

LEAD INDUSTRIES ASSOCIATION, INC.

222 MADISON AVENUE

NEW YORK 17, N. Y.

November 26, 1962

To Members of the Health and Safety Committee:

Enclosed for your information is the material on the Expanded Research Program promised by Dr. Radtke and made available to us by him.

I believe the material is self-explanatory, but Dr. Radtke will be pleased to answer your questions and send you additional information if you write or call him.

The E.R.P. Research Digest is the latest issue of this report. If you wish copies of individual reports or papers mentioned in the Digest, please contact me directly and I will see that you get them.

All research developed in the Expanded Research Program is available for review by our industry associates on request.

Very truly yours,

Don C. Fowler
Don C. Fowler
Secretary

DCF:md

Enc. 4

cc: Dr. Y. E. Lebedeff

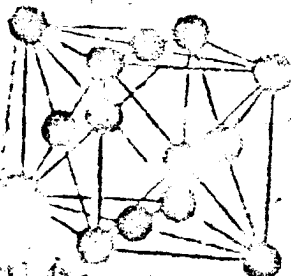
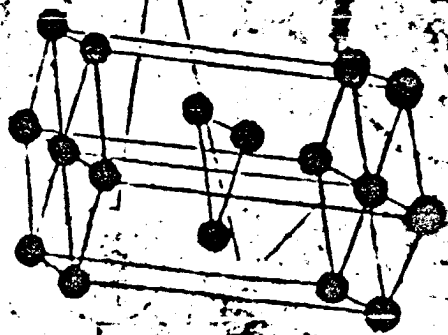
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2/14/61

Agreement

Standard Operating Procedure, ERP, June 1962
ERP Research Digest No 10 (October 1, 1962)



Lead Ahead with Lead



EXPANDED RESEARCH PROGRAM



AZI-LIA EXPANDED RESEARCH PROGRAM

**American Zinc Institute
Lead Industries Association
292 Madison Avenue
New York 17, New York**

Dr. S. P. Madhwa

ESP RESEARCH DIGEST NO. 10

October 1, 1962

TENTH RESEARCH DIGEST

ALI-LIA EXPANDED RESEARCH PROGRAM

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TENTH RESEARCH DIGEST

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ERP RESEARCH DIGEST NO. 10

AZI-LIA EXPANDED RESEARCH PROGRAM

I. INTRODUCTION

This tenth issue of the AZI-LIA Expanded Research Program presents a digest of the research work which has been actively pursued in the period April 1, 1962 to October 1, 1962. Individual research projects are reviewed as to their progress during the past six months and brief mention is made of their over-all objectives.

Project numbers are prefixed by ZM, ZC, and ZE to indicate zinc metallurgical, chemical and electrochemical research and by LM, LC and LE to indicate lead metallurgical, chemical and electrochemical research.

An abstracting service for the review of lead and zinc literature is being conducted by the Zinc Development Association - Lead Development Association in England. More than 200 technical and scientific journals throughout the world, along with published research work, are being reviewed. Abstracts of important articles are presented in two monthly companion publications titled "Zinc Abstracts" and "Lead Abstracts" and distribution has begun with the January 1962 issues. It is hoped that these abstracts and bibliographies will aid lead and zinc users in keeping abreast of the latest developments and will contribute to the promotional activities of AZI and LIA.

The ERP "RESEARCH DIGEST" is based on data received from the research project contractors and has been prepared and edited by Mr. Louis Kettler of the Expanded Research Program.

II. LEAD RESEARCH PROGRAMS

A. METALLURGICAL PROGRAMS

1. LM-4. - A Study of Lead Base Alloys, Armour Research Foundation, Mr. C. J. Reichel, Mr. C. R. Simcoe

Studies of the effect of alloying elements on the mechanical behavior of lead were continued and additional experimental work was performed on ternary alloys containing larger quantities of alloy additions.

Tensile properties were determined after extruding, after annealing the extruded rod at 100°C for one hour, and after solution heat treating at 230°C for 45 minutes and aging at several elevated temperatures. Strength levels of about 8,000 to 10,000 psi were obtained in a number of alloy compositions containing barium or calcium in combination with tin or cadmium, in the extruded or the extruded and annealed conditions. In some instances the strength remained constant or decreased slightly after the 100°C anneal; in others, there was an appreciable increase in strength. Many alloys apparently recrystallize during or immediately after extruding, as indicated by low strength levels in both conditions of treatment.

A series of alloys containing lithium in combination with tin, cadmium, thallium, or zinc showed exceptionally high strength after quenching from near or above the melting point. A tensile strength of 15,070 psi and 41% elongation was obtained for an alloy of Pb + 1.93 v/o Sn + 0.61 v/o Li after quenching from 300°C (approximately 70°C above the first signs of melting in this alloy). Other alloys containing about one-half per cent lithium with cadmium, thallium, or zinc varied in cast strength from 12,590 to 10,870 psi. Examples of the microstructures of these lithium-bearing alloys are presented. Other ternary systems containing barium, calcium, or sodium in place of lithium did not exhibit unusual strengthening in the as-cast structure.

2. LM-7 - Lead Asbestos Pads for Vibration Attenuation, Lewis S. