AZI-LIA EXPANDED RESEARCH PROGRAM

AMERICAN ZINC INSTITUTE, INC.
LEAD INDUSTRIES ASSOCIATION

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Director of Research

July 1, 1959

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

Gentlemen:

The second quarterly report of the AZI-LIA Expanded Research Program is attached. We hope that the first report met with your approval and has been useful to you. It is our desire that you be kept fully aware of the progress and nature of the many individual projects as well as the over-all direction of the total program.

Four additional research contracts have been initiated in the last quarter and several existing programs have been extended. The objectives of these are summarized in the respective Lead Research and Zinc Research sections.

The format of the resume has been changed so that the report may be readily separated into lead and zinc sections with individual tables of contents, and the individual programs have been catagorized into Metallurgical, Chemical, and Electrochemical disciplines. This was done to facilitate the use of the report by reviewing personnel, and we hope you find that these changes increase the utility of the report.

We look forward to receiving your comments and suggestions.

Sincerely yours,

Schrade F. Radtke

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AZI-LIA EXPANDED RESEARCH PROGRAM

American Zinc Institute
Lead Industries Association

Quarterly Report No. 2
July 1, 1959

Second Quarterly Report

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I INTRODUCTION

This Second Quarterly Report of the American Zinc Institute and the Lead Industries Association Expanded Research Program briefly summarizes the progress that has been made on the many research programs in the period April 1, 1959 to July 1, 1959.

During this period four new programs have been initiated, and the objectives of these are outlined. Extensions of several existing programs have also been made and are noted in the summary of the appropriate projects.

To facilitate the use of the report by the personnel of the sponsoring companies, the format has been changed so that the report may be readily separated into Lead Research Program and Zinc Research Program sections with a separate table of contents for each. The Program summaries have also been classified into Metallurgical, Chemical, and Electrochemical disciplines, depending on the nature of the individual investigations. By this arrangement, the Expanded Research Program hopes to achieve maximum utility of the report by the Program's sponsors.

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ALI-LIA EXPANDED RESEARCH PROGRAM

II - LEAD RESEARCH PROGRAM

A. PROGRAMS RECENTLY INITIATED

1. Fundamental Investigation of Lead Powder Metallurgy (LP-8-59) (Rensselaer Polytechnic Institute, Dr. F. V. Lenel)

A program to investigate the fundamentals of lead powder metallurgy was initiated June 18, 1959 for a one-year period. Rensselaer was chosen to perform this investigation from the four research organizations who submitted proposals in respone to the Expanded Research Program's invitation to bid. Dr. Lenel has been associated with the science of powder metallurgy for some time and therefore brings a broad background of experience with him to apply to this research program.

The primary objective is to investigate dispersion hardening techniques for producing stronger and more creep-resistant wrought lead products. The first part of the project will be to determine the relationship between the degree of dispersion of a second phase in a lead matrix and the strengthening effect thus produced. This study will be made by extruding alloys made up from a series of compounds, including lead oxide, and lead powders of different particle size. Powders of lead alloys which have improved creep strength will also be incorporated into mixtures with a second dispersion phase to determine the extent of additional strengthening obtained.

Another recently developed method of obtaining very fine second phase dispersions in lead powders will be investigated. This consists of atomizing a lead alloy in which the alloying element is soluble in the liquid phase but practically insoluble in the solid phase. This method produces a powder in which the alloying element is distributed in the form of a very fine dispersion. The creep properties of a wrought product fabricated in this way will be investigated, as well as tensile and corrosion performance.

As a result of these initial studies, it is anticipated that techniques will be developed for producing wrought lead alloys possessing tensile and creep strengths superior to the known alloys of lead.

2. Investigation of Methods for Producing Lead Coated Steel (LP-26-59) (Expanded Research Program Supervision)

A program has been initiated to evaluate the various methods for producing lead-coated steel. An immediate objective is to determine the most economic method of producing lead-coated can stock for nonfood containers. Supervision of this project will be handled by the Expanded Research Program staff which will let feasibility study and sample production contracts to organizations that have particular skills in the various techniques.

Initially it has been proposed that the techniques of vacuum metallization, direct cladding by powders, foil or sheet cladding, electroplating, and hot dipping will be investigated.

A contract has been let to National Research Corporation to produce lead-clad steel by the vacuum metallization process. Lead lends itself well to this technique and advances in production equipment are making this method of deposition competitive to older processes in certain areas. If no difficulties are encountered in vacuum metallization, delivery of the coated steel should be made in the near future.

Other organizations have been approached for the procurement of lead-coated steel by the other processes.

The materials produced by the various methods will be evaluated by a major container organization.

B - ACTIVE METALLURGICAL PROGRAMS

1. Continuous Extrusion of Lead Cable Sheathing (LP-15-59)
(John Robertson Company)

Three additional lead cable sheathing alloys have been extruded on the Robertson machine since the last report period. The operating characteristics of the machine have been determined for the antimonial alloy, tellurium alloy, and Habirloy. These alloys were shown to be extrudable on the modified continuous machine of Robertson with varying degrees of ease depending on the alloy. The limited runs performed are believed to be ample indication that they can be continuously extruded into cable sheathing on a commercial basis.

Metallurgical evaluations of these alloys are being performed by Mr. Snyder of the Anaconda Wire and Cable Company's Laboratory.

Future work will include the preparation of a technical brochure to sum up the operating characteristics of the machine and the metallurgical evaluation of the sheathing produced from each of the alloys. This will include a discussion of commercially pure lead, F-3 arsenical alloy, Habirloy, tellurium alloy, copper-bearing alloy, and the antimonial alloy.

2. Study of lead Base Alloys (LP-4-59)
(Armour Research Foundation, C. R. Simcoe, Supervisor)

This is a fundamental study of the recrystallization kinetics of binary lead alloys involving approximately 15 high purity alloy systems and a total of some 80 composition ranges.

Essentially, all the chosen compositions have been melted, cast, and prepared for the recrystallization studies. The procedure chosen to study recrystallization kinetics involves cold pressing prepared ingots at -110°F and then measuring hardness changes with a specially developed hardness tester as the samples warm to room temperature. The cold worked samples will also be up-quenched and held at various temperatures to make isothermal hardness measurements.

Preliminary measurements indicate that the recrystallizatic. temperature of 99.9999% lead is -60°F. Initial results of the lead 1% antimony alloy have shown the competing processes of softening due to recrystallization and hardening due to aging, phenomena which are expected in several of the alloy systems.

The lov recrystallization temperatures and hardness of the high purity alloys have necessitated the development of special techniques. Now that successful procedures have been worked out, the recrystallization measurements will be rapidly carried out. Future work will consist of alloying the remaining few systems and performing and analyzing the recrystallization studies.

Consolidated Mining and Smelting Co., St. Joseph Lead Co., and American Smelting and Refining Corp. have contributed much to this program by supplying high purity lead and alloying additions and technical data to Armour.

3. Fiber-Reinforced Lead (LP-9-59)
(Armour Research Foundation, R. H. Read, Supervisor)

Development of methods for producing self-supporting lead products by reinforcement with metal fiber mattes is the object of this project.

A study of lead infiltration conditions leading to maximum impregnation of a phosphor-bronze fiber structure of varying densities is being performed by immersing the fiber mattes in molten lead with and without trays to minimize lead run out. Conditions found to promote impregnation are high lead bath temperature, tin additions to the lead, pre-fluxing of the mattes, and mechanical vibration of the lead bath. 80 to 90% infiltration of the matte voids was obtained by immersing zinc chloride-ammonium chloride fluxed mattes into a 750°F lead bath for three minutes with attendant 60 cycle vibration of the lead bath. As-fabricated composites of various lead-tin alloys exhibited tensile strengths ranging from 3140 to 6400 psi compared to the component strengths of 1480 psi for a 20% dense phosphor-bronze fiber structure and 2230 to 4900 psi for 99.9% lead and 90% lead - 10% tin alloys respectively. The strength of the composites was essentially equal to the additive strengths of the components. This is less than theoretical calculated strength --a fact attributed to incomplete bonding between the fiber and matrix phases and to the formation of a brittle intermetallic phase, believed to be $Cu_{31}Sn_8$.

The intermetallic phase was also believed responsible for the surface cracking of these composites which resulted from cold working by pressing and rolling. Per cent reduction possible before cracking occurred varied from 23 to 75%. The higher ductilities were shown by the lower density fiber mattes.

Future work will consist of modifying the lead alloys to minimize intermetallic phases, developing techniques to improve infiltration efficiency, and preparing steel fiber-lead composities.

4. High Spot Investigation of Lead for Sound Attenuation (LP-16-59)
(Bolt Beranek & Newman, Inc.)

This project entails a feasibility study for employing lead products in architectural structures for sound isolation. It is to be exploratory in nature; intended to give direction to further development in the promising area of lead as a sound isolation medium.

The investigation is expected to be completed prior to the next quarterly report.

C. ACTIVE CHEMICAL PROGRAMS

1. Lead Chemicals (LP-10-59)
(Arthur D. Little, Inc., Dr. C. R. Morgan, Supervisor)

The current areas of research in this program are a study of the compound dicyclopentadienyllead, the preparation of p-styrenyllead and hexaphenyldilead monomers and their polymers, and a continuing literature search of current organolead chemistry.

