AZI-LIA EXPANDED RESEARCH PROGRAM

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Director of Research

April 1, 1959

To All Members of the American Zinc Institute and the
Lead Industries Association

Gentlemen:

Our Expanded Research Program sponsored by the producers of slab zinc and pig lead, has been increasing continually in size and scope since its original inception. It is believed that the time has been reached when the members should be notified of the progress of the Program and this is being accomplished by submitting to you a copy of our First Quarterly Report.

The first report is somewhat longer than subsequent reports will be; however, it was felt advisable to provide you with background information concerning the many projects that are now under way.

Additional reports will follow each quarter and we look forward to receiving your comments and suggestions.

Sincerely yours,

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enc.

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American Zinc Institute
Lead Industries Association

Quarterly Report No. 1
April 1, 1959

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I INTRODUCTION

This is the first of the quarterly reports to be prepared and distributed as a part of the AZI-LIA Expanded Research Program. The purpose of these reports is to summarize the progress achieved on the many research projects sponsored by the American Zinc Institute and the Lead Industries Association and to advise of research initiated during the intervening period.

While the members of technical committees and subcommittees are kept informed of progress on the individual projects with which they are directly concerned, it is believed desirable to distribute an all-inclusive report such as this for the general membership of the Lead Industries Association and American Zinc Institute and cooperating organizations here and abroad.

These quarterly reports will be general in nature, relating only progress achieved in the last report period with emphasis being placed on the general rather than the detailed accomplishments of the individual research. This first report will also include the objectives and some background information on each program as well as a brief summary of projects in existence for sometime.

The report will appear under two headings entitled, "Lead Research Program" and "Zinc Research Program".

II LEAD RESEARCH PROGRAM

A. Continuous Extrusion of Lead Cable Sheathing - (LR-15-59)

Partial support for development of an extrusion press capable of continuously extruding lead cable sheathing alloys has been given to the John F. Robertson Company since May, 1958 and will continue through June, 1959 under present arrangements. Extruders now available are capable of producing pure and copper-bearing lead cable sheathing but have proven unsatisfactory for the arsenical and antimonial alloys. Lead Industries Association support partially covers supplies and labor to prove out extruding the press for arsenical and antimonial cable sheathing alloys. Press development, manufacture, and modification have been financed by the Robertson Company.

Prove-in of the press was accomplished using pure lead, and from this base point, extrusion of the F-3 arsenical lead alloy was accomplished. Continuous production rates of 62 to 65 pounds per minute were obtained on pure lead corresponding to linear rates of 18 to 19 feet per minute of 2" O. D. sheathing. F-3 alloy could be continuously produced at a rate of 43 pounds per minute, corresponding to 12 to 13 feet per minute for 2" O. D. sheathing.

Samples of the sheathing taken during the run-in on F-3 alloy have been evaluated with respect to composition, tensile properties, and grain structure at the Anaconda Wire and Cable Company Laboratories. Composition of the alloy was maintained essentially constant after many repeated extrusion, melting, and freezing cycles. All samples of the sheathing were air cooled during manufacture so that strengths obtained were comparatively low. When treated and quenched to

simulate rapid cooling, strengths increased to normal values without significant loss of ductility. Elongation was similar to those of sheathing extruded on conventional hydraulic presses. The grain structure was similar to that of lead samples produced on screw-type presses, except that smaller grain size was obtained. Shadow patterns on tongue-shaped flow lines were evident on either side of the top of the section which resembled, in appearance, the charge welds produced by a hydraulic press and die block but were not severe enough to restrict grain growth across them, and for this reason should not be harmful to mechanical performance of the sheathing. No streaks or patterns appeared that were attributable to alloy segregation.

Future work will consist of determining operation conditions for the antimonial alloys and evaluation of the resulting sheathing with respect to composition, tensile properties, and grain structure.

B. Study of Lead-Base Alloys - (LR-4-59)

This research is being carried out at Armour Research Foundation under the supervision of C. R. Simcoe. The investigation began in July, 1958, and will continue until July, 1959 under the present agreement.

It is believed that the poor creep and tensile properties of lead mitigate against its use in many applications and that improvement of these properties in homogeneous alloys will produce new market areas. For this reason, a rigorous study of lead alloys was believed necessary to uncover alloy systems showing potential for improvement in this area.

