assumed serious proportions. Not only has corrosion of the containers caused difficulty in commercially available products with subsequent financial loss, but it has prevented marketing of some products which are still in the experimental stage. Fortunately, the corrosion problem appears to be limited to those formulations which use water as either the sole solvent or as a cosolvent. Experience indicates that, in general, the nonaqueous formulations do not cause corrosion of the containers. An exception to this is the effect of ethyl alcohol on aluminum containers. Under certain conditions, there is a comparatively rapid reaction between the aluminum and the alcohol, with subsequent failure of the container. This type of corrosion may be considerably reduced, and even eliminated, by using some less reactive alcohol such as isopropyl alcohol.

A large number of the cosmetic formulations are aqueous solutions, or contain water as a cosolvent. In addition, many of

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[3] Aerosol Pressure Product Survey, Chemical Specialties Manufacturers Association, Inc. (1953).

these preparations contain relatively reactive ingredients.[4] As a consequence, severe corrosion problems have been encountered in the packaging of many of these products. In addition, since most cosmetic preparations contain some type of perfume, the presence of dissolved iron is highly undesirable because of the tendency for reaction between the dissolved iron and some perfumes to form very unpleasant-smelling compounds. Many perfumes are highly susceptible to this type of reaction, and will tolerate only very low concentrations of dissolved iron, in some cases as low as a few parts per million. As a consequence, corrosion of a tin-plated, mild-steel container by any formulation containing one of these susceptible perfumes would rapidly make the formulation unmarketable.

The most serious corrosion problems appear to occur in containers used to package aqueous formulations, of which the various cosmetic preparations are the most common. Many of these cosmetics are neutral or nearly neutral solutions of salts which have ionic properties. Since the majority of the many products available are packaged in some type of tin-plated, mild-steel

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[4] "Package for Profit," E. I. DuPont de Nemours Co., Inc., Kinetic Chemicals Division, Wilmington, Delaware, p. 20.

container, one step toward the solution of the problem of corrosion in aerosols has been made by studying the corrosion processes in tin-plated containers, both lacquered and unlacquered, containing some of the more common cosmetic preparations. In this investigation, a commercial shampoo was used as an example of a formulation highly corrosive to tin-plated containers, and a commercial shaving cream was used as an example of a relatively noncorrosive formulation. Both of these preparations were obtained from the G. Barr Company of Chicago, Illinois.

The corrosion of the tin-plated containers used in packaging aerosols appears to be due to a galvanic effect. By this it is meant that the dissolution of the metal components of a container is directly due to the passage of an electric current in a short-circuited galvanic cell. Due to pores in the tin plate,[5] which allow the mild-steel base stock to come into contact with the contents of the container, one of the requirements for galvanic corrosion is fulfilled. The two metals in contact with the formulation (i.e., tin and steel) will usually have differing tendencies to enter solution. Thus, an electrical potential difference will be produced across the bimetallic system,

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[5] H. H. Uhlig, Corrosion Handbook, John Wiley and Sons, Inc., New York, 1948, p. 830.

which is a function of the nature and concentration of the constituents in the solution in the container, and which also depends upon the nature, purity, and surface condition of the metals in the system. This potential difference may further be modified by the occurrence of polarization of one or both of the metal electrodes due to the flow of current. Polarization may be thought of as a potential produced by the flow of current in a galvanic cell which opposes the normal or instantaneous potential produced upon first immersing the electrodes of the cell in the electrolyte. Polarization may be due to the local build-up of reaction products at one or both electrodes, the local reduction in concentration of one or more reactants at one or both electrodes, or it may be due to the overvoltage effects due to the evolution of a gas at one or both electrodes. The phenomenon of polarization is a common one in electrochemical reactions in which a current is allowed to flow. Polarization tends to reduce the potential difference across a galvanic cell, and thus tends to retard the reactions taking place by retarding the flow of current. Conversely, the presence of any constituent in the contents of a corroding container which would function as a depolarizer would cause an increase in the flow of current, and hence an increase in the rate of corrosion.

Because of the phenomenon of polarization, the irreversible potential, i.e., the potential measured across a galvanic cell when current is flowing, may be quite different from the reversible potential, i.e., the potential measured across a galvanic cell when no current is flowing. Because of this, the potential measured across a short-circuited galvanic corrosion cell may be quite different from the value calculated from the electrochemical series of metals.

In this investigation, the purpose has been to determine first the corrosion process or processes, and second, the corrosiveness of any formulation relative to some standard formulation of noncorrosive character. The corrosiveness of a formulation toward tin-plated containers has been commonly determined by packaging samples and shelf-testing them for extended periods of time. Subsequent opening of these samples and inspection of the interior indicated whether the product was marketable or not. Since this type of testing required long-term storage, in some cases over a year's interval or more, due to the low reaction rate in some corrosion processes, it was unsatisfactory under the highly competitive conditions existing in the industry.[6] Attempts were made to accelerate

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[6] "Package for Profit," E. I. DuPont de Nemours Co., Inc., Kinetic Chemicals Division, Wilmington, Delaware, p. 12.

the corrosion processes by storing the sample packages at elevated temperatures, so that the time required for an accurate estimate of corrosiveness would be reduced.[7] The results of many of these accelerated tests were found to be anomalous, and the accelerated test is regarded with suspicion today.

Three types of measurements were utilized in this investigation. Since this investigation was limited to corrosion of tin-plated containers, samples of pure tin foil and the mild-steel base stock normally used in the production of tin cans were used. The measurements consisted of weight loss measurements of standard size samples of both metals, reversible potential measurements across tin-steel electrode systems immersed in various solutions, and polarization measurements on short-circuited tin-steel electrode systems immersed in various solutions. Corrosion tests on standard tin cans obtained from the G. Barr Company were also run as comparisons.

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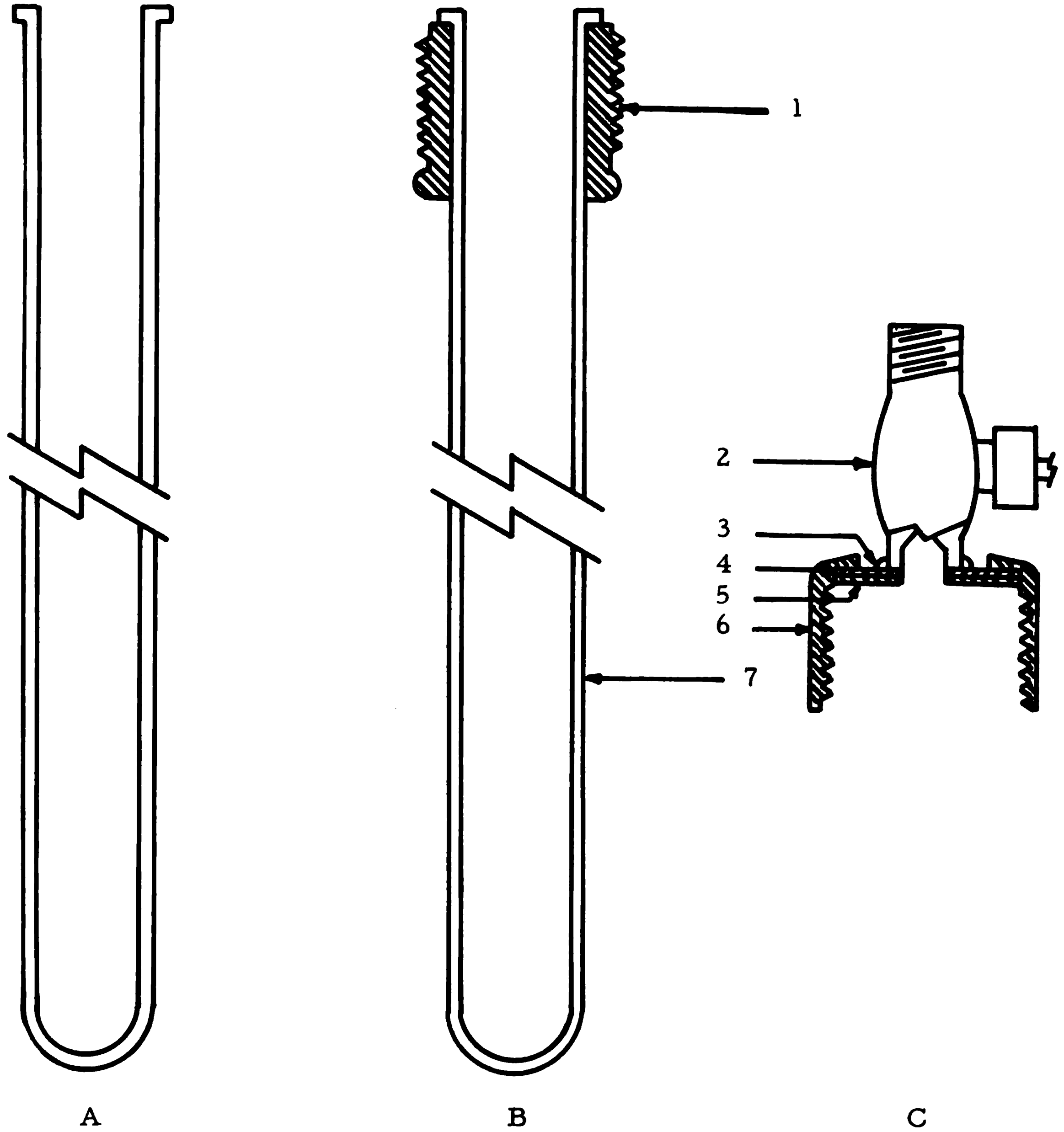
[7] "Package for Profit," E. I. DuPont de Nemours Co., Inc., Kinetic Chemicals Division, Wilmington, Delaware, p. 12.

APPARATUS AND METHODOLOGY

The apparatus used in conducting this investigation was of simple construction, and could be easily duplicated in any laboratory. Since the corrosion of aerosol containers occurs in systems under pressure, it was necessary to devise equipment in which the various measurements could be made, which would withstand the pressures involved. Two types of glass pressure tubes were utilized in those experiments in which the weight loss, due to corrosion of standard metal strips, was measured. The first type of tube used consisted of a test tube constructed of 19 millimeter O.D. pyrex medium-wall tubing. These tubes measured eight inches long, and had a wall thickness of 1.5 to 2.0 millimeters. They were made with a standard test-tube type round bottom, and the lip was turned so as to present a flat surface, two or three millimeters wide, which was perpendicular to the longitudinal axis of the tube (Figure 1A). These tubes were fitted with modified brass three-quarter inch hose couplings (Figure 1B). The male portions of the hose couplings were slipped over the bottoms of the tubes, and up to the lips, where they were in contact with the flat undersurfaces of the lips. The female portions of the couplings were fitted with internal steel washers to



1 - Brass male hose fitting, 3/4-inch
2 - 1/8-inch baby Hoke needle valve
3 - Soldered joint
4 - 1-inch steel washer
5 - Resistoflex gasket
6 - Brass female hose fitting, 3/4-inch
7 - 19 millimeter O.D. heavy-wall pyrex tube

Figure 1. Pressure tubes.

which were silver soldered one-eighth inch baby Hoke needle valves, so that the valve bodies extended through the outlet openings of the female portions of the couplings. Gaskets of one-eighth inch thick "Resistoflex," a polyvinyl alcohol resin, were prepared and inserted into the female portions of the couplings so that they made firm contact with the steel washers bearing the valves. When the female portions of the couplings were screwed onto the male portions, these gaskets produced a tight seal between the lips of the glass tubes and the steel washers bearing the needle valves. Upon filling these tubes with standard metal samples, the corrosive formulation under consideration, and the "Freon" mixtures, the only metals other than the corrosion samples to come into contact with the corrosive media were the brass bodies of the needle valves, and here the contact was only with the vapor phase. These tubes had the advantage of being reusable, they could be filled in such a way as to exclude air, and it was possible to withdraw portions of the corrosive media after various time intervals.

The second type of pressure tube used in the corrosion measurements was made in such a way that the standard metal strips and the corrosive media were completely enclosed in glass. These tubes consisted of eight inch long sections of heavy-wall pyrex tubing, with a wall thickness of 2.5 to 3.0 millimeters. One end of each of these tubes was drawn into a round, test-tube type bottom. The standard metal samples were then placed in the tubes. These tubes were then heated at a point about six inches from the bottom, and drawn into a constricted neck. The fluid ingredients were then added through the constricted neck by means of a small funnel which was drawn down to a long thin tip. When the "Freon" mixtures were added, in liquid form, the bottoms of these tubes were immersed in liquid nitrogen in order to freeze these compounds. The constricted necks of these tubes were then heated and sealed off, while the lower portions of the tubes were immersed in liquid air. These tubes were stored by encasing them in sections of steel water pipe to eliminate the danger of flying glass in the event of an explosion.[8] Care was taken in the production of these tubes to insure uniform wall thickness throughout, and the tubes were thoroughly annealed before use. Figures 2A, 2B, and 2C show the various steps in the construction and sealing of these tubes. Since the seals on these tubes sometimes cracked upon cooling, it was found necessary to flame-anneal them to insure against failure of the tube.

A piping network attached to a laboratory rack was constructed for the handling of the "Freon" propellents. The cylinders of the

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[8] Kinetic Technical Bulletin KTM-14, E. I. DuPont de Nemours and Co., Inc., Wilmington, Delaware, 1953, p. 3.

compressed gases were held in an inverted position on the rack, to allow the "Freons" to be drawn off in a liquid state. The piping network was constructed of one-quarter inch copper tubing, and utilized one-quarter inch baby Hoke needle valves as control valves. The system was divided into two parts, one part of which was fitted with cooling coils immersed in a bath of solid carbon dioxide and isopropyl alcohol. The other part of the system was fitted with electric heaters, made of nichrome wire, so as to insure complete vaporization of the compressed gases. In this way, the gases could be delivered in either a liquid or gaseous state.