P-styrenyltriethyllead monomer has been isolated and polymerized to a hard, transparent plastic. The monomer, which contains 53 wt-% lead, was produced by the reaction of triethyllead chloride and a styrenyl Grignard reagent. It was isolated by room temperature-high vacuum distillation. On standing at room temperature, in the absence of inhibitors, the monomer became viscous and on exposure to high intensity ultra-violet light, it polymerized. A new monomer, p-styrenyltriphenyllead, has been prepared by reaction of triphenyllead chloride and styrenyl Grignard reagent but it has not as yet been polymerized. This monomer contains 38.3 wt - % lead.

A study of the compound dicyclopentadienyllead (DCL) indicates that it forms an adduct with maleic anhydride. DCL is of interest because of its relatively good thermal stability compared to previously known divalent organolead compounds, and it will be studied further.

Hexaphenyldilead - maleic anhydride adducts have been prepared and a preliminary study of its esterification with ethylene glycol made. Analysis of the adducts do not agree with a previously reported structure. Before additional work on condensation polymerization of the adducts is carried out, the structure must be established.

In the future these compounds will be investigated further and greatly increased effort will be directed towards application research on available chemicals A. D. Little and others have prepared.

This program has been supported by the cooperation of National Lead Company and Ethyl Corporation who have furnished bibliographies on organolead chemistry and samples of organolead compounds.

2. High Emission Lead Compounds (LP-11-59)
(New York University, Professor I. B. Cadoff, Supervisor)

A fundamental study of the thermal and spectral emissivity of lead compounds is being carried out on this research investigation.

This program, initially contracted for the academic year 1958-1959, has recently been renewed for the academic year 1959-1960.

Work has been concentrated on obtaining the room temperature emission properties of lead telluride, the compound which is expected to have the highest emissivity in the series being investigated, which consists of PbSe, PbS, PbO, and PbTe. To avoid absorption, refraction, and reflection at grain boundaries, measurements are being made using PbTe single crystals which have been prepared. Preliminary emission data have been obtained on PbTe samples. These have shown that reflectivity is nearly independent of wave length with a slight minimum at about 5 microns. The absorption values indicate that the sample must be approximately 500 microns thick to absorb all the incident radiation and therefore have emissivity properties of the bulk material. Materials used as surface coatings must be quite substantial in thickness to completely mask the properties of the underlying material and have diffuse rather than spectral reflection.

3. Lead in Ceramic Materials

Research on ceramics is being carried out by means of fellowships in seven universities. Recently all the fellowship programs were extended to include the academic year 1959-1960. The reports of progress since the last report period are summarized below.

(a) Effects of Lead Oxide in Porcelain Enamels (LP-19-59)
(University of Illinois, Dr. A. I. Andrews, Supervisor)

The investigation is being continued on the effects 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.

(b) Lead Glazes for Ceramic Whiteware Bodies (LP-20-59)
(Ohio State University, Dr. R. Russell, Jr., Supervisor)

The object of this fellowship is to determine the relative effects of varying compo-

sitions on the properties of typical lead glazes when tested as glass samples--the results to be used in the formulation of glazes having certain desirable properties when applied to typical ceramic whiteware bodies.

The fellow performing the investigation on this program was unable to continue the work after April, 1959 and no replacement was available until July, 1959. At this time Fellow Edwin L. Rogers accepted the LIA fellowship and will continue the investigation for the academic year 1959-1960.

(c) Wettability of Lead Glazes upon Structural Clay Bodies (LP-12-59)
(Clemson Agricultural College, Professor G. C. Robinson, Supervisor)

This program entails a study of wettability of lead glazes upon structural clay bodies with respect to clay body composition, lead composition of the frit, and firing atmosphere.

A thesis by Fellow E. K. MacFarlane written in partial fulfillment of the requirements for a Master of Science Degree has been received. It covers the investigation he has performed in 1958-1959 academic year on the LIA fellowship.

The general conclusions of the effects of the variables studies on wettability are summarized:

Initial liquid formation of a glaze was relatively independent of the firing atmosphere and the clay body composition, and initial wetting occurs at a considerably higher temperature than required for liquid formation. It was dependent on firing atmosphere and body and glaze composition. A slightly oxidizing atmosphere promoted wetting of the evaluated bodies and glazes, and a reducing or oxidizing atmosphere containing water vapor raised the wetting temperature. Reducing atmospheres were specifically disadvantageous for leaded glazes because they tended to reduce the oxide to metallic lead, causing spotting and reducing the flux content of the glaze.