The objectives of this program are two-fold. First, the existing state of knowledge concerning the physical and mechanical properties of lead is to be extended, and second, with this knowledge alloys superior to those now known are to be developed.

Progress to date included a survey of available literature and, based on this, a number of binary lead-base alloys have been chosen for study. Preliminary work will be directed toward a systematic evaluation of the recrystallization kinectics of the selected binary alloy compositions. Promising compositions will be subject to further study.

Future work will consist of melting, casting, and cold-rolling of alloys followed by a study of recrystallization kinectics at three temperature levels.

C. Fiber-Reinforced Lead - (LR-9-59)

Research in developing fiber-reinforced lead materials is being conducted at Armour Research Foundation under the supervision of R. H. Reed. The investigation began in January of 1959 and is expected to continue until January of 1960 under the existing contractual arrangements.

The objectives of this research are to develop lead-metal fiber composites which demonstrate better strength and creep resistance than homogeneous lead products, yet still exhibit the virtues of lead with respect to resistance to

chemical attack, nuclear shielding capacity, etc., so that these inherent properties can be more universally applied in chemical and atomic energy industries. The poor creep performance of lead has mitigated against its use in many applications in these industries.

The initial approach will be to investigate methods of impregnating fibre metal mattes with lead, and study strength and creep properties of these composites. The lead-wettability of various metal matte compositions will be determined as well as the effects of matte fibre content, size, and yield strength on the mechanical properties of the lead containing composites.

Work now in progress consists of developing techniques to produce composites of lead and tin bronze felts. Good impregnation has been accomplished by immersion of the bronze felts in charcoal-covered lead - 1% tin baths subject to mechanical vibrations. Pores have been found to open up in the composites on solidification, and methods of eliminating the porosity or healing the porosity by working are being investigated.

D. Lead Chemicals - (LP-10-59)

This phase of the research program is being conducted by Arthur D. Little, Inc. under the supervision of Dr. Morgan. Under the present contract, this program covers a period of one year, beginning December 15, 1958.

The field of lead chemicals should hold considerable promise for further commercial exploitation as sizeable tonnages of lead organic and inorganic salts are used presently. A two-phase investigation has been initiated, both phases being carried out concurrently. One phase will consist of a study of the fundamental chemistry of lead, its bonding characteristics in organic and inorganic compounds and application of this knowledge in the synthesis of new compounds. The second part of the program will be an attempt to synthesize polymers and related complex structures, considering the commercial application for these materials.

Progress to date includes a review of pertinent literature to plan the initial experimental effort. Underway is an effort to synthesize and polymerize styrl lead derivatives. A similar investigation is being carried out on the adduct of hexaphenyl di-lead and maleic anhydride, the synthesis of dicyclopentadienyl lead and its polymerization by the ferrocene-type reaction or the maleic anhydride adduct.

E. High Spot Investigation of Lead for Sound Attenuation - (LP-16-59)

This investigation is to be carried out by Bolt Beranek and Newman, Inc. The project will require little time, and the investigation is expected to be completed prior to the next quarterly report.

Lead has long been known to possess excellent sound attenuation characteristics, but little use has been made of this inherent property in architecture. The superiority of lead for sound isolation is manifested by the fact that one producer of passenger aircraft used lead-coated fabrics as a cabin

lining to reduce the noise level. In spite of the apparent weight penalty, lead was actually lighter in the final analysis because of its accoustical efficiency.

This contract is to be a feasibility study for employing lead products in architectural structures for sound isolation. It is to be exploratory in nature, pointing out the most promising areas for the development of markets for lead accoustical panels, encompassing:

(a) A comparison of transmission loss of common architectural partition constructions with simple lead sheets.

(b) A compilation of a list of possible applications in which lead will be the most economical, the lightest, or the thinnest material which would satisfy the accoustical requirements.

(c) Designing of a typical building partition employing lead.

F. High Emission Lead Compounds - (LP-11-59)

This investigation is being carried out via fellowship support at New York University under the direction of Professor I. Cadoff. Fellow E. Miller is performing the laboratory work during the academic year 1958-1959.