The part of the system designed for handling the propellents in a gaseous state was connected, through a needle valve, to a copper "T," one end of which was attached to a female fitting which was tapped to fit the threads of a one-eighth inch Hoke needle valve. By means of this arrangement, it was possible to attach the pressure tubes fitted with Hoke valves to the system, evacuate all of the air in the tube, and fill the tubes with mixtures of the "Freon" compounds by freezing the gases into the pressure tubes with a dry ice and isopropyl alcohol bath.

The "Freons" used in all of the experiments were Freon-11 and Freon-12, the most commonly used propellents in packaging aerosols. These compounds were used in a 1:1 ratio, by weight, which gave a mixture with a vapor pressure of approximately forty pounds per square inch gauge. Approximately 10 milliliters of this mixture was added to each pressure tube in all of the experiments, a volume which comprised one-half of the total volume of the contents of the pressure tubes. Each tube was calibrated so that by introducing the correct volumes of Freon-11 and Freon-12, the correct weight ratio was obtained.

Electromotive force and polarization measurements were made on various formulations as a method of following the corrosion processes involved. Since many of these measurements were made on formulations containing mixtures of "Freon" compounds, it was necessary to devise a cell which would withstand the internal pressure. This cell was constructed of heavy-wall pyrex tubing with a diameter of 19 millimeters, and was of typical test-tube shape. A piece of pyrex tube of 7 millimeter O.D. was sealed through the bottom of the test tube, and the other end connected to a stopcock. The other side of the stopcock was connected through a salt bridge to a saturated calomel half cell. An aluminum collar, which was made of one-quarter inch thick aluminum sheet stock, was placed around the pressure tube below the lip. The tube was closed by bolting a cap plate, bearing the electrode assembly and a "Resistoflex" gasket, to this collar, so that the gasket made a tight seal with the upper surface of the lip of the pressure tube (Figure 3A).

The electrode assembly consisted of a piece of pyrex tubing containing two copper wires. One end of the glass tubing was sealed to the cap plate with "Apiezon W" cement, and the other end was sealed with a "Resistoflex" plug through which the copper wires extended. The copper wires extended through the cap plate, and were insulated from the cap plate and each other by a polyethylene grommet. The tin and steel electrodes were soldered to the copper wires extending through the "Resistoflex" plug at the lower end of the assembly, and the soldered joints coated with a cellulose acetate stop-off lacquer (Figure 3B).

The electromotive force measurements were made with a Leeds and Northrup Student Potentiometer, utilizing a galvanometer with a sensitivity of 0.0012 microamperes per millimeter deflection. The current flow during the polarization measurements was found by measuring the voltage drop across a known external resistance with the same potentiometer. All electrical measurements were made at 25° centigrade, unless otherwise designated.

Standard size strips of tin foil and mild-steel can stock which measured 0.5 by 2.5 centimeters were cut. These strips were electrolytically cleaned before use by being made the cathode in an

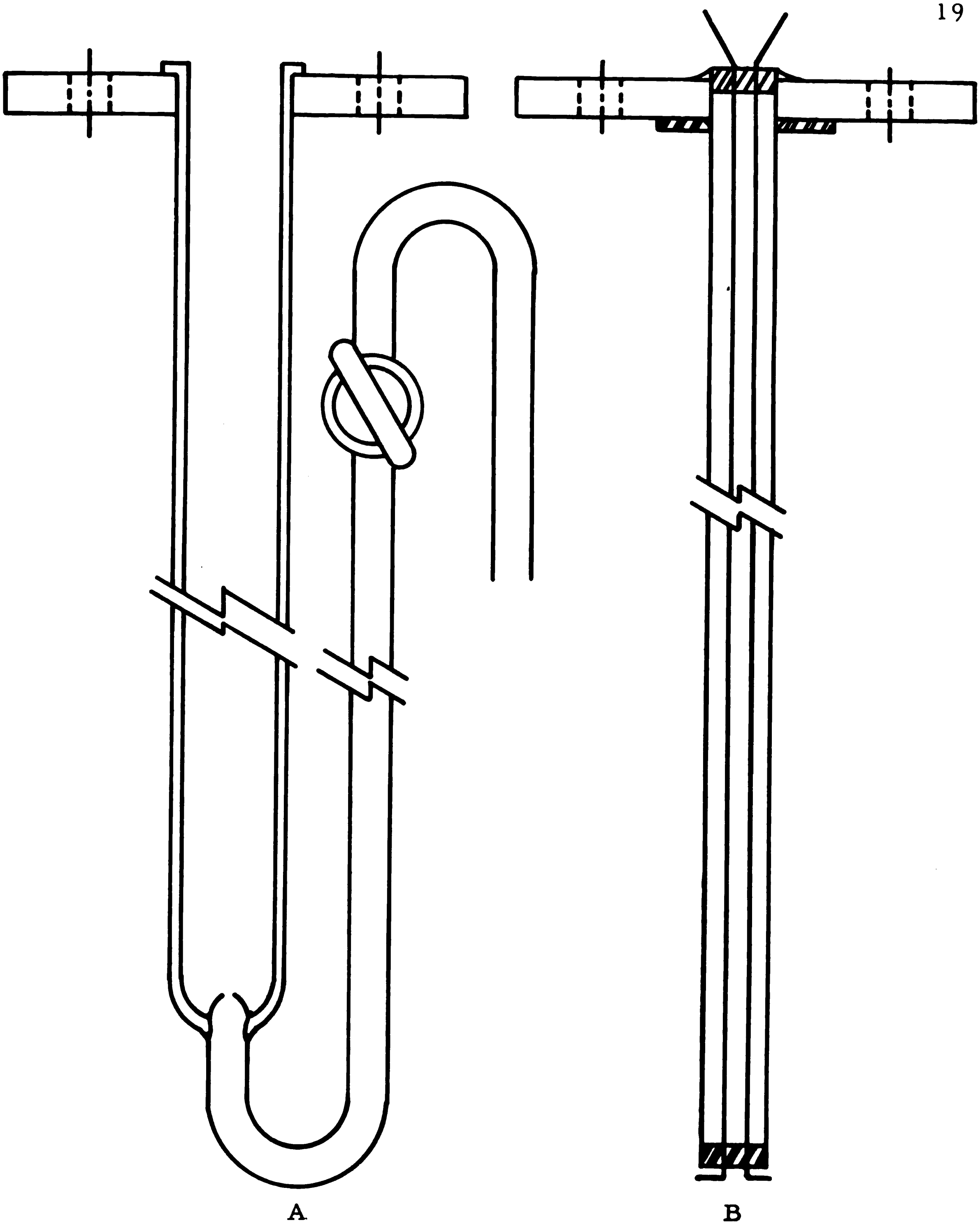

Figure 3. Pressure cell and electrodes.

alkaline cleaning bath. After thirty seconds in this cleaner, the strips were rinsed thoroughly in cold running water, immersed for five seconds in 20 percent by volume hydrochloric acid, and rinsed again in distilled water. The strips were used immediately after cleaning.

Strips prepared in this manner were used for corrosion specimens in various formulations. The strips were cleaned, dried, weighed, and then immersed in the corrosion media. After various time intervals, the strips were removed, rinsed, freed from any loosely adhering corrosion product, dried, and reweighed. The loss or gain in weight was taken as a measure of the corrosion. These experiments were run on tin alone, steel alone, tin and steel together but insulated from each other, and tin and steel in contact with each other. These experiments were run in formulations with and without the "Freons" present, and with and without air present.

The electrode potentials of both tin and steel were measured in various solutions, against a saturated calomel half cell. These measurements were made on formulations with and without the "Freons" present, and with and without the presence of air. Since it was noticed that the reversible potential of either a tin or steel electrode was not always the same in a given formulation, potential measurements were made on each of these electrodes over an extended period of time, for various solutions. These data yielded valuable information as to changes occurring at the electrodes.

Polarization effects were determined for tin and steel electrodes in various formulations. The electrodes were connected through a variable external resistance which could be set at known values. The current flow was found by measuring the voltage drop across the known external resistance value with a potentiometer, and applying Ohm's Law. For a given value of external resistance, the current, and the irreversible potential of each of the electrodes were measured. The irreversible potential for each electrode was measured against a saturated calomel half cell. These measurements were conducted at 25° centigrade. These data were plotted graphically to obtain the polarization curves for both tin and steel electrodes immersed in various solutions. Once again, these measurements were run in both the presence and absence of air, and in the presence and absence of "Freon" compounds.

Tests were made to determine the porosity of the tin plate in commercial containers. Samples of both the standard tin-plated cans and the lacquered cans were obtained, and filled with a saturated solution of sodium chloride. These samples were then placed in a constant-temperature oven at 96° centigrade. Samples of each type of can were removed after twenty-four and seventy-two hours.

The solutions from each can were transferred to beakers, made acid with two normal sulfuric acid, 2 milliliters of 30 percent hydrogen peroxide added to each, and boiled until the peroxide was essentially destroyed. A small quantity of potassium ferrocyanide was then added to each beaker. The presence of a blue precipitate indicated the presence of iron. Visual inspection of the cut-open containers revealed the points at which attack had occurred.

Tests using similar reagents were made, in which strips of filter paper soaked in a saturated solution of sodium chloride containing 2 percent potassium ferricyanide were applied to sections cut from can walls. The presence of blue spots on the paper indicated corrosion of the steel. In all of these tests, there appeared to be little or no attack of the tin plate. As a consequence, it appears the attack of the steel could only have occurred through pores in the tin plate. The lacquered cans also indicated some porosity of both the lacquer and the tin plate, but this was of a considerably lesser degree.

Two short pieces of 15 millimeter diameter standard-wall pyrex tubing were drawn down to fine capillary tips on one end. These tubes were then clamped so that the capillary tips were in contact with different points on a strip of mild-steel base stock. The tubes were then filled with various formulations, with care being taken to insure good electrical contact between the liquid in the capillary tips and the steel surface. Saturated calomel half cells were then inserted into the upper ends of these tubes, and the potential across the system was measured with a potentiometer. By moving the strip of steel so that other points on its surface came into contact with the capillary tips containing the corrosive media, it was possible to show that the potential of steel, in contact with an electrolyte, is not the same at all points on the metal surface.

EXPERIMENTAL DATA

Corrosion Tests on Standard Specimens

A preliminary experiment in this investigation indicated that the corrosion of tin and steel by an aqueous aerosol formulation known to be corrosive toward tin-plated containers was due to an electrochemical action. This was brought about by placing two species of metal in contact with each other and in contact with an electrolytic solution. A strip of tin foil and a strip of mild-steel can base stock were crimped firmly together at one end, and the joint coated with electroplating stop-off lacquer. This bimetallic couple was then immersed in a sample of the shampoo formulation received from the G. Barr Company. No attempt was made to exclude atmospheric oxygen. An interval of 24 hours was allowed to expire, at which time the bimetallic couple was removed, rinsed in distilled water, and examined visually to detect any indication of corrosion. In this case, the metal area exposed to the shampoo was approximately five square centimeters for both the tin and the steel. It was easily seen that the surface of the tin strip was uniformly etched, while the surface of the steel strip was covered with a dense, blue-black coating. Addition of a few drops of cacotheline test solution[9] indicated the presence of stannous tin in the shampoo. No test for tin was obtained in the original shampoo sample.

A similar experiment was conducted in which a strip of tin foil and a strip of steel base stock were insulated from each other, and the bimetallic specimen was immersed in a sample of shampoo. No attempt was made to exclude atmospheric oxygen. After 24 hours, the bimetallic specimen was removed, and the surfaces of the metals examined for indications of corrosion. The metal surfaces exposed to the shampoo comprised an area of approximately five square centimeters for both the tin and the steel. Visual inspection of the metal strips showed, again, a dense, blue-black film over the steel, but no attack of the tin. A few drops of cacotheline test solution added to the shampoo sample indicated the absence of stannous tin.

A portion of the shampoo from each of these experiments was treated with acid and hydrogen peroxide, boiled to destroy the peroxide, and then a few drops of potassium ferrocyanide solution added. A test for dissolved iron was obtained in both cases.

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[9] Feigel, Qualitative Analysis by Spot Tests, Elsevier Publishing Co., N. Y. (1946), p. 87.

The results of these experiments indicated that the corrosion of tin in the shampoo formulation occurred only when the tin was in contact with steel, and this fact pointed to a galvanic corrosion process.

The fact that the tin had undergone attack indicated that the tin functioned as the anode in the tin-steel couple. This phenomenon was not to be expected from an examination of the electrochemical series of metals which places the oxidation potential of iron above that of tin. However, a consideration of the conditions present in the experiment served to dispel the apparent anomaly. The standard oxidation potentials of metals were determined under reversible conditions; i.e., essentially no current flowing. These potentials were also measured for systems in which a metal electrode was immersed in a solution of its own ions at unit activity. In the case of a system of two metals in contact with each other, and both in contact with an electrolytic solution, there will be a current flow, at least initially, and hence the condition of reversibility does not apply. There will be some polarization of one or both metal electrodes, which will alter the respective potentials. It must also be remembered that in the two experiments outlined above, there were no ions of either metal initially present in the electrolyte. As a consequence, the discrepancy between the actual behavior of the electrodes and the theoretical behavior is not surprising.

In order to place the observed results from the preliminary experiments on a quantitative basis, a series of metal specimens was prepared, and immersed in portions of both the commercial shampoo and a commercial shaving cream of noncorrosive character, which was also obtained from the G. Barr Company. Both the tin and steel strips were degreased with carbon tetrachloride followed by an acetone rinse, and then weighed. They were then immersed in the formulations in both a coupled and uncoupled condition. After varying periods of time, the metal specimens were removed, rinsed in distilled water, freed from loosely adhering corrosion products, dried, and reweighed, after the coupled strips were once more separated. The results of these experiments are listed in Tables I and II.

Several facts were noted from the results of these experiments. It was shown that, in the shampoo, the tin did not undergo attack unless it was in contact with steel. It was also noted that the steel corroded more rapidly when by itself than when coupled with tin. From the data it was apparent that the shaving cream was indeed a noncorrosive formulation.

TABLE I

THE CORROSION OF TIN AND STEEL BY COMMERCIAL SHAMPOO IN THE PRESENCE OF AIR

(specimen areas = 2.5 square centimeters; weights in grams)

Weight Record	Days				Comments
	1	3	6	12	
			Tin in Shampoo		
Before	0.0430	0.0466	0.0451	0.0455	No attack
After	0.0430	0.0465	0.0448	0.0452	
Loss	0.0000	0.0001	0.0003	0.0003	
			Steel in Shampoo		
Before	0.5939	0.5693	0.5699	0.5764	Severe pitting, 12 days
After	0.5922	0.5661	0.5633	0.5704	
Loss	0.0017	0.0032	0.0066	0.0060	
			Tin, Coupled with Steel, in Shampoo		
Before	0.0480	0.0474	0.0456	0.0431	Tin etched
After	0.0474	0.0459	0.0433	0.0394	
Loss	0.0006	0.0013	0.0023	0.0037	
			Steel, Coupled with Tin, in Shampoo		
Before	0.5624	0.6343	0.6089	0.5332	Some pitting, 12 days
After	0.5617	0.6329	0.6071	0.5312	
Loss	0.0007	0.0014	0.0018	0.0020	

TABLE II

CORROSION OF TIN AND STEEL BY COMMERCIAL SHAVING CREAM IN THE PRESENCE OF AIR

(specimen areas = 2.5 square centimeters; weights in grams)

Weight Record	Days				Comments
	1	3	6	12	
Tin in Shaving Cream					
Before	0.0460	0.0447	0.0471	0.0460	No attack
After	0.0460	0.0446	0.0469	0.0459	
Loss	0.0000	0.0001	0.0002	0.0001	
Steel in Shaving Cream					
Before	0.5656	0.5836	0.5807	0.5657	No attack
After	0.5656	0.5838	0.5806	0.5658	
Loss	0.0000		0.0001		
Gain		0.0002		0.0001	
Tin, Coupled with Steel, in Shaving Cream					
Before	0.0443	0.0481	0.0448	0.0458	No attack
After	0.0443	0.0481	0.0447	0.0457	
Loss	0.0000	0.0000	0.0001	0.0001	
Steel, Coupled with Tin, in Shaving Cream					
Before	0.4903	0.6205	0.6325	0.5331	No attack
After	0.4903	0.6212	0.6324	0.5330	
Loss	0.0000		0.0001	0.0001	
Gain		0.0007			

If it is assumed that the tin functioned as the anode in the tin-steel couple immersed in the shampoo formulation, the more rapid destruction of the tin when coupled with steel may be explained. This assumption is borne out by the fact that the steel corroded more rapidly when alone than when coupled with tin; an example of cathodic protection being furnished to one metal by another metal to which it is coupled and which functions as an anode.

It must be remembered that the conditions under which these experiments were conducted are not the same as the conditions which prevail in a closed aerosol package. There were, of course, no Freon compounds present in the experimental systems, and, as a consequence, the corrosion processes which occurred did so at atmospheric pressure. The corrosive effect of the various Freons has been studied exhaustively by the E. I. DuPont de Nemours Corporation,[10] and further tests were run by the author, with negative results for tin and steel in Freon-11 and Freon-12 both from the storage cylinders, and saturated with water. More important perhaps is the fact that in the experimental systems, the exposed

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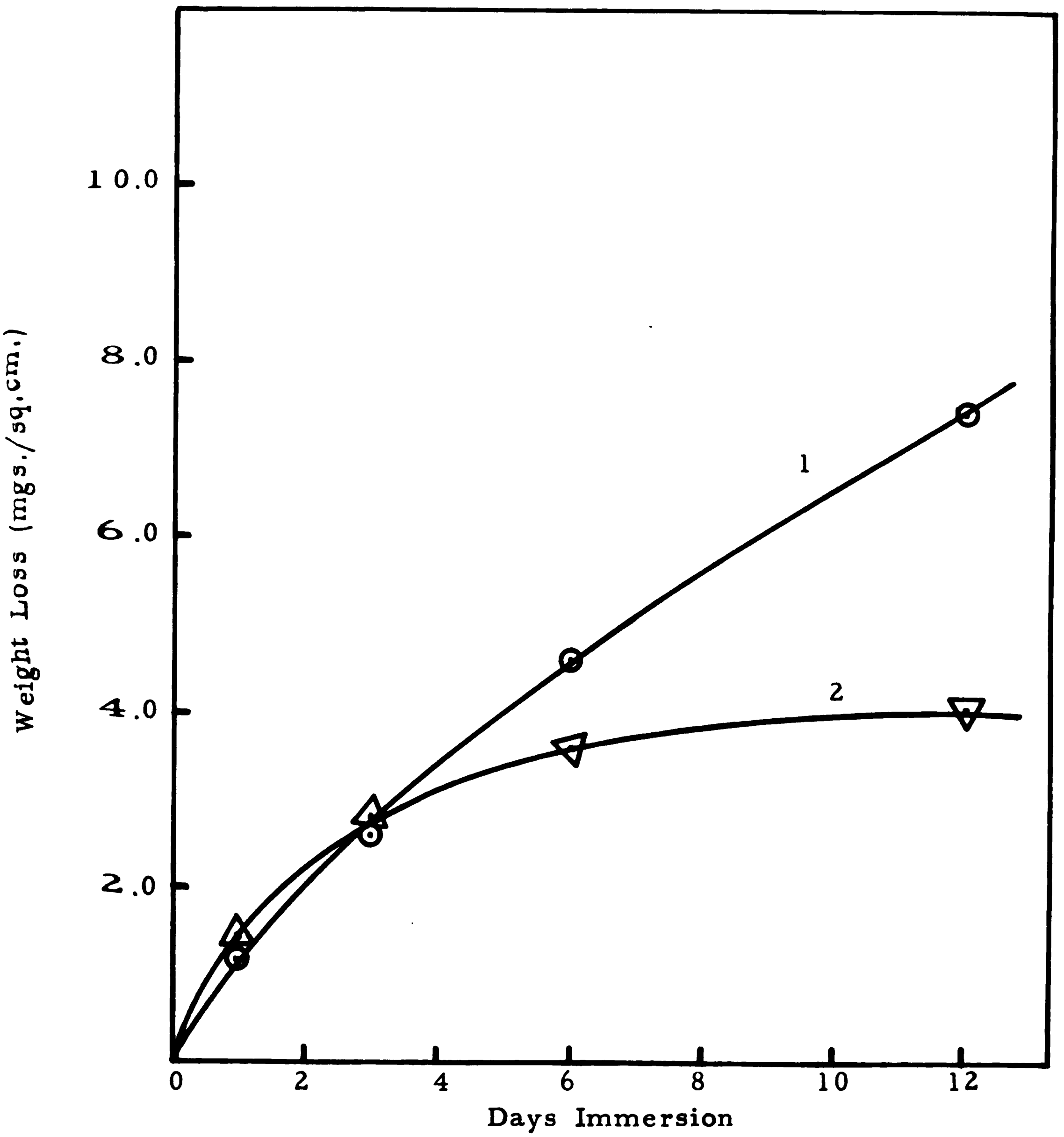
[10] Parmlee and Downing, Soap and Sanitary Chemicals, XXVI, No. C.Sm. A. (2), 1950.

surface areas were essentially the same for both the tin and the steel. Such is not the case in a tin can. In a tin can, the steel would be exposed only through fractures and scratches in the tin plate caused by forming the container, and through pores and other inadequacies produced during the tinning of the steel base stock. In such a case, there would exist only small cathodic areas and large anodic areas. As a result, it may be expected that the galvanic corrosion processes would be controlled by the degree of polarization of the cathodic areas.

A curve was drawn in which the weight loss per square centimeter was plotted against the time of immersion, for both the coupled tin and steel strips immersed in commercial shampoo (Figure 4). The slope of the curve at any point is, of course, the rate of destruction of the metal involved. From this curve, it may be seen that the rate of destruction of both metals decreases with time. This point is interesting, since it indicates that the corrosion reactions involved are self-limiting. Unfortunately, in a tin-plated container, the tin plate is quite thin, and the tin is very likely removed from large areas of the surface of the steel base stock before the rate of the corrosion reaction is decreased sufficiently.

Experiments of a similar nature were run, in which the metal specimens were immersed in shampoo with an equal quantity



1 - Tin coupled with steel in commercial shampoo
2 - Steel coupled with tin in commercial shampoo

Figure 4. Corrosion rate curves.

of a mixture of 50 percent Freon-12 + 50 percent Freon-11 added. These samples were sealed in glass pressure tubes, and then placed in sections of steel pipe, which acted as safety shields. In these experiments, a further modification was made in that some of the samples were packaged in such a way as to eliminate as much atmospheric oxygen as possible. This was accomplished by sweeping all containers out with dry nitrogen. The shampoo formulation was heated to 90° centigrade for thirty minutes in order to expel as much dissolved air as possible. This was done under reflux to eliminate the loss by vaporization of any of the volatile constituents. The Freons which were added were vaporized in a heated section of the piping system, bubbled through a heated solution of alkaline pyrogallol, passed through a tube containing glass wool, and finally dried by passage through a tube of anhydrous calcium chloride. This treatment did not cause any apparent decomposition of either of the Freons. After removal of dissolved oxygen from the Freon compounds, they were recondensed by passage through cooling coils immersed in a mixture of solid carbon dioxide and isopropyl alcohol.

In all cases, in this experiment, the metal specimens used were strips of tin and mild steel, crimped firmly together at one end, and the crimped joint coated with electroplating stop-off lacquer. The metal strips were once again degreased with carbon tetrachloride followed by an acetone rinse. The strips were then individually weighed, coupled together, and immersed in the various formulations. The mixture of Freons was added, and the pressure tubes sealed with an oxygen-gas torch. The results are listed in Table III.

From these data several facts may be noted. In the presence of atmospheric oxygen, the corrosion of the tin strips was greater than in formulations in which the amount of air present, either in the vapor phase or dissolved in the liquid phase, was kept at a minimum. In those systems in which the tin was most readily attacked, the steel strips were corroded to a somewhat lesser extent.

The fact that the steel strips coupled with rapidly corroding tin strips suffered a lesser degree of attack than those steel specimens which were coupled to slowly corroding tin strips once again indicated that the tin, by acting as the anode, furnished cathodic protection to the steel. The presence of atmospheric oxygen increased the flow of current in the galvanic couple, most likely by serving as a depolarizer and reducing the hydrogen overvoltage at the cathode, thus imposing cathodic properties on the steel specimen and reducing the corrosion of the steel. The effect appeared to be sufficiently great to overcome the normal enhancement of the corrosion

TABLE III

CORROSION OF COUPLED TIN AND STEEL STRIPS IN COMMERCIAL SHAMPOO IN THE PRESENCE OF FREON-11 AND FREON-12, WITH AND WITHOUT THE PRESENCE OF AIR

Conditions	Metal Specimen	Weight (grams)		
		Before	After	Loss
Shampoo + air + Freons, at room temp. 2 days, metals in contact	Tin Steel	0.1020 0.4774	0.1014 0.4769	0.0006 0.0005
Shampoo + Freons, air-free, at room temp. 2 days, metals in contact	Tin Steel	0.0980 0.5091	0.0976 0.5087	0.0004 0.0004
Shampoo + air + Freons, at room temp. 7 days, metals in contact	Tin Steel	0.1012 0.4849	0.0986 0.4830	0.0026 0.0019
Shampoo + Freons, air-free, at room temp. 7 days, metals in contact	Tin Steel	0.0993 0.5116	0.0972 0.5103	0.0021 0.0013
Shampoo + Freons + air, at room temp. 14 days, metals in contact	Tin Steel	0.0998 0.4495	0.0966 0.4475	0.0032 0.0020
Shampoo + Freons, air-free, at room temp. 14 days, metals in contact	Tin Steel	0.1008 0.4639	0.0982 0.4621	0.0026 0.0018

of steel in the presence of oxygen. The terms "rapid" and "slow" corrosion are used here strictly in a relative sense.

Porosity of Tin Plate in Commercial Containers

The results of the preceding experiments indicated that the corrosiveness of certain aerosol formulations toward tin-plated containers was due to the formation of a galvanic cell between the components of the container and the fluid ingredients. A necessary requirement for the destruction of the tin plate is that both the tin and the steel base stock come into contact with the formulation. A second requirement is, of course, that the formulation be capable of carrying a current of electricity. In order to establish the possibility of corrosion of commercial containers by galvanic action, it was necessary to show that the coating of tin on the steel base stock did not form a continuous protective covering. Two possibilities exist as to the cause of flaws in the tin plate. Firstly, during the fabrication of the container, scratching and fracturing of the tin plate very probably occurs. These flaws would undoubtedly appear at those points where the metal is joined together; namely, the side seam, and the crimped areas where the top and the bottom of the container are affixed. In the case of the Crown Container, which is produced by a deep-drawing process and which, consequently, has

no side seam, there undoubtedly is a flow of the tin plate during the drawing process which would lead to very thinly tinned areas over the metal surface. These thinly tinned areas would be expected to contain flaws in the tin plate, and indeed corroded containers of this type show corrosion along vertical striations on the can wall, i.e., in the direction of the drawing. Once again, in this type of container, the bottom is crimped into place, a process which could lead to flaws in the tin plate along the crimped joint.

The second possibility for the cause of flaws in the tin plate is that the tin does not cover the steel base stock completely during the tinning process. This could be caused by the steel surface not being completely clean prior to tinning, or by the presence of small inclusions of slag or other impurities in the steel surface, which would not be removed by the cleaning process. Previous investigations have shown that there is indeed a certain area of steel base stock which is left exposed after the tinning process.[11] It would be well to point out that although tinning of steel base stock by electrodeposition gives a more nearly continuous coating of tin than do hot-dip methods in which steel sheets are immersed in a bath of

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[11] H. H. Uhlig, Corrosion Handbook, John Wiley and Sons, Inc., New York (1948), pp. 829-36.

molten tin, the possibility of flaws still exists for the reasons cited above.[12]

It is possible to obtain tin-plated containers commercially which have been internally coated with a lacquer to further increase the resistance to corrosion. Although it is difficult to state exactly what the lacquers used are composed of, it is probable that they are various phenolic resins, or possibly mixtures of phenolic and epoxy resins. It has been found that, while the internally lacquered cans do undoubtedly have a higher corrosion resistance, there are still flaws present through which the steel base stock is exposed.

An experiment designed to show the presence of exposed steel in tin-plated containers of both the lacquered and unlacquered types was run, using commercial containers obtained from the G. Barr Company. Twelve containers of each type were filled to the top with a nearly saturated solution of sodium chloride. The containers were closed with one-hole rubber stoppers bearing six-inch sections of glass tubing of seven millimeter outside diameter. The purpose of these seals was to minimize evaporation of the contents of the containers. These containers were then incubated in a

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[12] H. H. Uhlig, Corrosion Handbook, John Wiley and Sons, Inc., New York (1948), pp. 829-36.

constant-temperature oven at 90° centigrade. Four samples of each type of container were removed at the end of 24 hours. A 100-milliliter aliquot was taken from each sample, and placed in 250-milliliter beakers. The solutions were acidified with 2N sulfuric acid, and five milliliters of 30 percent hydrogen peroxide added to each. These solutions were boiled until the peroxide was destroyed. After cooling, an excess of potassium ferrocyanide was added to each, and the relative intensity of the resulting Turnbull's blue precipitate approximated visually. This procedure was repeated with samples withdrawn at the end of forty-eight hour and seventy-two hour incubation periods. In all cases, a blue precipitate was formed, indicating the presence of dissolved iron. A reagent blank was run in each case on the original sodium chloride solution, with negative results for iron.

The sample containers were cut open, after the aliquot portions were removed, and after rinsing with distilled water and drying, were examined under a microscope. Numerous black spots could be seen over the interior surfaces of the containers, and relatively large black areas discerned around the crimped joints. No apparent attack of the tin plate could be detected, as the tin remained quite bright and shiny.

Although some of the results were slightly erratic due to the statistically small number of samples, it was possible to establish definite trends. The longer the period during which the containers were in contact with the corrosive medium, the greater was the concentration of dissolved iron in the solutions. Those containers in which the higher concentrations of dissolved iron were detected showed more pronounced black spots over the internal surfaces when examined microscopically than those containers in which only a small iron concentration was detected. The results indicated that the lacquered containers indeed suffered less corrosion than the unlacquered samples, but still the presence of dissolved iron in the contents of the lacquered containers was readily demonstrated. These results serve to indicate that there definitely are areas of tin-plated containers which are not covered by protective coatings.

Further experiments were conducted, in which strips of filter paper were soaked in a solution saturated with sodium chloride and containing 5 percent of potassium ferrocyanide. These strips of filter paper were then applied, in a still wet condition, to the interior surfaces of both lacquered and unlacquered cans which had been cut open longitudinally and rolled out flat. These metal samples covered with the filter paper strips were then placed in a desiccator containing distilled water in the bottom, and the desiccator then placed in an incubating oven at 80° centigrade for twenty-four hours. The water in the desiccator served to saturate the air space with water vapor, and thus prevent the strips of filter paper from drying. After the twenty-four hour interval, definite blue spots could be seen on the filter paper, indicating the presence of ferric iron at those spots. Visual inspection of the metal surface under the filter paper revealed dark spots which apparently extended through the tin plate, and whose positions coincided with the blue spots on the filter paper. In the case of the lacquered containers, blue spots were noted on the filter paper which were of a much smaller number and extent, and it was difficult to ascertain the presence of dark spots on the metal surface beneath the filter paper. It was observed that the blue spots on the filter paper strips were not limited to those areas where the metal was subjected to machining, i.e., the points where the side seam was formed and where the ends of the container were crimped into place. Similar methods of determining the porosity of tin plate have been applied by previous investigators, and values have been determined for the area of exposed steel base stock over a given area of tin plate for varying thicknesses of tin.[13]

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[13] H. H. Uhlig, Corrosion Handbook, John Wiley and Sons, Inc., New York (1948), pp. 829-36.

Electrical Measurements on Tin and Steel Electrodes

When a metal is immersed in a liquid medium, there will exist a tendency for the metal to dissolve. During this process of dissolution, metal ions will migrate across the metal-liquid interface, leaving an excess of electrons at the metal surface. As the metal surface builds up a larger excess of electrons, it will become more difficult for ions to leave the metal surface, and at the same time some of the ions in solution will tend to return to the metal surface and be discharged. At equilibrium, the number of ions leaving the metal surface will equal the number of ions returning to the metal surface and being discharged. Under these conditions of equilibrium, the metal surface will contain excess electrons which will give the metal an electrical potential. The tendency for metal ions to dissolve or plate out has been termed the "escaping tendency."[14] At equilibrium, the escaping tendencies of the metal ions in the metal and in the solution are equal.

The potential attained by a metal specimen immersed in a solution at equilibrium will be a function of the nature of the metal, the composition of the solution, and will also depend on the surface

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[14] Pollitt, The Causes and Prevention of Corrosion, D. Van Nostrand Co., N. Y. (1923), p. 19.

of the metal. For a given metal immersed in a given solution, the potential of the metal may be varied considerably by variation in the surface condition.

When two metals are immersed in the same solution, they will attain different electrical potentials, and if they are connected by means of an external wire, a current of electricity will flow. The metal with the higher oxidation potential will dissolve as the anode of the bimetallic couple, while the metal with the lower oxidation potential will function as the cathode. It should be pointed out that due to polarization of one or both electrodes, the potentials of the electrodes under conditions of current flow will be different than the reversible potentials under conditions of no current flow. Because of this, reversible potential measurements may not be used as a basis for determining how fast corrosion will proceed.

In connection with the corrosion of tin-plated containers by aqueous aerosol formulations, reversible potential measurements were used to determine the relative electromotive forces of mild steel and tin under various conditions. These measurements were made with a Leeds and Northrup Potentiometer utilizing a galvanometer with a sensitivity of 1.2×10^{-3} microamperes per millimeter deflection. The potentials of the respective metals were measured at various times in several formulations.

It was noted early in the investigation of the electrode potentials of tin and steel in various formulations, that differing values could be obtained for the potential of a given metal in a given solution, depending upon the treatment of the metal electrode prior to immersion in the solution. In the original measurements, the metal electrodes were degreased prior to immersion by washing in carbon tetrachloride followed by an acetone rinse and drying in air. The values obtained varied for samples cut from different areas of the same strip of metal, and there was also a variation which was a function of the time of immersion in the solution.

Metal electrodes were cut from strips of mild-steel base stock and tin foil, and cleaned electrolytically by being made the cathode in an alkaline cleaning solution. The composition of the solution was as follows:

Sodium carbonate	23 gms./liter
Trisodium metaphosphate	23 gms./liter
Sodium metasilicate	2 gms./liter
Sodium hydroxide	15 gms./liter

The metal electrode to be cleaned was connected to the cathode of a six-volt storage battery. The anode of the current supply was connected to a steel plate immersed in the cleaning solution. The solution was heated to approximately 96° centigrade. The electrode was inserted into the cleaning solution and the current turned on for thirty seconds. The electrode was then immersed in cold running water, dipped in 20 percent by volume hydrochloric acid for five seconds, and then rinsed in distilled water. Without drying, the cleaned electrode was immediately immersed in the formulation under consideration, and a potential measurement made immediately. Further potential measurements were made as the time of immersion increased, and the data thus obtained were plotted on graphs. This procedure was followed for both tin and steel electrodes in various formulations. By this means, it was possible to cut specimens of tin from various areas of a strip and obtain essentially the same reversible potentials for the different specimens. This was not possible with the steel base stock samples, due, undoubtedly, to local variations in the composition of the metal, and the presence of strains. The tin which was used was quite pure so that there was little, if any, variance in local composition. Furthermore, tin, being a relatively soft metal, would not retain strains, in the thin samples that were used.

The presence of localized strains in a metal specimen may lead to intense attack of the metal in the strained areas. The distorted material is analogous to a compressed spring, and will contain stored up energy due to the strain.[15] As a first approximation,

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[15] U. R. Evans, Metallic Corrosion Passivity and Protection, Edward Arnold and Co., London (1937), p. 473.

the corrosion of the strained areas will result in a larger release of energy. Thus, it would be expected that the strained areas would be anodic to unstrained areas. Other conditions which control the corrosion of metals may conceal this effect, however. The electrode potential behavior of a metal specimen will be determined, to an appreciable extent, by the number and respective potentials of the microanodes and microcathodes over the metal surface. Thus strained areas, which will represent microanodes, will vary the potential behavior of the entire metal specimen. In general, an increasing potential indicates predominance of anodic processes, and a decreasing potential shows predominance of cathodic processes.[16]

As previously stated, a metal electrode, immersed in a solution, will exhibit an electrode potential which is determined by the escaping tendency of the metal in that solution, and the activity of the metal ions in that solution. Therefore, any factor which influences either the metal escaping tendency or solution activity will cause a change in the electrode potential. The presence of a surface film is one such factor which, in general, will decrease the electromotive force of a metal. In practice, a large number of metals

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[16] Gatty and Spooner, The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions, Clarendon Press, Oxford (1938), p. 24.

attain a surface film of oxide due to reaction with atmospheric oxygen. This oxide film may be quite protective and will prevent further corrosion of the metal, as in the case of aluminum and, under certain conditions, iron.

In order for an oxide film to be protective, it must fulfill two conditions. It must be adherent to the metal surface, and it must be dense enough to prevent further penetration of the corrosive agent. The surface oxidation of a heavy metal yields an oxide of a greater volume than that of the original unoxidized metal. Thus the surface film, if it is adherent, must be under lateral compression.[17] This compression results in a film with a close-packed molecular structure, which will be relatively impervious to further penetration. In general, then, if the ratio of the density of a metal to the density of its oxide is greater than one, the oxide film will be protective. If the ratio is less than one, the oxide film will be discontinuous and not protective.

Although oxide films are commonly found on metals which resist corrosion, they are by no means the only protective films which may be formed. Sulphide films have been shown to be

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[17] U. R. Evans, Metallic Corrosion Passivity and Protection, Edward Arnold and Co., London (1937), p. 68.

protective in some instances, as have sulfate films. The same considerations apply, however, as to adherence of the film and the protection offered against penetration by a corrosive agent.

In the measurement of the reversible electrode potentials of tin and steel specimens in various formulations, the specimens were immersed in the formulations in as film-free a condition as possible, due to the cathodic cleaning process. Any change in electrode potential with time was then taken as an indication of the occurrence of two processes: (1) the production of a protective film over the metal surface; and (2) polarization of the microanodes and microcathodes on the metal surface. In some respects, the polarization of a microelectrode might be considered as the production of a protective film due to the adsorption at the surface of either ions or a gaseous material such as hydrogen, or possibly the presence at the interface of a film of liquid in which the concentration of the electrolyte promoting corrosion is depleted. In the case of a pure metal surface on which microelectrodes would not be found initially, the build up of a protective film may result in some areas which will be cathodic with respect to other unprotected areas of the same metal.

All metals appear to have a surface film of oxide after exposure to moist air.[18] It follows, therefore, that an initially film-free metal will build up an oxide film upon being immersed in a liquid containing dissolved air, as long as the oxide film is not soluble in the liquid. The oxide film produced in a liquid medium may be in a different form from that produced in moist air, as for example, the production of a solvated oxide. For this reason, the initial electrode potential of a metal may be of a considerably different value depending upon whether the metal is covered by an air-formed oxide film or an oxide film formed by immersion in a liquid containing dissolved air. However, the electrode potential of a metal specimen covered by an air-formed oxide film, and which is immersed in a liquid containing dissolved air will tend to stabilize at approximately the same value as the potential of a specimen bearing an oxide film formed by immersion in the same liquid containing dissolved air, providing the time of immersion is sufficiently extended.

The results of the electrode potential measurements on cathodically cleaned tin and steel electrodes are shown in graph form

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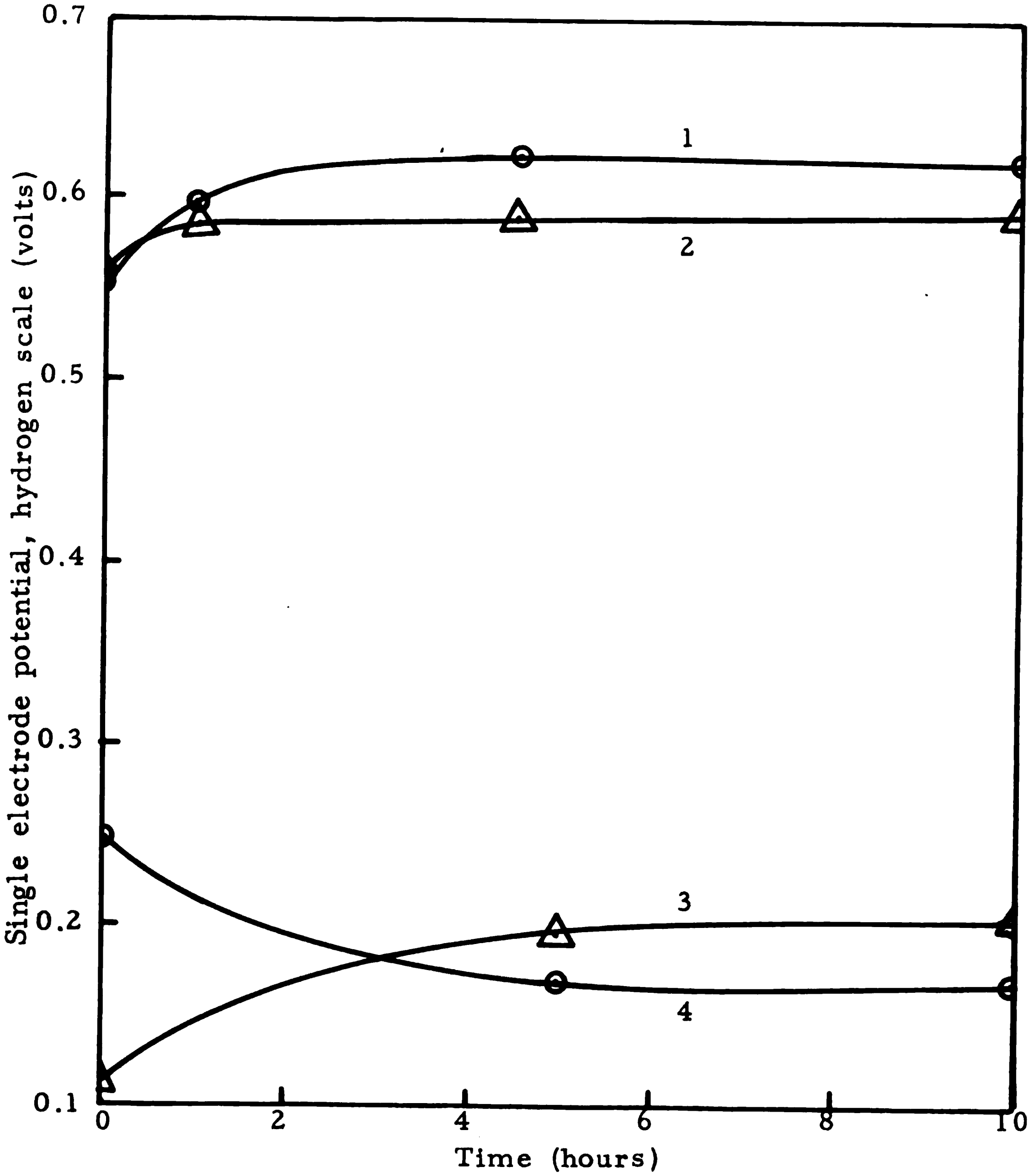
[18] Gatty and Spooner, The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions, Clarendon Press, Oxford (1938), p. 91.

in Figures 5 through 9. The commercial shampoo and shaving cream formulations were obtained from the G. Barr Company. The formulation designated as Shampoo A was a noncommercial preparation of the following composition:

Sodium lauryl sulfate	105 gms.
Polyethylene glycol 400	9 gms.
Magnesium stearate	3 gms.
Water	223 gms.

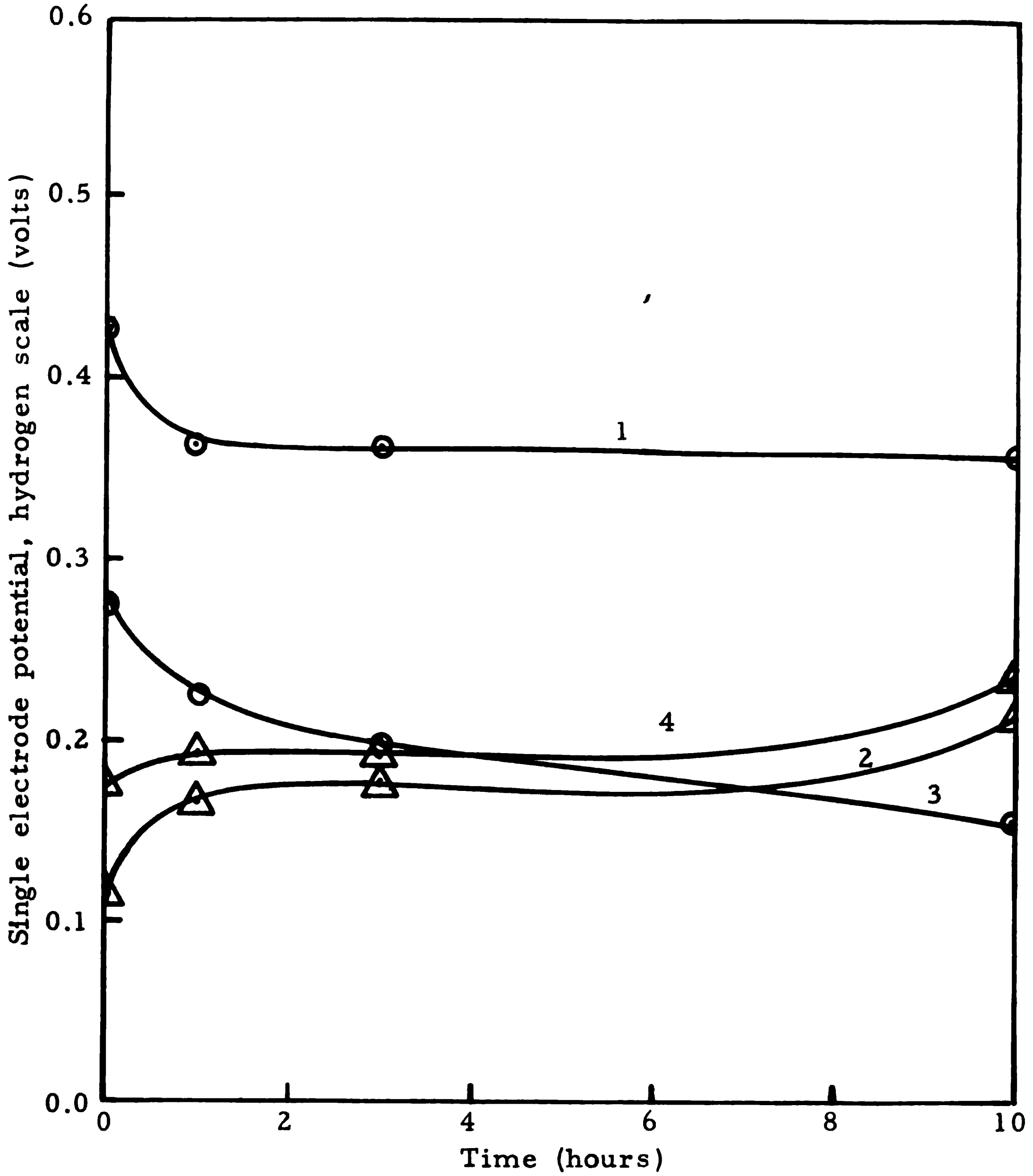
The measurements made in the 10 percent sodium lauryl sulfate solution were for the purpose of investigating the effect of a surface active agent. The measurements in saturated potassium chloride served to show the effect of a high concentration of chloride ion, which has the ability to penetrate the oxide film on many metals. These measurements were made in the presence of both low and high concentrations of dissolved oxygen.

Figure 5 shows that tin was anodic to steel in commercial shampoo with a low dissolved oxygen concentration, although initially the polarity was reversed. With a high oxygen concentration, the tin was initially anodic to steel, but the polarity reversed after approximately three hours' immersion. Since during the filling operation for an aerosol container the air in the container will be swept out by the boiling of the propellant mixture prior to sealing of the container, the only air which will be present in the container will be



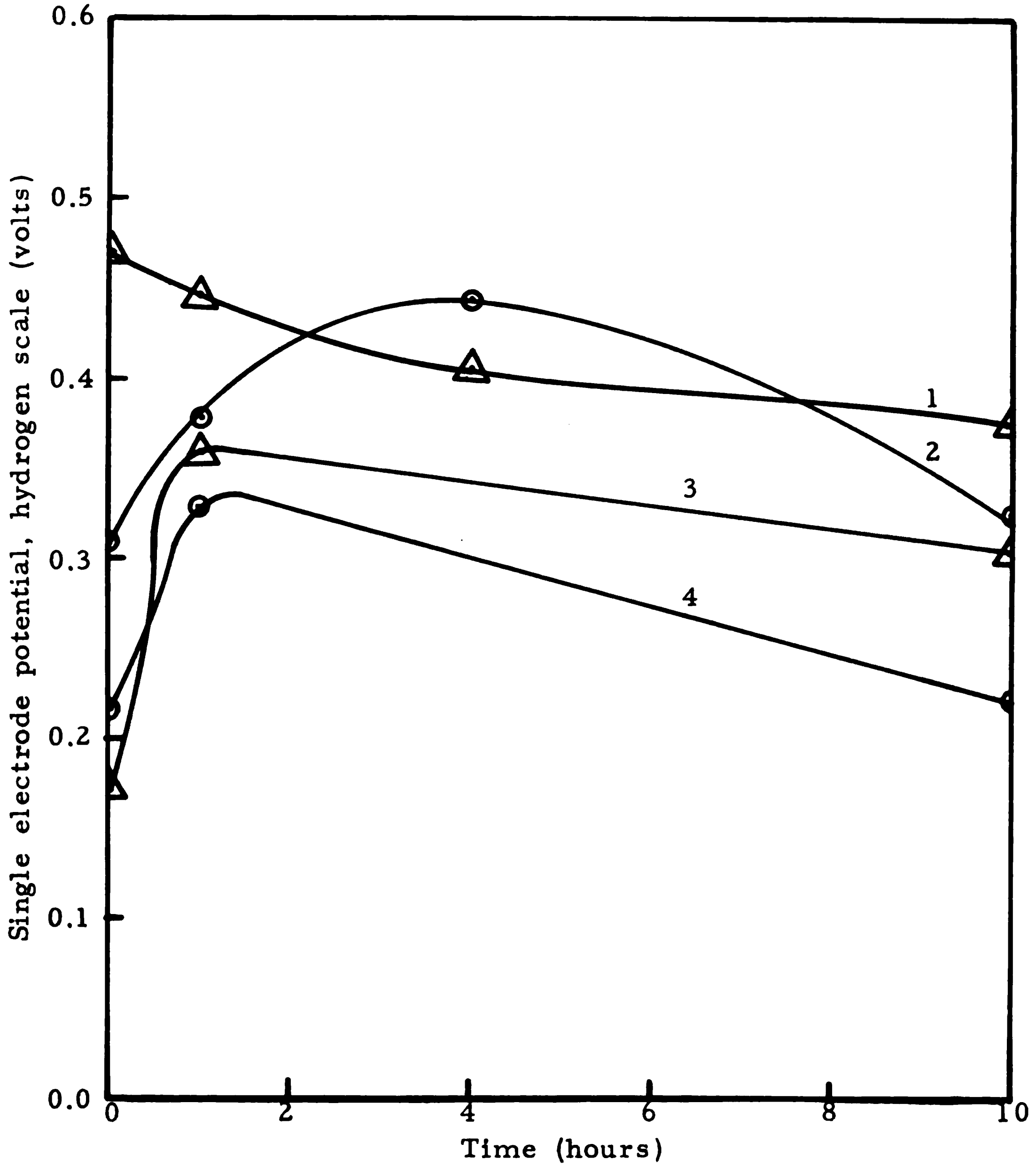
1 - Tin electrode in commercial shampoo (low oxygen)
2 - Steel electrode in commercial shampoo (low oxygen)
3 - Steel electrode in commercial shampoo (high oxygen)
4 - Tin electrode in commercial shampoo (high oxygen)

Figure 5. Potential-time curves.



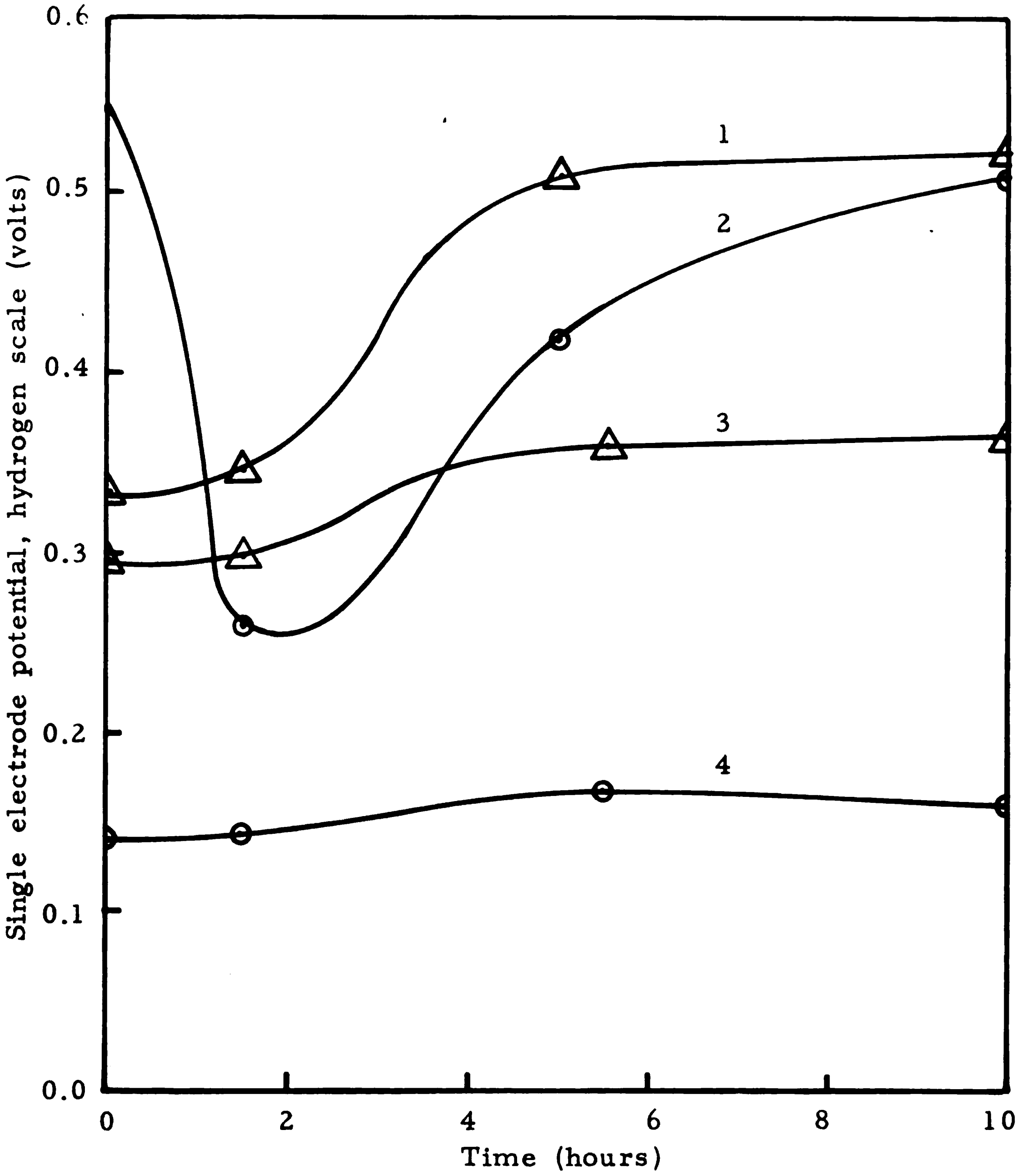
1 - Tin electrode in commercial shaving cream (low oxygen)
2 - Steel electrode in commercial shaving cream (low oxygen)
3 - Tin electrode in commercial shaving cream (high oxygen)
4 - Steel electrode in commercial shaving cream (high oxygen)

Figure 6. Potential-time curves.



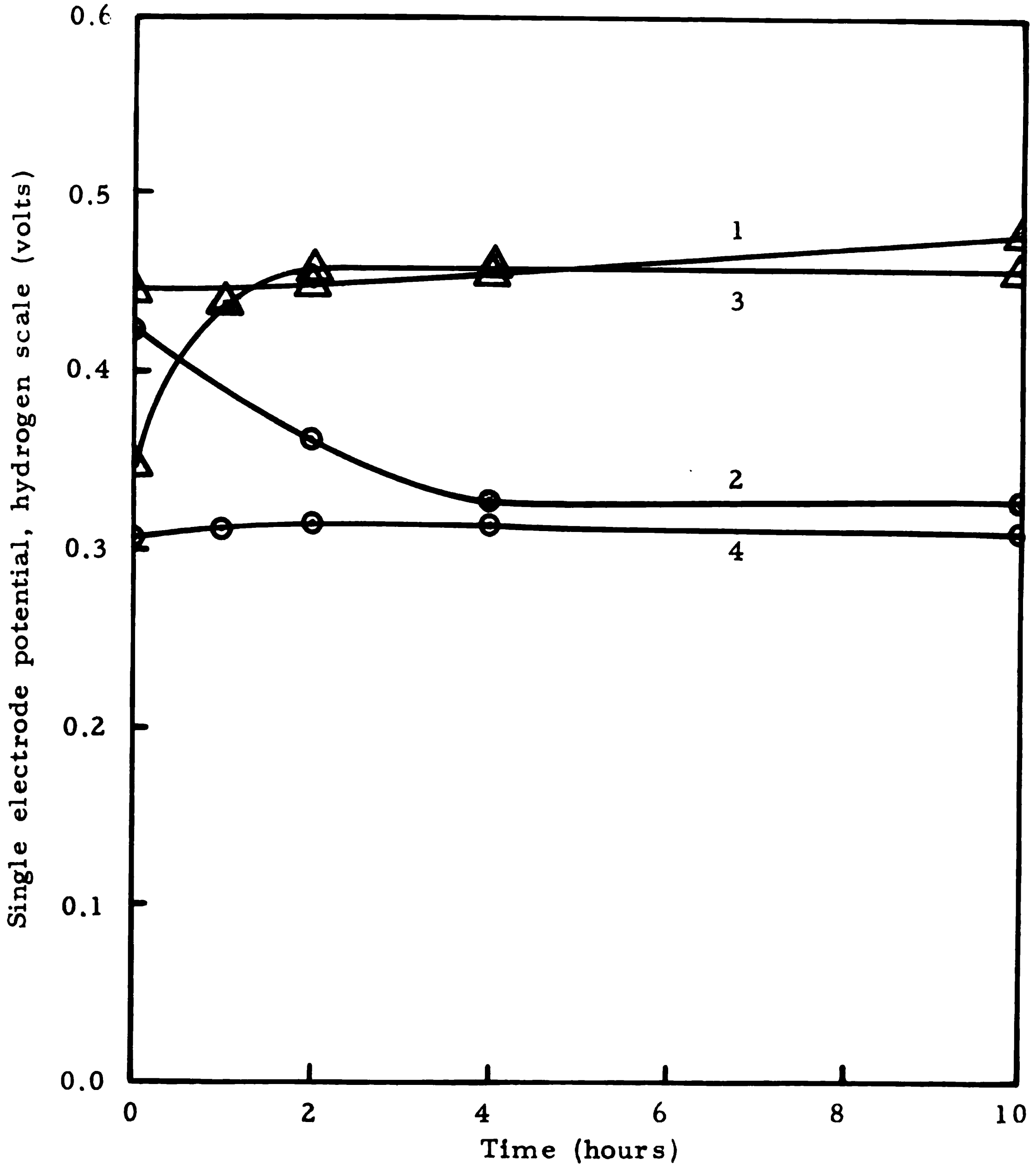
1 - Steel electrode in Shampoo A (low oxygen)
2 - Tin electrode in Shampoo A (low oxygen)
3 - Steel electrode in Shampoo A (high oxygen)
4 - Tin electrode in Shampoo A (high oxygen)

Figure 7. Potential-time curves.



1 - Steel electrode in 10 percent sodium lauryl sulfate (low oxygen)
2 - Tin electrode in 10 percent sodium lauryl sulfate (low oxygen)
3 - Steel electrode in 10 percent sodium lauryl sulfate (high oxygen)
4 - Tin electrode in 10 percent sodium lauryl sulfate (high oxygen)

Figure 8. Potential-time curves.



1 - Steel electrode in saturated KCl (low oxygen)
2 - Tin electrode in saturated KCl (low oxygen)
3 - Steel electrode in saturated KCl (high oxygen)
4 - Tin electrode in saturated KCl (high oxygen)

Figure 9. Potential-time curves.

that which is dissolved in the fluid contents. Thus, the electrode potentials for the tin and steel will be approximately the same as those given in Figure 5 for the low-oxygen curves after ten hours' immersion. Thus, initially, tin will be anodic to steel in the container, and the tin will dissolve.

Figure 6 shows that tin was seen to be anodic to steel under conditions of low oxygen concentration. When the oxygen concentration was increased, the polarity was initially the same, but reversed after about four and one-half hours.

Figure 7 shows that, at low oxygen concentration, the polarity reversed twice, ending up with tin cathodic to steel. At the high oxygen concentration tin was initially anodic to steel, but the polarity reversed after a very short time.

Figure 8 shows that, at low oxygen concentration, the electrode potential of tin underwent a considerable change, and, as can be seen, had still not stabilized after ten hours' immersion. The potential of the steel also changed by quite a bit, but eventually stabilized after approximately six hours. At high oxygen concentration the fluctuations in potential for both metals were reduced to a large extent.

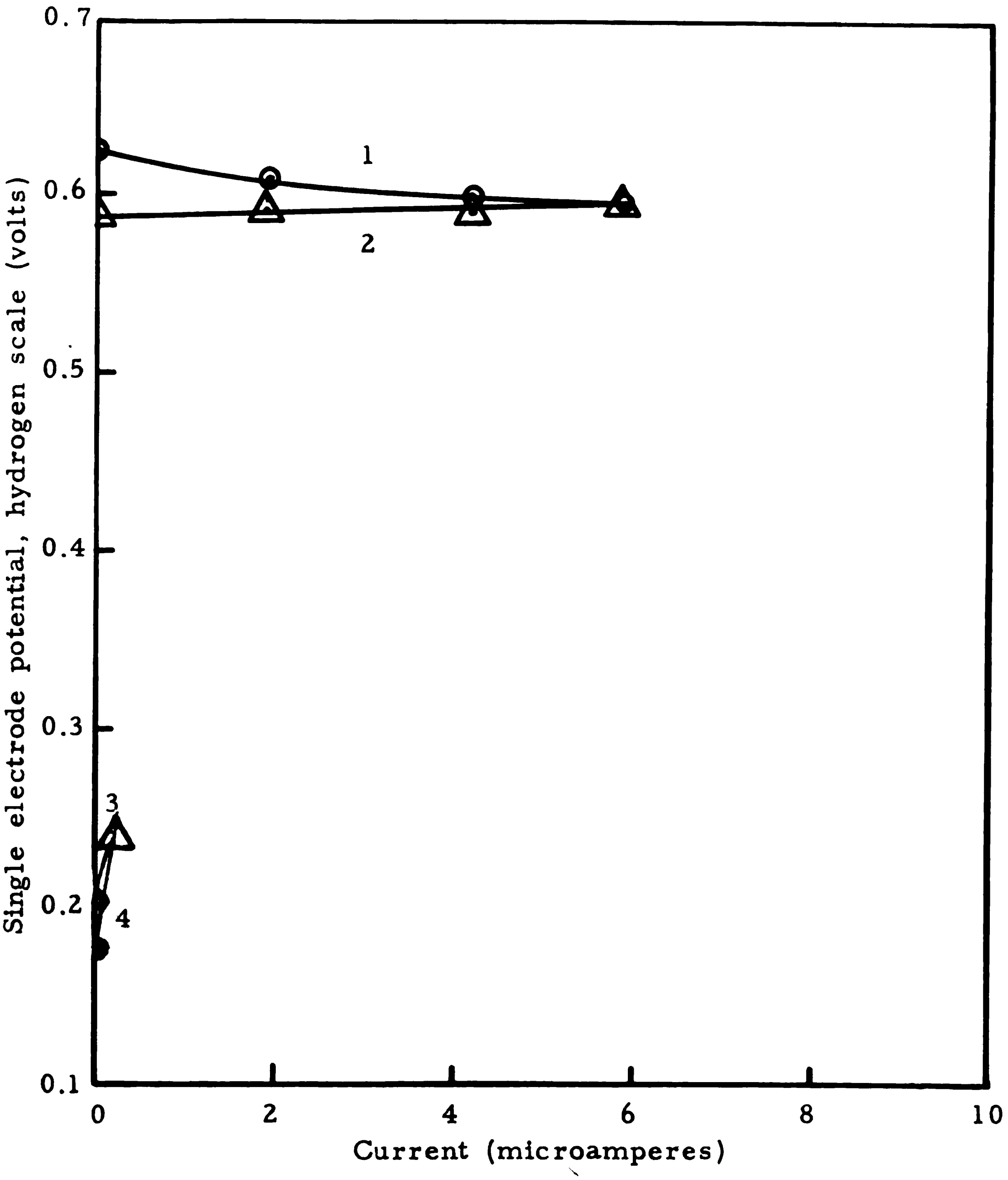
Figure 9 shows that, in saturated potassium chloride, the oxygen concentration produced little variation in the final potential attained for both metals, although a low oxygen concentration exerted a

pronounced effect on the potential of the tin, while the high oxygen concentration caused a variation in the potential of the steel.

Each of these solutions was neutral or nearly neutral with respect to pH. The shampoo formulations had pH values of 8.0 to 8.5, while the sodium lauryl sulfate solution had a pH of 9.0. The commercial shampoo was at a pH of 7.8, while the potassium chloride had a pH of 7.0.

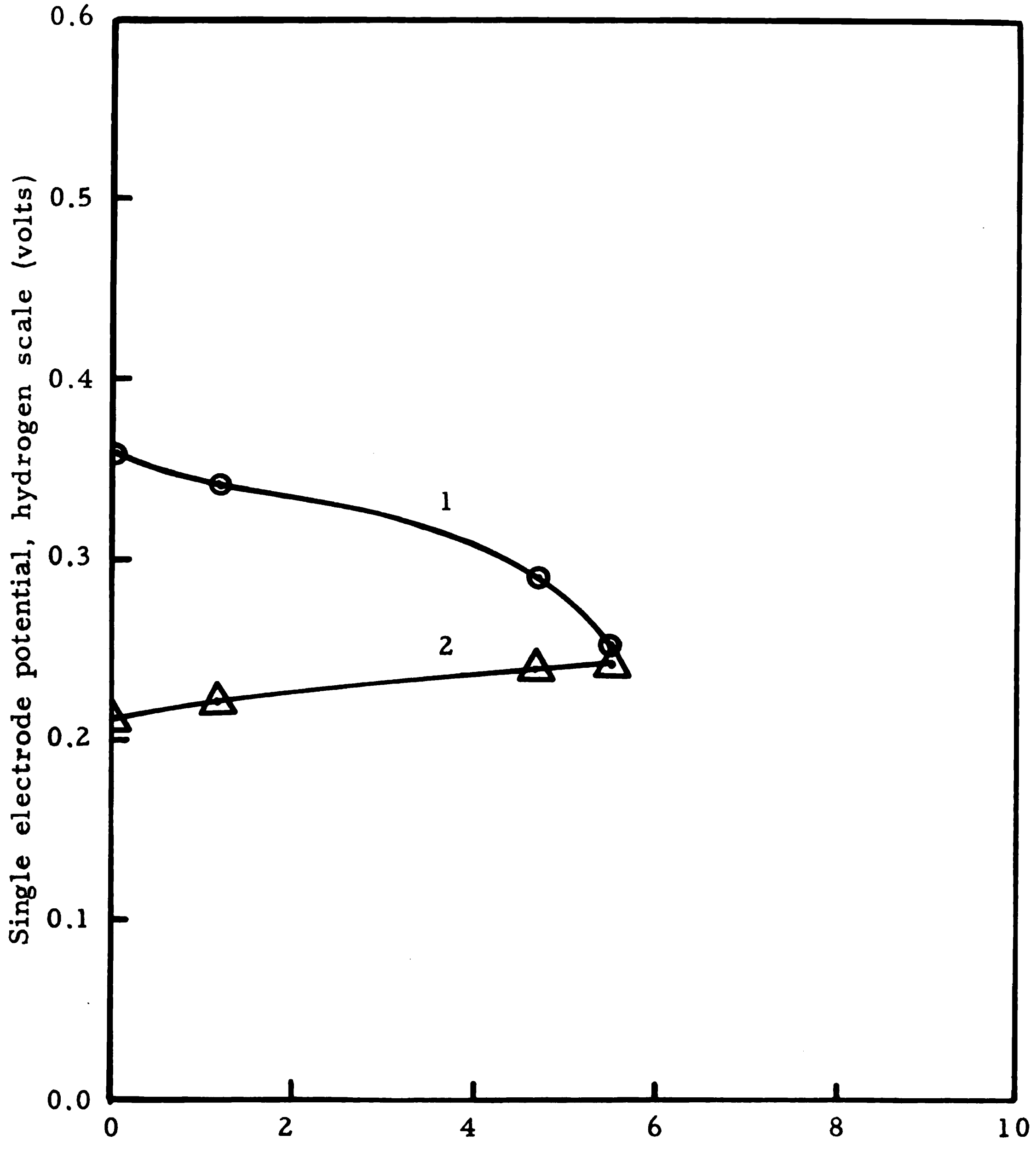
Figures 10 through 15 show the results of the polarization measurements on tin and steel electrodes immersed in various solutions. The metal electrodes were cathodically cleaned, rinsed in distilled water, and immediately immersed in the various formulations. The electrodes were connected through an external resistance which could be set at specific resistance values. The current flowing through the cell was found by measuring the voltage drop across the known external resistance with a potentiometer. The potential of each electrode was found by measuring the reversible potential across the metal electrode under consideration and a saturated calomel electrode by means of a potentiometer.

In every case, except that of distilled water, the presence of a large amount of dissolved oxygen reduced the limiting current of the corrosion cell. From the corrosion tests on standard metal specimens it was found that decreased amounts of oxygen reduced the corrosion.



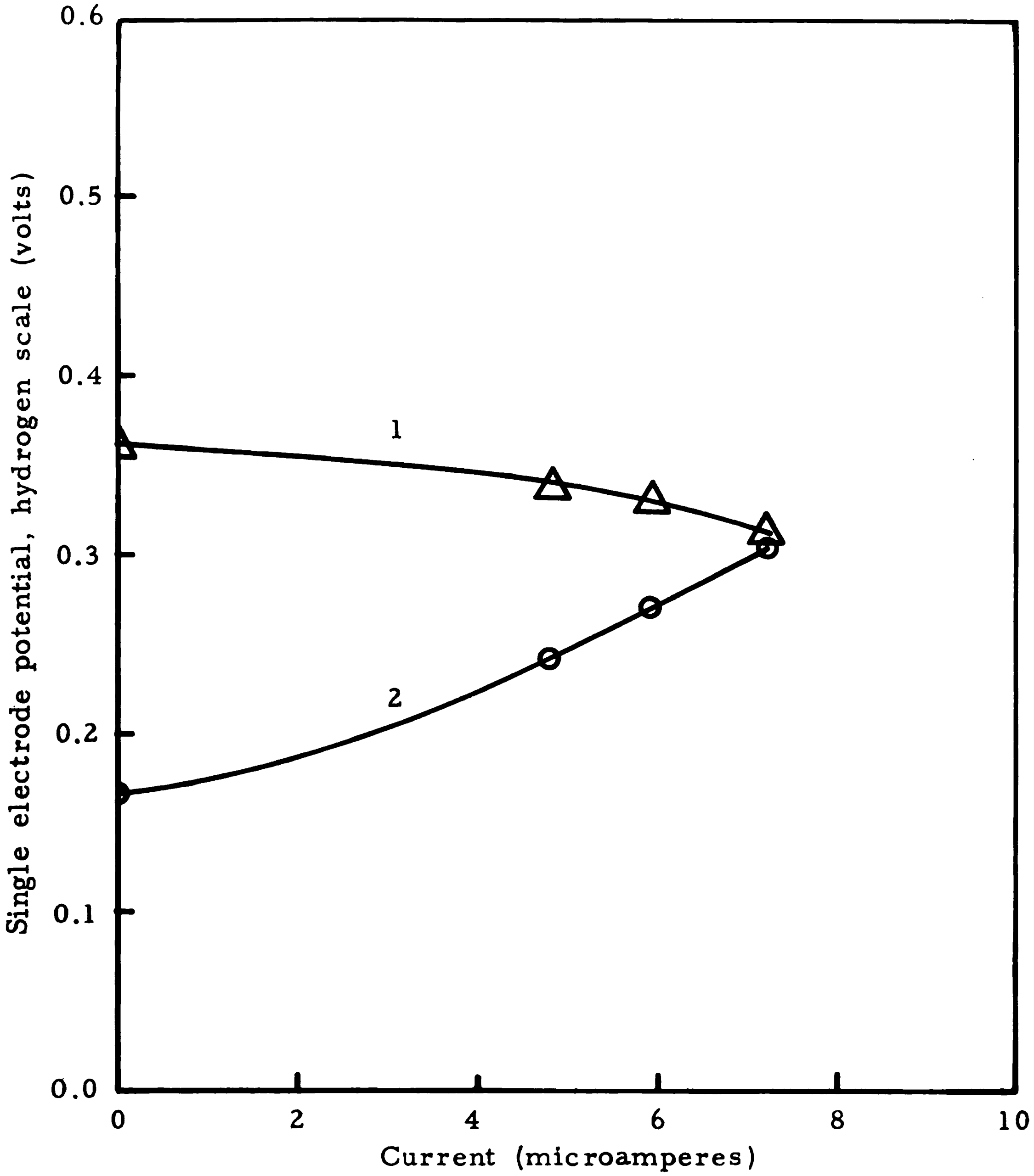
1 - Tin electrode in commercial shampoo (low oxygen)
2 - Steel electrode in commercial shampoo (low oxygen)
3 - Steel electrode in commercial shampoo (high oxygen)
4 - Tin electrode in commercial shampoo (high oxygen)

Figure 10. Polarization curves.



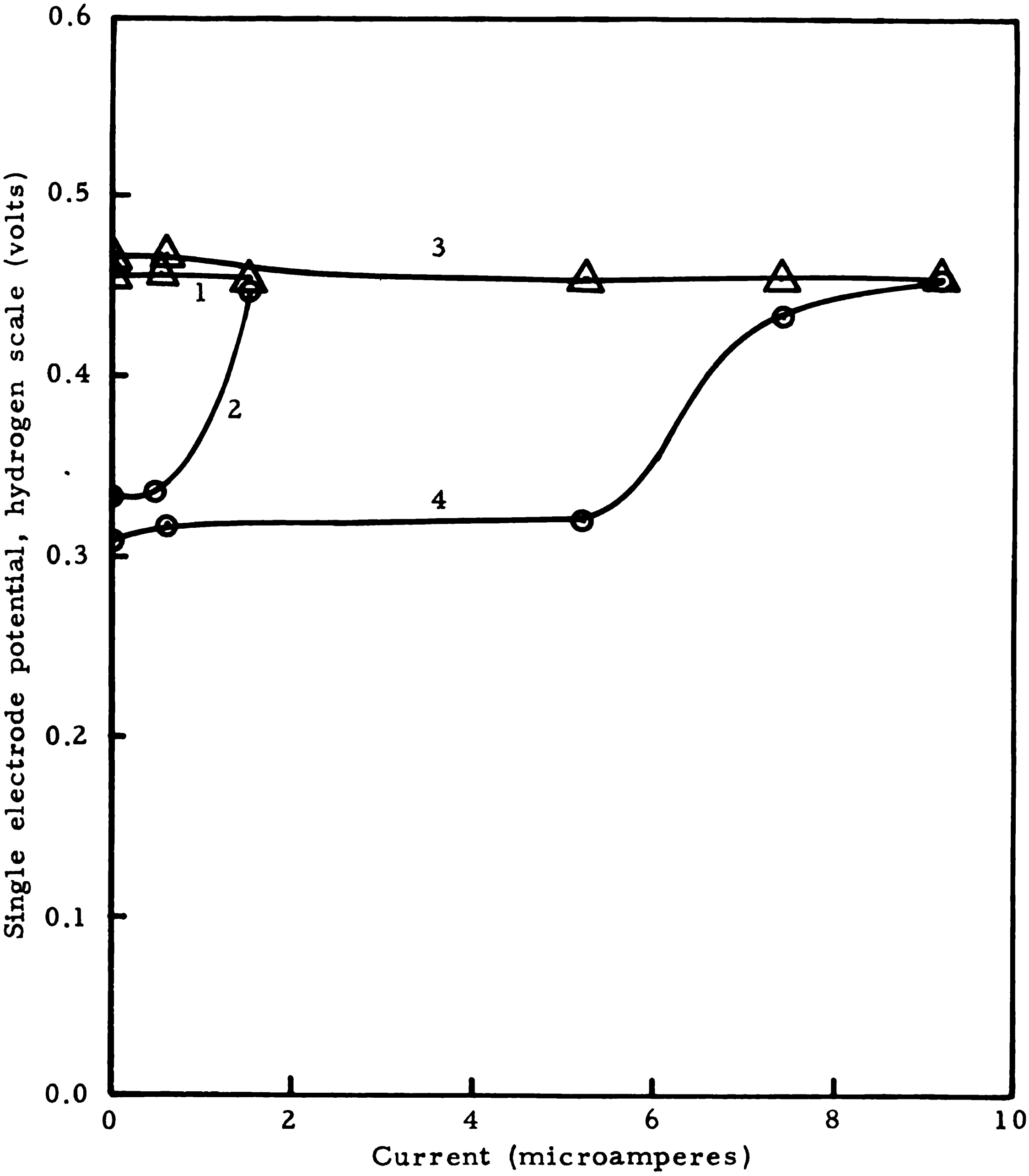
1 - Tin electrode in commercial shaving cream (low oxygen)
2 - Steel electrode in commercial shaving cream (low oxygen)

Figure 11. Polarization curves.