Lead oxide substituted for other fluxes in the glaze definitely lowered the melting and wetting temperature of the glaze due to the better fluxing properties of PbO.

An increase in silica content of the body caused a slight lowering of the wetting temperature in dry air and moist air atmosphere and had little effect in reducing atmosphere. An increase in calcium content lowered the wetting temperature in all atmospheres and generally the high calcium content bodies were the most easily wetted. The wetting range, however was decreased in those bodies by the rapid penetration of glaze into the body. Any effect caused by the change in iron content was offset by the effects of the fluxes and silica, the compositions of which were proportionally increased when iron was reduced. Iron displayed its maximum effect under a reducing atmosphere, demonstrating that as the oxidation state of iron was decreased, the wetting temperature was decreased. In general, body composition affects wettability by the promotion or retardation of the solid-liquid interfacial reaction.

(d) Phase Relationships & Properties of Selected Ceramic Systems (LP-14-59)
(Pennsylvania State University, Professor F. A. Hummel, Supervisor)

Investigation of the physical properties of the lead silicate, lead phosphate, lead borate, lead phosphate-silicate, lead aluminum-silicate, and lead borate-silicate compounds are being carried on concurrently with a study of the phase relationships of the ternary systems PbO - La_2O_3 - SiO_2.

The compound $3PbO\text{-}2SiO_2$ has been suggested. An attempt to verify its existence by X-ray diffraction patterns did not show that it was present. Samples prepared by both solid state reaction and devitrification of glass showed only mixtures of $2PbO\text{-}SiO_2$ and $PbO\text{-}SiO_2$.

Six lead phosphate compounds and one lead phosphate-silicate ternary have been prepared and are under study. One lead borate-silicate and four lead borate compounds are also being investigated as are three lead-aluminum silicate compounds.

The ternary system, PbO-La_2O_3 - SiO_2, is being investigated in the low silica region since this is where the six binary compounds are thought to exist. Present work has indicated that one ternary compound exists. It seems highly probable that several more will be found.

A new lead compound, 4 PbO - La_2O_3 which may have interesting dielectric properties has been found. These properties will be investigated at a later date.

(e) Development of Ultra Low-Loss Ceramic Dielectrics (LP-21-59)
(Rutgers University-Dr. J. E. Koenig, Supervisor)

The successful development of ultra low-loss ceramic dielectrics based on low loss glass binders and fused quartz crystalline components as reported in the last quarterly report is being augmented by a study of dielectrics incorporating alumina as the main crystalline compound.

Using an alumina crystalline phase and the low-loss silicate glasses containing lead, barium, bismuth, and calcium which were previously developed in the fused quartz studies, several dielectric bodies were investigated. Firing of these bodies proved difficult. Anomalous dielectric properties and water absorption values were obtained depending on the firing conditions. Conditions which produced good dielectric properties caused high water absorption because the bodies did not vitrify. An increase in firing temperature and time produced vitrification but the dielectric properties were markedly inferior.

An investigation of the causes for this was made, and it was found that poor dielectric properties were accompanied by the recrystallization of the alumina into large grains. From an examination of the system it was found that after the lead frit melted, further heating caused the glass to gradually dissolve the alumina crystals. The initial firing conditions, 2160 to 2200°F, no soak at temperature and fast cooling, gave bodies containing alpha alumina and lead aluminum silicate crystals having good dielectric properties but poor vitrification. Soaking at 2200°F for one hour caused considerable solution of the alumina which recrystallized into large alpha-alumina crystals on slow cooling. When these large crystals formed, no lead-aluminum silicate crystals were present, indicating that the glass composition had shifted into the corundum field of the $Al_2O_3\text{-}SiO_2\text{-}PbO$ system due to the solution of alumina. Several possibilities were proposed to explain the poor dielectric properties in the presence of the large recrystallized alpha-alumina crystals. A study of these possibilities will be undertaken.

(f) Fundamental Behavior of Lead in Glass (LF-22-59)
(Alfred University, Professor C. Greene, Supervisor)

This investigation of the fundamental behavior of lead in a glass system is being carried forward by a study of the $PbO-K_2O-SiO_2$ system. Apparatus for producing the glasses under controlled conditions have been constructed and 18 compositions have been prepared. The thermal expansion of 13 materials have been measured in the temperature range, 0-300°C by use of a dilatometer, and it has been found that in the area of the system from which manageable glasses can be obtained, the coefficient of expansion appears to be a linear function of the compositions. From this the coefficients for the three components may be calculated and these calculations are being carried out.