The objective of this program is to study the thermal and spectral emissivity of lead compounds. New advances in heat transfer and electronic devices suggested the investigation of the properties of lead compounds for use in these areas.

The program consists of determining the emission spectra of the group of compounds, PbO, PbS, PbSe, and PbTe. The experimental procedure will be to detect the radiation emanating from the samples by means of a Beckman IR-2 infrared spectrophotometer. At room temperature, where radiation is negligible, the emission properties will be obtained from the absorption spectrum using the relation that emission must equal absorption in order for the sample to remain at room temperature.

Progress to date consists of procurement of the spectrophotometer, development of techniques for obtaining room temperature absorption characteristics, and sample preparation (i.e., thin wafers of the compounds) for transmission studies.

It is expected that test procedures will be finalized and preliminary data obtained by the next report period.

G. Lead in Ceramic Materials - Introduction

Research for furthering the role of lead in ceramics is being carried out at seven universities on a fellowship basis. At present nine fellowships are being supported covering broad areas of investigation of the effect of lead and its compounds in ceramic materials of all types.

1. University of Illinois - (LP-19-59)

Two fellowships have been awarded under the direction of Dr. A. I. Andrews.

A thesis covering the work performed by Fellow D. Kessel during the 1957-1958 academic year has been submitted, and the work is summarized below.

Recent interest in low firing temperature frits has been intensified because of the wider use of porcelain enamel on steel and aluminum for building panels. Lead oxide is an effective agent for reducing firing temperature, and therefore is of importance for minimizing distortion and simplifying the coating process.

The study was concerned with "Some Effects of Lead Oxide in Porcelain Enamels", particularly the effect of lead oxide on the recrystallization of crystalline opacifiers in enamels and the reduction of reflectance produced by mill-added opacifiers due to solution in high lead enamel glasses. The plan of attack was to add lead oxide to existing enamel compositions rather than make an extended compositional study of lead oxide-bearing enamels. A literature survey and bibliography was included.

Tentative conclusions arising from this work were: 1) additions of red lead to leadless enamel in general tend to decrease the acid resistance, but lead bearing enamels can be balanced to give acid resistance as indicated by two lead compositions having excellent corrosion resistance; 2) crystallization of opacifiers in enamels of high lead content is possible but reflectance of an enamel, in general, decreases when lead oxide is used; 3) firing temperatures of enamels containing lead oxide as an additive will not be as low as lead oxide-bearing enamels specifically formulated to have low firing temperatures; 4) solution rate of mill-added opacifiers in lead oxide-bearing enamels is not very sensitive to heat treatment but prolonged heating periods or higher firing temperatures than normal cause rapid rate of solution; 5) color of enamels containing lead oxide depended on compositions of the enamel, amount of lead oxide, and type of opacifying crystal. There was a tendency toward yellow coloration when lead oxide was added, but Uverite, zirconium silicate, tin oxide, and recrystallized ZrO_2 produced white coatings with lead oxide-bearing enamels.

Extension of this work is being carried on by Fellow R. C. Capek in the 1958-1959 academic year.

Although a second fellowship was given to the University of Illinois, work has not been initiated as yet.

2. Ohio State University - (LP-20-59)

One fellowship under the direction of Dr. R. Russel, Jr.

Work on this fellowship was carried out by Fellow T. W. Latimer during the 1957-1958 academic year and is being continued by him through the 1958-1959 academic year.

The objective of this study is to determine the relative effects of varying compositions on the properties of typical lead glazes when tested as glass samples and to investigate the possibility of using this information in the formulation of glazes having certain desirable properties when applied to typical ceramic whiteware bodies.

The first phase is being carried out by studying: 1) the system PbO - Al_2O_3 - SiO_2; 2) the effect of additions of B_2O_3 to selected compositions of the above system; and 3) substitution of RO and R_2O oxides for PbO in glasses of selected RO-Al_2O_3 - B_2O_3 - SiO_2 ratios.

The effect of the above changes in composition will be determined with respect to thermal expansion, strain point, annealing point, hardness, solubility in weak acids, and density.

Information derived from the above studies will be utilized in the formulation of lead glazes for whiteware bodies possessing desirable characteristics such as resistance to crazing, acid attack, abrasion, and adequate strength.