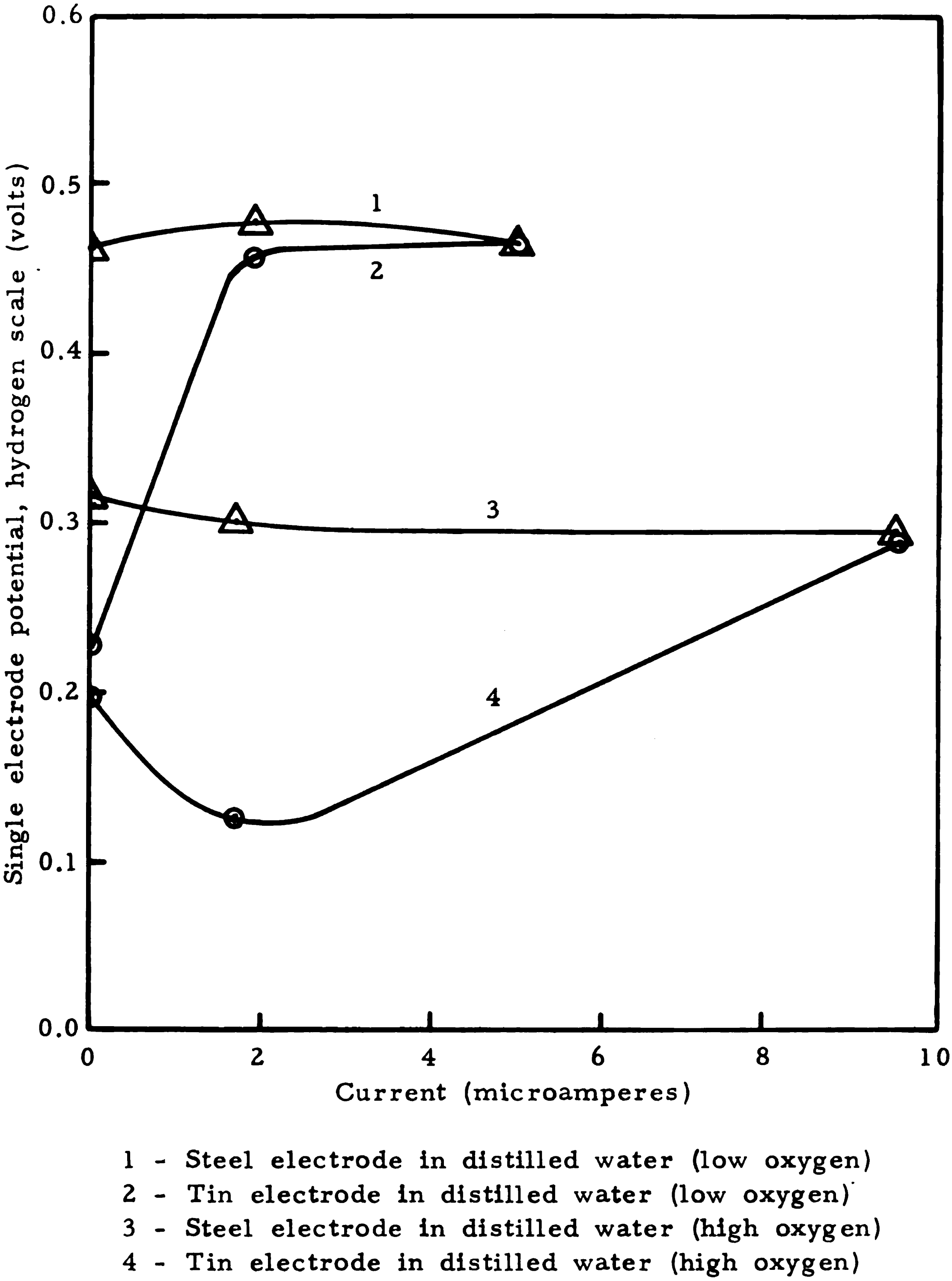
1 - Steel electrode in 10 percent sodium lauryl sulfate (high oxygen)
2 - Tin electrode in 10 percent sodium lauryl sulfate (high oxygen)

Figure 12. Polarization curves.



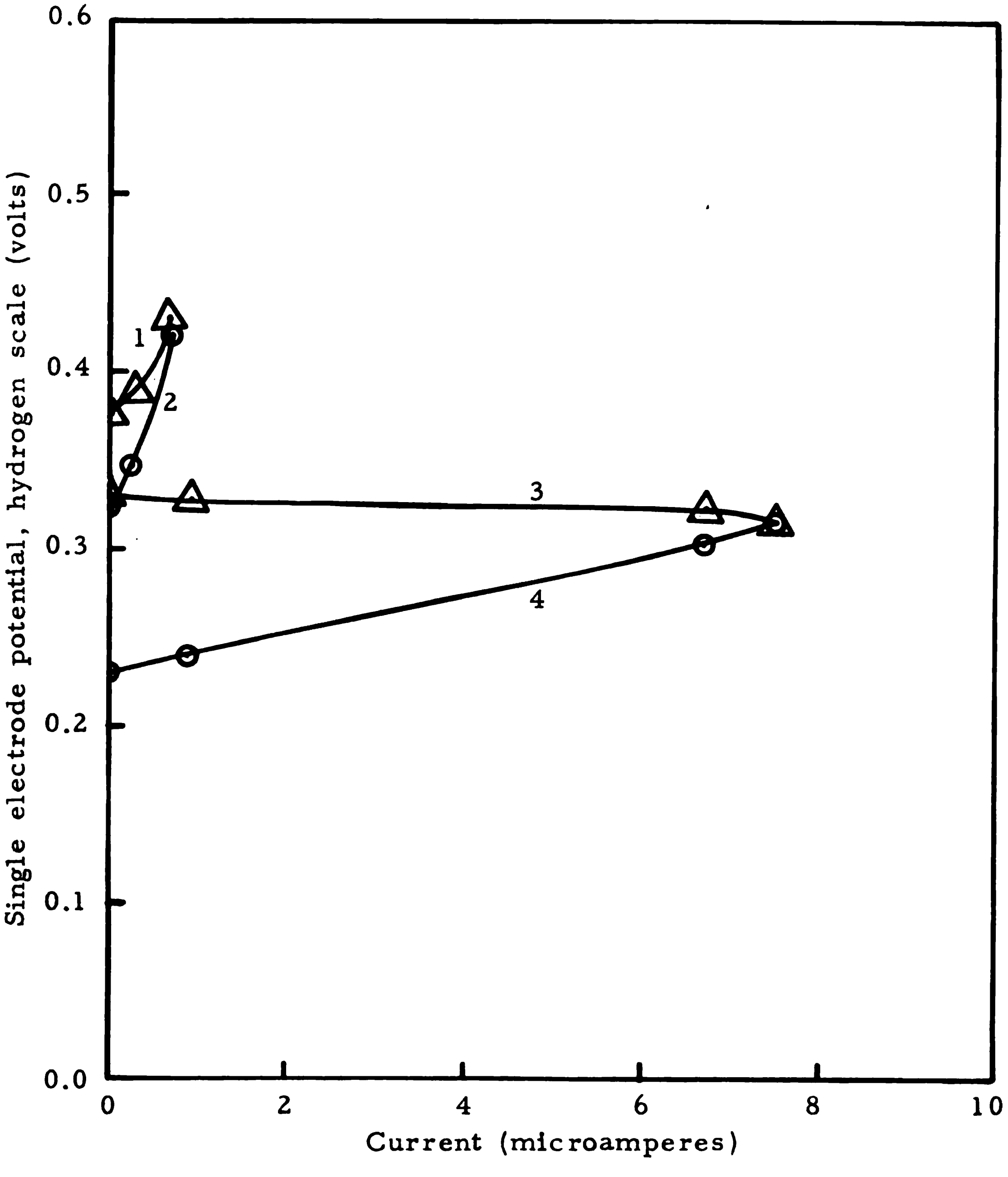
1 - Steel electrode in saturated KCl (low oxygen)
2 - Tin electrode in saturated KCl (low oxygen)
3 - Steel electrode in saturated KCl (high oxygen)
4 - Tin electrode in saturated KCl (high oxygen)

Figure 13. Polarization curves.



1 - Steel electrode in distilled water (low oxygen)
2 - Tin electrode in distilled water (low oxygen)
3 - Steel electrode in distilled water (high oxygen)
4 - Tin electrode in distilled water (high oxygen)

Figure 14. Polarization curves.



1 - Steel electrode in Shampoo A (low oxygen)
2 - Tin electrode in Shampoo A (low oxygen)
3 - Steel electrode in Shampoo A (high oxygen)
4 - Tin electrode in Shampoo A (high oxygen)

Figure 15. Polarization curves.

It was apparent from these data that there was an optimum concentration of oxygen at which the corrosion process proceeded most rapidly. This was interpreted as showing that a certain amount of oxygen was necessary for the corrosion process, but that a large excess of oxygen resulted in the formation of a protective film over the metals which was kept in repair by the presence of a large excess of oxygen, and which reduced the rate of corrosion.

In those cases of corrosion in which the tin served as the anode of the galvanic couple, it was found that as corrosion proceeded, the pH of the corrosive media increased. In no case was there an increase in the internal pressure during corrosion in a sealed container. Thus the possibility of the discharge of hydrogen ion to gaseous hydrogen was eliminated. In any case, the various media were slightly alkaline, a factor which would cause the potential necessary for the production of hydrogen to rise to a prohibitive level. However, it was found that the single electrode potentials involved were such as to allow the reaction

$$1/4\ O_2 + 1/2\ H_2O + e = OH^-$$

to proceed. This reaction is then, apparently, the cathodic reaction.

The relative conductance values were measured for various formulations by means of a conductance cell with fixed platinum electrodes, and a Wheatstone Bridge. The source of current was an oscillator with an output frequency of one thousand cycles per second. These values are listed in Table IV. The values were determined at 25° centigrade. Since they are only relative values, they can only be compared to each other.

As may be seen from these data, the commercial shaving cream has a low conductivity as compared to the commercial shampoo. Thus, it would be expected that the shaving cream would be less corrosive. In addition, it may be seen from the polarization curves that in the shaving cream the tin underwent polarization. It was noted that in the shaving cream, a jelly-like layer of the formulation covered the tin specimen quite soon after the coupled tin and steel were immersed. The jelly was colloidal in nature, and appeared to have migrated to the tin anode by an electrophoretic effect. This layer apparently accounted for the pronounced polarization of the tin anode, and the low rate of attack of the metallic components.

Two glass tubes were prepared each with one wide-mouthed end and one end drawn down to a fine tip. These tubes were affixed with the capillary tips in contact with a strip of mild-steel tin-can stock. The points of contact of the two tips were within one-half inch of each other. These tubes were filled with the commercial shampoo formulation, and the shampoo allowed to make contact with

TABLE IV

RELATIVE CONDUCTANCES OF VARIOUS FORMULATIONS AT 25° CENTIGRADE

Formulation	Relative Conductance
Commercial shampoo	0.0357 $ohms^{-1}$
Commercial shaving cream	0.0004 $ohms^{-1}$
Shampoo A	0.050 $ohms^{-1}$
10 percent sodium lauryl sulfate	0.0166 $ohms^{-1}$
Saturated KCl	0.128 $ohms^{-1}$

the steel specimen through the capillary tips. A saturated calomel electrode was then inserted into the upper end of each tube. The electrode potential was then measured across this system by means of a potentiometer. This procedure was repeated over several points on the surfaces of each of several different specimens. Both degreased and cathodically cleaned specimens were used. Potential differences between various points were recorded which ranged from zero volts to 0.75 volts. The recorded values were taken after sufficient time was allowed for the system to come to equilibrium. This indicated the definite possibility of local action on the steel surface.

CONCLUSIONS

Several conclusions may be drawn from this study. The corrosion process is primarily of an electrochemical nature. The tin-plated containers have flaws in the tin coating, and these flaws are necessary for the galvanic action to commence. In order for the corrosion process to proceed, the formulation must be able to conduct an electric current. The greatest difficulty with corrosion has been found in those instances where tin is anodic to steel. Of practical importance to the aerosol packaging industry is the fact that it appears possible to use electrical measurements coupled with electrochemical theory as a criterion for the determination of the relative corrosiveness of a given formulation. Thus, the need for long-term shelf tests on packaged units as a means of studying the corrosive action may be eliminated.

The corrosion process in the case of the commercial shampoo appears to be due to the following factors:

1. The tin metal in the container is anodic to the steel base metal, which is exposed through faults in the tin plate. The tin undergoes anodic dissolution due to galvanic action.

2. The steel, which is exposed only at small faults in the tin plate, is subjected to a high cathodic current density, which prevents the corrosion of the steel.

3. Due to the thinness of the tin plate, larger areas of steel base metal are exposed as the tin dissolves. This results in a continually decreasing cathodic current density over the steel surface.

4. Eventually, the current density over the steel surface decreases to the point where local microanodes and microcathodes due to strains and impurities in the steel begin to take effect. This local action is characterized by intense corrosion at small areas resulting in pitting of the steel base stock. The pitting leads to perforation and failure of the container.

As stated earlier, the cathode reaction appeared to be the production of hydroxyl ion from water and oxygen by electrochemical action. If a hypothetical system is imagined in which the tin is cathodic to the steel base metal, then it is readily seen that the steel will suffer anodic dissolution at the small faults through which it is exposed. The corrosion product at the anode will most likely be ferrous ion. The tin surrounding the small anodic area will be the site of the cathodic production of hydroxyl ion, which will react with the ferrous ion to produce hydrated ferrous oxide. The ferrous hydroxide will very likely undergo further oxidation by the dissolved oxygen in the formulation to ferric hydroxide, which will be precipitated in the fault through tin plate. In the absence of any ion able to penetrate the ferric hydroxide film thus formed, such as chloride ion, the anodic dissolution of the steel will most likely be prevented, thus preventing further corrosion. In practice, it has been found that tin cans suffer little serious corrosion by liquids in which tin is cathodic to steel, except in certain cases with acid liquids. The above explanation, of course, is for neutral, aqueous aerosol formulations containing some dissolved oxygen.

The presence of dissolved oxygen in the fluid ingredients in the aerosol container has been found to exert a twofold effect. The oxygen serves to promote the cathodic reaction, and thus promote corrosion. The second function of the oxygen is to produce a protective film over the exposed surfaces of the metal components of the container, which serves to retard the rate of the corrosion. However, the presence of a large amount of oxygen in the sealed container is not recommended as a means of inhibiting corrosion.

The effect of the colloidal material in the shaving cream formulation in reducing the attack by electrophoretic migration of the colloid toward the tin anode, is of interest, and may well point one direction toward inhibition of the corrosion reaction. In the case of those formulations which are not capable of attacking tin directly, the corrosion process may be eliminated by eliminating the flaws in the tin plate, either by increasing the thickness of the tin plate, or by more careful fabrication of the tin-plated metal into containers. The use of baked resinous enamels as a protective coating over the interior surfaces of the containers has certainly reduced corrosion, and, with further study, may result in total elimination of the problem.

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