(g) Study of Ferroelectrics Containing Lead Compounds (LF-23-59)
(University of California, Professor J. A. Pask, Supervisor)

The magnetic ferrites have been developed only recently and have shown a combination of very useful electric, dielectric, and magnetic properties. The lead ferrites subject of this program, have found extensive use in permanent magnets because of their high intrinsic coercive force and relatively high remanence. They are derived from magnetite by the substitution of lead atoms in the magnetite cubic crystal.

A literature survey of the lead ferrites has disclosed considerable divergence of opinion as to compounds formed in the ferric oxide-lead oxide system. In view of this, the initial area of investigation of the program is to determine which lead ferrites do exist.

Lead ferrites are being produced by sintering chemically pure mixtures of PbO and Fe_2O_3 powders which have been pressed into cylindrical slugs. The slugs are sintered at fixed temperatures for known times and rapidly air quenched. During sintering, exothermic and endothermic reactions are recorded by differential thermal analysis. The sintered slugs are ground and then analyzed by X-ray diffraction techniques. Lead loss during sintering is measured.

Using these techniques on a powder mixture of 1:4 molar ratio of PbO: Fe_2O_3, it was found that; (1) at 705° sintering temperature, only alpha-Fe_2O_3 and $2PbO-Fe_2O_3$ are present; (2) with increasing temperature $PbO-6Fe_2O_3$ begins to form (800° C upward); (3) at 840°C and 875°C, $PbO-6Fe_2O_3$, $PbO-2Fe_2O_3$, and Fe_2O_3 are present, and (4) at 910°C - 915°C, the compound $PbO-6Fe_2O_3$ is still present but X-ray peak intensities are decreasing, possibly due to the vaporization of PbO.

These results are not in full agreement with those of other investigations. The possibility of the occurrence of solid solutions will be investigated in the continuing study of the lead oxide-iron oxide system.

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III - ZINC RESEARCH PROGRAM

A. PROGRAMS RECENTLY INITIATED

1. Zinc Anodes for Protection of Crab Pots (ZP-16-59) (Virginia Institute for Scientific Research, W. R. Buck, Supervisor)

An applied program to investigate the use of zinc anodes for protection of galvanized wire crab pots used in the Chesapeake Bay area was initiated on May 18, 1959 with the Virginia Institute of Scientific Research. The Virginia Fisheries Laboratory is an equal co-sponsor of the program, and the special zinc anodes to be used in the program were furnished through the courtesy of the American Smelting and Refining Company.

Corrosion of galvanized iron crab pots is estimated to cost half-million dollars annually in the Chesapeake area alone, and although some crabbers have used zinc anodes to extend pot life, no study has been made of the anode size, lifetime, fouling, protection achieved, nor the effect of the anodes on the crab catch. The purpose of the program is to supply this information through laboratory experiments and field work so that it can be widely disseminated to the crabbing industry.

The program is expected to be completed prior to the end of the year.

2. Fundamental Investigation of Zinc Powder Metallurgy (ZP-17-59) (Rensselaer Polytechnic Institute, Dr. F. V. Lenel, Supervisor)

A program to study the fundamental characteristics of zinc powder metallurgy was initiated at Rensselaer on June 18 for a period of one year under the present contract. Dr. Lenel, who is to supervise the investigation, has been associated for many years in the field of powder metallurgy and has a broad background of experience to apply to this research.

The initial objectives of this program are to investigate suitable methods of consolidating zinc powders into semi-fabricated products for further working to the wrought condition and of directly converting powder to wrought products. These studies will be preliminary to the main objective of finding techniques for producing zinc base alloys having finely-divided, insoluble second phases to impart superior strength and creep properties than are currently available in alloys fabricated by conventional methods. This will include a study of the available commercial and laboratory grades of zinc powders with regard to their oxide content and fineness. The effect of addition of zinc oxide and other compounds to zinc powders will be determined to find combinations producing dispersion strenthened alloys.

A recent development for producing very fine dispersions of practically insoluble intermetallic compounds in powders will be evaluated as to its applicability to zinc powder metallurgy. The method consists of atomizing an alloy of the matrix metal with an alloying element which is almost insoluble in the matrix metal at ambient temperature but soluble in the molten state. Rapid solidification produces a finely precipitated dispersion in the powder. Zinc-nickel alloys are a candidate for this procedure.

In the evaluation of the alloys developed, particular attention will be paid to creep. Other mechanical properties and corrosion resistance will also be evaluated.

B. ACTIVE METALLURGICAL PROGRAMS

1. Development of Improved Zinc Die Casting Alloys (ZP-5-59)
(New Jersey Zinc Company, Mr. E. A. Anderson, Supervisor)

The initial phases of the die casting alloys program are nearing completion and work will soon begin on the casting and mechanical evaluation of high aluminum-zinc alloy compositions.