A bibliography on lead glazes was prepared.

3. Clemson Agricultural College - (LP-12-59)

One fellowship under the direction of Professor G. C. Robinson.

This investigation is being carried out by Fellow E. K. MacFarlane during the academic year, 1958-1959.

The wettability of lead glazes upon structural clay bodies is being studied to develop glazes having superior wetting characteristics. The approach selected is to evaluate the effect of clay body composition, frit composition with respect to lead content, and firing atmosphere on the wettability of the frit.

A base clay body composition has been selected and compositions will be varied by 1) raising silicon content; 2) raising calcium content; and 3) lowering iron content, in each case holding the proportions of the other constituents constant.

Pemco P-239 glaze composition will be used as a base, to which will be added .15, .30, and .45 equivalents of PbO.

Firing will be done in: 1) a reducing atmosphere of carbon monoxide; 2) an oxidizing atmosphere of dry air; and 3) a second oxidizing atmosphere of air saturated with water vapor (at 25°C).

4. Pennsylvania State University - (LP-14-59)

One fellowship under the direction of Professor F. A. Hummel.

This investigation is being performed by Fellow J. Argyle during the academic year 1958-1959.

A basic study of the phase relationships in the ternary systems PbO - MgO - P_2O_5, and PbO - La_2O_3 - SiO_2, is being undertaken as well as the thermal expansivity of the lead crystalline compounds of silcates and phosphates, and the ternary compounds consisting of lead-aluminum-silicates and lead-boron-silicates.

Primary attention is to be given to the thermal expansion measurements and the ternary phase system PbO - La_2O_3 - SiO_2.

Work so far completed indicates that a ternary compound may exist in the system PbO - MgO - P_2O_5, but this conclusion is tentative pending further analysis and a survey of the system PbO-MgO.

The binary system PbO - La_2O_3 is being studied as well as compositions on the join between PbO - SiO_2 and La_2O_3 - SiO_2. Tentative data indicate the extent of liquid immiscibility in the ternary system and the possible existence of a ternary compound.

5. Rutgers University - (LR-21-59)

Two fellowships under the supervision of Dr. J. H. Koenig.

The object of the study on both fellowships is to develop ultra low-loss ceramic dielectrics using ultra low-loss glasses as binders for Wollastonite or fused quartz for the main component. The work was started by Fellow M. M. Bunag during 1957-1958 academic year, and she is continuing the work during the present year with E. Sawaguchi.

Wollastonite and fused silica were chosen as the principle components of the dielectric body, because each is known to have ultra-low dielectric loss characteristics. Primary consideration has been given to developing glass binders with low dielectric losses.

Theoretical considerations as to the cause of dielectric losses enter into the realm of solid state physics. Most glasses contain Si-O networks, and other positive ions in the glass compositions are bound to the Si-O networks with rather weak forces which may be of ionic or covalent character. Weakly bound ions are assumed to exist in shallow potential wells such that when an electric field is applied to the glass there will appear dielectric polarization composed of electronic and ionic polarization, P (elec) and P (ion) respectively. P (ion) is due to the shifting of ions and P (elec) is due to distortion of the ion's electron cloud. At low frequencies P (ion) will appear, but as frequency is increased, P (ion) begins to decrease because it cannot follow the rapidly changing a.c. field. Around the frequency range where the dielectric constant begins to decrease, the P (ion) is out of phase with the applied field, and as a result, high dielectric loss appears. If ions are bound to the Si-O network so that deep potential wells exist, then dielectric loss appears only at very high frequencies because the restoring force for the shift of the ion is strong in the deep potential well and P (ion) is maintained in phase over a broader frequency range. One component of P (ion) may appear at low frequencies but disappears at higher frequencies because the rate of transfer of the ion causing this component is so slow compared to high frequency applied fields that ion shifts are not made.

Decrease of dielectric loss at radio frequency ranges is the objective of the present research and from the above described theory of losses, this can be accomplished by producing deep potential wells for ions in the Si-O network. In general, deep potential wells are realized if the valency and polarizability of the ions are large. Lead ions have valency twice that of sodium and the polarizability is two to three times as large; hence the depth of the potential well for lead would be considerably greater than that for sodium. Glasses containing lead can be expected to show a maximum dielectric loss at low frequency and very low loss at higher frequencies - the desired range.

Experimental work conducted to date has included the fabrication of dielectrics using glasses composed of lead, barium, and bismuth ions in the Si-O network as the binder for Wollastonite components, and the evaluation of these dielectrics with regard to power factor, dielectric constant, and dielectric loss factor. Seven glasses were evaluated, varying the lead, barium and bismuth compositions, and results were compared to a standard binder glass having the alkaline metals, sodium and potassium. In all cases, the elimination of sodium and potassium and the inclusion of ions forming deep potential wells caused significant decrease in the dielectric loss factor. All seven of these bodies have ultra low dielectric loss, having a JAN-I-10 specification rating greater than L-7. The body having the lowest loss factor developed to date consists of 55% #4248 Wollastonite, 20% #4 ball clay, 15% barium carbonate and 10% lead bisilicate.

Future work will consist of evaluation of other compositions for producing extra low dielectric bodies, and studies of other applications where bodies having these characteristics may be used. Also the wider use of lead-flexed bodies will receive attention.

6. Alfred University - (LF-22-59)

One fellowship under the guidance of Professor C. Greene.

Work is being carried out in the present academic year by Fellow C. Lieser.

The object of this research is to study the fundamental behavior of lead in glasses. The use of lead oxide has been of considerable importance to the glass industry primarily because of its great solubility and fluxing action. Characteristics ascribed to the presence of lead oxide in glass are high index of refraction, large dispersion, low melting point, wide softening and working range, adaptable coefficient of expansion, resistance to devitrification, and high capacity to absorb radioactive energy.

The many beneficial characteristics attributed to lead could lead to a broad program of investigation if the effects of lead on each of these properties were to be studied. To narrow down the field of investigation to that area or those areas where the greatest contribution can be made, an exhaustive literature study has been prepared.

7. University of California - (LF-23-59)

One fellowship under the supervision of Professor J. A. Pask.

This research is concerned with a study of ferroelectrics containing lead compounds with particular attention being given to investigation of the lead oxide-iron oxide system.

A literature search is now being made, and from this will come final definition of the program.

III ZINC RESEARCH PROGRAM

A. New Finishes for Zinc Die Castings - (ZP-12-59)

Research to improve the corrosion resistance of chromium-plated zinc die castings is being carried out by Battelle Memorial Institute under the supervision of Mr. Safranek. Work has been in progress since April, 1956 and will be carried out until July, 1959, under the present agreement.

Many plating systems have been evaluated during this period and two systems appear to produce corrosion resistance which is far superior to industrial chrome plating as it now exists. Test panels have been exposed at two sites, some for over a period of fifteen months, and the superiority of these two systems is apparent. The first of these is called the "duplex nickel process", which is a commercially available system in which bright nickel is deposited over dull nickel, affording superior corrosion resistance at areas of local defects in the chrome plating. The other system approaches this problem from another standpoint, and improved corrosion resistance is predicated on a defect-free chrome plating. This system has been termed "bright, crack-free chromium". The evaluation of both these methods of improving corrosion resistance of zinc-based die castings has indicated that either method combined with conventional practice will produce a far superior product. Test panels will remain on exposure and new panels reflecting improved, bright, crack-free chromium are being placed on test.

Recent work at Battelle has been concerned with determining plating conditions that yield improved, bright, crack-free chromium. The variables of chromic acid concentration, plating temperature, and current density, as well as chromic acid sulphuric acid ratio, are being studied with respect to continuity of the chromium plate. Information on these variables is desired to define why some sets of plating conditions are better than others for plating corrosion protective chromium for the guidance of industry in selecting the best over-all plating process.

Studies of plating thickness have shown that porosity of plating is dependent somewhat on thickness when plating conditions are such as to produce bright, crack-free chromium. Cracking of chrome plate was found to be dependent upon the plating bath temperature and to a lesser extent on the chromic-sulphuric acid ratio and chromic acid concentration. Deposits made from baths operated at 130oF containing 45 oz. chromic acid concentration and a high chromic-sulfuric acid ratio were found to produce superior films.