Design of the experimental die, which includes a round and flat tensile bar and an impact bar, has been completed. Fabrication of the die has begun and is expected to be completed in July.

A selection of elements to be considered as ternary additions to the zinc-aluminum binary system has been made, considering such factors as solubility, toxicity, cost, availability, oxidation rate in the melt, and tendency to promote intergranular corrosion. From these initial considerations, it was decided that the first experiments would incorporate copper, magnesium, silicon, titanium, zirconium, vanadium, molybdenum, tantalum, chromium, tungsten, manganese, iron, cobalt, nickel, antimony, and possibly hafnium.

The liquid solubility of many of these elements was screened in Zn-8% Al and Zn - 14% Al alloys by performing melt analysis of samples taken 50°C above the binary liquidus. The quantity of each element retained in solid solution and as a finely precipitated compound after slow cooling was measured. Only in the cases of copper and silicon did the amount held in liquid and solid state appear to be approximately the same. Iron, manganese, titanium, zirconium, vanadium, molybdenum, cobalt, nickel, and tantalum all showed a sharp drop in solubility during alloy solidification at slow rates.

Future work will include a study of the interaction of a combination of selected elements to determine which will form compounds between themselves rather than with zinc or aluminum during solidification. The silicides in particular will be investigated.

2. Improvement of Zinc Lithographers' Plates (ZP-4-59)
(Lithographic Technical Foundation, Mr. M. Bruno, Supervisor)

This investigation, since its initiation in March, has been proceeding along many lines concurrently. Its goal is to improve the characteristics of zinc lithographic plates. Creep and bending tests have shown that a titanium-copper alloy plate possesses mechanical characteristics far superior to regular zinc plates, and a few surface treatments have shown promise of improving the water-receptivity of these zinc plates.

Co-sponsors of the program furnished titanium-copper alloy materials for evaluation, and one of these materials showed markedly improved creep resistance over conventional zinc plates, which often exhibit objectionable creep during long runs. The superior alloy contained 0.14% titanium and 0.35% copper and was heat treated at 480°F. Extensive press runs indicated a negligible amount of creep, amounting to only 0.02% compared to approximately 0.2% for regular zinc. The bending characteristics of the alloy were equivalent to those of the conventional material. Attempts to brush grain the zinc alloy plates, a method for producing a very fine grain, have shown that this process tends to polish the alloys (as it does regular zinc plates) instead of producing a fine grained surface. The plates could be tub-grained successfully, however.

The lithographic properties of the alloy plates were investigated in view of their superior mechanical performance, and no detrimental characteristics were found in making either albumin or deep-etch images. Six different desensitizing treatments were compared (treatments that produce water-receptivity in the nonprinting areas), and of these the Post-Nital treatment in conjunction with cellulose gum proved superior and gave better scumming resistance to the alloy than to regular zinc plates.

Investigation of surface treatments to develop better water-receptive surfaces without destroying the excellent ink-receptivity of zinc were carried out by measuring, as a screening test, the contact angle of water on the treated zinc surface in air and the contact angle of oleic acid on the surface in water. A 140°F acid bichromate solution treatment followed by a 140°F 5% oxalic acid solution treatment showed promise of producing a lasting oleophobic treatment.

3. Development of Improved Dry Cell Battery Anodes (ZP-18-59)
(Cooperative Program)

A performance test for rating pinhole perforation of zinc battery cans is under evaluation by the cooperating participants in the program. The test procedure was submitted by Bright Star Industries and consists of determining the perforation rate of battery cans in a heated solution of zinc and ammonium chlorides. To determine if the test will give reproducibility of results, each participant will conduct the test on battery cans furnished by Ball Brothers. The cans sent the various participants were manufactured from the same lot of zinc to reduce the possibility of material variation.

After the testing procedure is standardized, the chemical and metallurgical aspects of battery cans relative to perforation will be investigated.

4. Rolled Zinc in Architecture (ZP-20-59)
(Cooperative Program)

The over-all object of this program is to evaluate the performance of various rolled zinc alloys in exterior architectural applications. Rolled zinc products have enjoyed relatively large markets in many European countries for roofing, flashings, downspouts, and gutters, and an evaluation of its performance in the varied climatic conditions and atmospheres in the United States is being carried out on a cooperative basis by the rolled zinc producers, building contractors, and the AZI.

Zinc alloy gutters and downspouts for private homes are being fabricated and installed at Daytona Beach, Florida and Syracuse, New York. The alloys being used for fabrication of the components are the titanium-copper alloys and the 1% Cu alloy. Standard galvanized steel components are to be installed at the same locations to serve as performance controls. It is anticipated that the original installation will be completed in August.

C. ACTIVE CHEMICAL PROGRAMS

1. Exposure Tests on Zinc Oxide Containing Exterior House Paints (ZP-22-59)
(Cooperative Program)

The outdoor exposure test on numerous formulations of zinc oxide exterior house paints is continuing. Many factors are being studied in these tests, including vehicles, extenders, substrates, and zinc oxide content. Panels are being evaluated with respect to checking, cracking, peeling, chalking, tint retention, and mildew resistance. Panels have been on exposure for approximately one year and recent inspections have indicated that significant performance differences between the many formulations are being manifested. The data obtained is now in the process of analysis and results will be reported in the near future.

D. ACTIVE ELECTROCHEMICAL PROGRAMS

1. Finishing of Zinc Die Castings (ZP-12-59)
(Battelle Memorial Institute, Mr. W. H. Safranek, Supervisor)

During the last quarter, further work has been carried out to determine the effects

of impurities on chromium plate continuity. Preliminary studies on direct plating of chromium on zinc casting were made. Evaluation of the outdoor exposure panels and accelerated-corrosion studies on plating systems was also performed. An evaluation of dual chromium electroplates was also initiated.

Trivalent chromium was found to be a beneficial impurity in high-temperature, high-ratio baths employed for producing bright crack-free chromium. Porosity and blistering during Corrodkote testing was reduced in deposits from baths containing 0.5 to 15.4 grams per liter of trivalent chromium. Zinc as an impurity was found to have very little influence on plate quality, and copper and nickel induced porosity as determined by electrographic printing and confirmed by Corrodkote testing.

A typical automotive part was plated directly with chromium followed by bright nickel and regular chromium to determine corrosion performance in the absence of the normal initial copper deposit used in conventional plating systems, the objective being the elimination of the cyanide waste disposal problem attendant with copper plating. The initial results indicated that the chromium-nickel-chromium system was more corrosion resistant than the copper-nickel-chromium one. The appearance of the parts was good except that nodules tended to develop at the edges. This plating system will be evaluated further in light of these initial results.

Evaluation of outdoor exposure panels incorporating various plating systems has shown that after 23 weeks of weathering at Kure Beach, Detroit and Columbus, the panels having .025 to .075 mil of bright, crack-free chromium (high temperature, high-ratio bath) over bright nickel were in good condition. Panels having regular chromium over duplex nickel were nearly as good. Earlier panels plated with bright, crack-free chromium deposited from a self-regulating bath, now on exposure for 70 weeks at these sites, are still in good condition.

An initial evaluation of the dual chromium plating system was made. This system consists of copper, bright nickel, and two layers of chromium deposited from two different self-regulating baths. Good resistance to copper-accelerated salt spray was obtained from the system and it will be evaluated further.

The Battelle program, which under the present contract terminated July 31, 1959, is being extended to December 31, 1959, under a new contract to investigate recent developments and continue the inspection of outdoor exposure panels. Among the phases to be studied are:

a. Evaluation, by accelerated and outdoor exposure, of systems involving duplex nickel and bright, crack-free chromium from high-temperature, high-ratio baths. Mobile exposure tests will also be conducted on trucks.

b. Further evaluation of the chromium-nickel-chromium system.

c. Further evaluation of the dual chromium system.

d. Evaluation of the practicality of plating bright, crack-free chromium in cold baths (at 90°F and lower).

e. Study the effects of cyclic heating and cooling on cracking of nickel-chromium deposits on zinc die castings.

f. Investigate electropolishing and leveling electroplating of zinc die castings as a practical procedure for eliminating buffing.

2. Corrosion of Hot Water Storage Tanks (ZP-20-59)
(Case Institute of Technology, Dr. R. C. Weast, Supervisor)

This investigation is proceeding along three main lines in a study to determine the mechanism of and overcome the premature failures of galvanized hot water storage tanks. They are:

a. Determination of the electrical potential of zinc in aqueous sytems under pressure.

b. X-ray studies of corrosion films formed on corroding zinc.

c. Use of cathodic protection to inhibit corrosion of galvanized hot water tanks.