One-year outdoor exposure tests have shown that outstanding performance can be obtained from a system having .4 mils of copper, .8 mils of bright nickel, and .08 mils of bright, crack-free chromium. Systems involving copper, duplex nickel, and regular chromium, also show good performance. These results correlated well with those obtained from CASS (copper accelerated salt spray) and Corrodekote tests. It appeared that these two accelerated tests correlated well with outdoor exposure tests.

Future work will be concerned with the study of plating bath variables on the continuity of chromium plate. Investigation of direct nickel plating on zinc die castings is also being studied as a possible means of eliminating cyanide waste disposal problems. Further evaluation of the corrosion protection afforded by duplex nickel as well as the combination of duplex nickel and bright, crack-free chromium, will also be carried out.

B. Development of Improved Zinc Die Casting Alloys - (ZP-5-59)

This program is being carried out in the research laboratories of the New Jersey Zinc Company under the direction of Mr. Anderson and, under the present agreement, will extend until February, 1960.

Work to date has consisted primarily of a literature survey and setting up experimental equipment. The research to be performed will consist of a study of alloys which can be hot chamber die cast, and which may contain aluminum in the range of 5 to 18%. The economic advantages of the hot chamber die casting process have dictated that alloy development be conducted with this process in mind. Improvement in die casting alloys is sought with regard to higher mechanical properties, wear resistance, creep strength, low temperature ductility, corrosion resistance, and thermoexpansitivity. The zinc-aluminum system seems to be the most likely candidate for improvement of these properties. Wrought zinc-aluminum alloys have excellent ductility and toughness at room temperature, and it is felt that use can be made of these characteristics to achieve the objectives outlined above.

The plan of attack proposed involves proceeding in three major phases: (a) the development of test bar die suitable for this type of alloy, (b) the preparation of die castings and evaluation of all reasonable alloy compositions (c) the more complete study, including the establishment of at least approximate composition limits of any alloys of sufficient interest which may be found in step (b). Such aspects as castability, corrosion resistance, platability, physical properties, and mechanical properties of promising alloys will be evaluated.

C. Corrosion of Galvanized Hot Water Tanks - (ZP-20-59)

This research is being conducted at the Case Institute of Technology under the supervision of Dr. Weast. It has been in progress since July, 1958 and is to be continued, under the present arrangement, until July, 1959.

The need for this research stems from the deterioration of the competitive position galvanized hot water tanks have suffered due to premature failure of tanks in critical locations throughout the country. Two factors which have led to this situation are believed to be the trend toward the use of soft water and higher operating temperatures. Whether these factors are indeed related to the problem remains to be proved, but it is apparent that some environmental change in conditions has caused, through early failures, a deteriorating market.

The object of this research is to obtain information which will permit development of zinc alloys possessing improved corrosion resistance to hot water. A plausible theory proposed to explain the corrosion of metals covered with a

continuous film of corrosion products is that theory concerned with the defect solid state. The basis of this theory is that the corrosion rate of a metal covered with such a film will increase as the number of defects in the film increases. Zinc oxide has been shown to be a metal excess compound in that it contains zinc ions located at interstitial sites. Wherever zinc ions are so located, there is an equivalent number of electrons in the crystal, and it is the migration of these ions from one interstitial position to another which permits continuous corrosion of zinc even though the metal is coated with a pore and crack-free film. In this film, the diffusion rate of zinc ions is the corrosion rate determining factor.

The experimental work now in progress is proceeding along two lines. First, photoconductivity studies and X-ray analysis of corrosion products obtained from alloys containing 99.99% zinc, 99.2% zinc, and 97.5% zinc with 2.5% aluminum in oxygenated distilled water are being undertaken.

It has been found from this study that zinc oxide was one of the corrosion products formed at all temperatures. At low temperatures, zinc hydroxide and hydrated zinc oxide formed as well. At 88°C, zinc oxide only was identified. At 100°C, there were at least three zinc oxide structures in evidence. One of these which formed slowly was colored black. The structures of the corrosion products formed at lower temperatures (20 to 30°C) were unstable at high temperatures (80 to 100°C) transforming to zinc oxide.

A second phase of the research involves determination of conditions which influence the electrical potential of zinc with respect to its environment with the object in mind of determining why the potential of zinc becomes so noble and to establish conditions under which this enoblement occurs. Previous research conducted at atmospheric pressure indicated that zinc became noble only in the presence of oxygen and bicarbonate ions and that the presence of even reasonably small concentrations of chlorides or sulphates prevented this tendency.

Sincezinc corrosion products in water always contain oxygen, the effect of pressure as a variable was investigated, and potential studies were made in pressurized systems. It was found that 30 psig caused zinc to become .1 to .3 of a volt more noble than when the system was not pressurized. In some of these experiments, zinc became more noble than iron in distilled water. From these data, there is indication that the reversal of potential of zinc with respect to iron is more common than predicted by research of earlier investigators and that pressure is a variable that affects potential reversal.

Future effort will be concerned with the pressure sensitivity of zinc corrosion in water as well as the development of alternate methods for minimizing the effects of potential inversion and the investigation of a system potentially capable of yielding long life regardless of geographic location and type of water.

D. Wet Storage Stain of Galvanized Sheet - (ZP-11-59)

This investigation is being carried out at Southern Research Institute under the supervision of Mr. Wilcox. The work has been in progress since February, 1957 and under the present arrangements is to continue until December, 1959.

Research has been primarily concerned with three topics:

a. The development of a rapid test procedure to determinethe susceptibility of galvanized sheet to wet storage stain.

b. The comparison of the developed test with existing stack tests now used in industry.

c. The evaluation of various protective films.

Of the various tests that have been investigated, the one that was found most likely to yield results comparable to those obtained in stack tests consists of immersion of galvanized samples in distilled water and measuring weight loss of the sample after corrosion products have been removed. This test produces quantitative results that may be valuable for differentiation of wet storage stain susceptibility. Previously used stack tests are not quantitative to this extent in that the susceptibility to stain is measured by the time required to stain 50% of the surface area.

Correlation between the immersion test and the stack test is still being carried out and for the most part has been found to be comparable. The comparison between the immersion method and industrial type method has been made with untreated, chromate-treated, and organic-coated specimens, and these two methods have generally rated the actual performances of various samples in the same way, with the exception that the chromate-treated specimens appear much better in relation to the organic-coated samples by the industrial method than by the immersion method. The immersion method is potentially of great value owing to its reproducibility and speed.

Recently susceptibility tests have been performed on treated and untreated galvanized samples submitted by seven galvanized steel producers. Susceptibility was tested by both the immersion test and the industrial stack test. Among the untreated samples, there was essentially no significant variation in corrodibility except that in one instance, where no aluminum was added to the galvanizing bath, susceptibility to wet storage staining was somewhat less. All treated samples showed some degree of protection. However, three treated samples seemed, from most of the data, to be superior to the group of the other four with regard to corrosion resistance.

A third phase of the research is concerned with determining the effectiveness of various organic coatings in inhibiting wet storage staining. Many products were shown to be ineffective. Two materials were found to be relatively protective but it should be noted that chromate, as applied in the laboratory, and as applied commercially by one manufacturer of galvanized sheet, showed superior inhibition to staining in the stack test than did the two organic compounds. Performance in the immersion test by these chromate-treated specimens was not outstanding, however.

Future work will be conducted to study an aging effect that appears to decrease the protection of chromate films. This phenomenon was recently found to be the cause of premature failure of some chromate films. Future testing of

industrial galvanized sheet will also be performed as well as electric diffraction experiments on the corrosion product known as black rust in order to identify the nature of the substance and develop information as to its cause.

E. Exposure of Competitive Sheet Materials - (ZP-1-59)

Tests are under way to compare the corrosion characteristics on continuous galvanized steel, semi-continuous galvanized steel, rolled zinc, and aluminized steel, at rural, industrial, and industrial sea-coast locations. The specimens were first exposed in March, 1958. The zinc sheet and galvanized steel specimens have darkened slightly since this date while the aluminized specimens show effects ranging from slight yellow staining near the edges to a more general yellow stain, with rust spots, on the lower side about 1/32" diameter at the rural site. The first specimens will be tested for physical properties as soon as significant corrosion has occurred in any one type of material.