Many measurements have been made to detect the change of zinc potential in distilled water and dilute solutions at various temperatures and under pressurized oxygen and nitrogen atmospheres. In distilled water pressurized to 30 psig with oxygen, the actual zinc potential was approximately 0.7 volt with reference to a calomel half cell. Normally, under atmospheric pressure, zinc exhibits approximately 1 volt potential to this reference, and reversal with respect to iron is considered to be in the 0.6 to 0.7 volt range. A 0.1 N KCL solution under this pressurization caused negligible zinc potential loss, but potentials in or below the reversal range were found in saturated solutions of $CaCO_3$ with additions of 10 ppm $SO_4^=$ 25 ppm $SO_4^=$ and 30 ppm Cl^-. Increasing the solution temperature caused a reduction in the zinc potential, and when oxygen was replaced by nitrogen in 10 ppm $SO_4^=$ (Sat. $CaCO_3$) solution, the potential in time returned to the normal value, indicating that even with a ZnO film, reversal will not occur in the absence of oxygen. These experiments show that the effect of oxygen concentration is a significant influence on the reversal phenomenon of zinc. The mechanism by which oxygen causes this effect will be studied further.

Further clarification of the corrosion products of 99.999% zinc in oxygenated distilled water showed that from 0 to 10°C zinc hydroxide and very small amounts of oxide formed at temperatures of 25 to 70°C the proportion of oxide markedly increased; and above 88°C only ZnO was detected. Between 70 and 90°C two layers of ZnO formed with the inner layer being much more adherent than the outer, although X-ray analysis indicated no difference between them. At 100°C a dense adherent black layer forms after corrosion has occurred for a month or more. Tests conducted to learn if the conversion of $Zn(OH)_2$ to ZnO in water is purely a thermal effect were affirmative. No measureable corrosion of zinc occurred in water through which nitrogen was bubbled.

Tests to determine the minimum current density necessary to protect galvanized steel are being conducted using platinum anodes, Cleveland tap water, and 140, 160, and 180°F temperatures. Initially, a current density of 12 milliampere per square foot has afforded complete protection. The current density will be reduced until the minimum for protection is found. Other waters will then be tested by the same procedure.

3. Wet Storage Staining of Galvanized Sheet (ZP-11-59)
(Southern Research Institute, Dr. W. S. Wilcox, Supervisor)

Three phases of this program were pursued during the last quarter. The evaluation of several protection coatings for inhibiting wet storage staining of galvanized sheet has been carried out as well as additional evaluation of the effectiveness of coatings used by commercial galvanized steel producers. Developments in testing procedures for determining the susceptibility of wet storage staining have also lead to a new and rapid method which is being correlated with existing test procedures.

Preliminary results have shown that citric acid additions to tannic acid greatly increased the protection effectiveness of tannic acid. A further investigation of citric acid alone showed that by itself it was ineffective in inhibiting wet storage staining. A propriety corrosion inhibitor, Anco C-203-1 "surfactant film", was evaluated and found to give protection equivalent to the best organic coating tested thus far. However, the recommended dilutent is toluene, and the acceptability of the material would be seriously limited because of its recommended application from a flammable solvent.

A satisfactory means of continuously measuring the progress of wet storage staining has been developed through use of light reflectance from the surface of the sheet under test. The apparatus consists of a collimated beam of light passing parallel to the surfaces of a galvanized panel in distilled water. The formation of white rust is detected by scattering of light which is picked up by a photodiode and continuously recorded against time by a recorder. At the beginning of a test the output of the photodiode is adjusted to produce a zero reading. Results obtained by this method show good agreement with those from other tests developed for determining the susceptibility of galvanized sheet to wet storage staining.

The light reflectance method, like the industrial stack test, gives a more exaggerated distinction between good and bad sheet than either of the weight loss methods. Its advantages are rapidity, objectivity, and simplicity; all three suggesting an attractive production quality control method. The correlation of this test to actual wet storage staining susceptibility will be evaluated more thoroughly.

4. Exposure of Galvanized & Competitive Steel Sheet (ZP-35-59)
(Cooperative Project - Formerly ZP-1-59)

Outdoor exposure of the panels and tensile specimens is continuing. The condition of the galvanized panels has changed little since the last report but some evidence has been reported that localized rusting of the aluminized panels is still occurring and in one instance the coating is peeling away around these localized areas. Sufficient corrosion has not occurred to begin the testing of tensile specimens that have been exposed concurrently with the panels. The material has been on exposure since March, 1958 in four locations.

5. Zinc Anode Installations for Maine Tankers (ZP-13-59)
(Cooperative Program)

The zinc anode installation in No. 9 cargo tank of Texaco's tanker Hull No. 4566, "S. S. Maine", has been completed and the ship is now in service for approximately two months. The completed installation included 222 type 2-30 zinc anodes conforming to MIL-A-18001, Type D. Five zinc reference electrodes are also installed at various locations in the tank, and these will be monitored by the crew of the "Maine" at various intervals to determine the degree of protection afforded by the system when the tank is in ballast. The initial results of the installation should be reported soon.

S. F. Radtke
Director of Research

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