F. Cathodic Protection of Marine Tankers - (ZP-13-59)

This program consists of installation and evaluation of zinc anodes for cathodic protection of No. 9 tank of Texaco Company's Hull No. 4566. The applicability of zinc anodes in protecting tanks under sea water ballast conditions will be determined in this study. The installation was designed by Ebasco Engineering Services who were also responsible for the actual installation. At this time the installation is practically completed with the exception that potential monitoring equipment is yet to be purchased and installed. The tanker is expected to be commissioned and put into service in May.

G. Improvement of Zinc Lithographers' Plates - (ZP-4-59)

This research is to be carried out under the technical supervision of the Lithographic Technical Foundation with metallurgical support from Ball Bros., Illinois Zinc Co., and Matthiessen & Hegeler Zinc Co. The contract was let in March of this year and, under the present arrangements, will run for a one-year period. It is being financed by the Lithographic Technical Foundation, the aforementioned companies, and the American Zinc Institute in a cooperative research venture.

The primary objective of this work will be to improve the nonprinting areas of zinc plates by conversion of the surface to a state in which it is highly hydrophilic. In the lithographic field, metals are classified as "more ink receptive than water receptive" or "more water receptive than ink receptive". Zinc is classified as one of the "ink receptive" metals. These terms are relative since a lithographic plate must have both ink receptive and water receptive areas, (the image and nonimage areas respectively). Of primary concern then, is the improvement of water receptivity of zinc plates.

Another area of investigation will be the development of a surface treatment on zinc which will enable the plates to be pre-coated with a diazolight-sensitive material to produce a presensitized lithographic plate or to be coated with a wipe-on type of diazo coating. These coatings are being used widely in the lithographic field and at present can be used only on specially treated aluminum plates.

Many possible approaches will be investigated for conversion of the non-printing areas to make them water receptive, and to enable zinc plates to be coated with diazo. Among these are acid and alkaline anodizing systems, the "Anozinc" process, and other chemical surface treatments with phosphates, oxylates, and silicates. These treatments will first be evaluated on a laboratory basis, and promising ones will be field tested in actual production.

Improvement of the mechanical properties of zinc plates by developing suitable alloys is also to be investigated with the objective in mind of producing fine-grain plates which have better printing characteristics and alloys with more creep resistance since one criticism of zinc plates is that they stretch during long press runs. This phase of the investigation will be carried out by the three participating companies, Ball Bros., Matthiessen & Hegeler and Illinois Zinc Co.

H. Zinc Battery Cans - (ZP-18-59)

Recognizing the superior properties of zinc for dry cells, and the desire to continually improve the quality and performance of this power package, the dry cell manufacturers and the fabricators of zinc sheet have joined together in a cooperative program directed towards the elimination of perforation of the dry cell container.

The first step in the program is to establish a yardstick for evaluating the relative performance of zinc cans when exposed to media equivalent to that encountered in the completed dry cell. Evaluation of the "yardstick", or corrosion test is underway. When this is completed, the chemistry of the cell as well as the metallurgy of the container will be studied.

I. Exposure Tests of Zinc Oxide Containing Exterior House Paints - (ZP-22-59)

This investigation is being carried out with the extensive cooperation of the American Zinc Oxide Co., The Eagle-Picher Co., The New Jersey Zinc Co., Sherwin-Williams Co., and St. Joseph Lead Co.

The objectives of this broad program are threefold: 1) the evaluation of new paint vehicle developments with zinc oxide pigment; 2) the evaluation of zinc oxide paint formulations with respect to zinc oxide content; and 3) evaluation of performance of zinc oxide formulations with respect to mildew resistance and comparison of performance with that of other paints containing chemical mildewcides.

Thousands of paint test panels have been exposed since August, 1958, at six sites representing different atmospheric conditions. These sites and their environments are: 1) Monaca, Pa. - city smoke;2) Joplin, Mo. - mining; 3) Columbus, Ohio - average residential; 4) Palmerton, Pa. - industrial smoke; 5) Coffeyville, Kansas - farm; and 6) Miami, Florida - marine and sun.

The six-month exposure results of these sites will be reported in the next quarterly report.

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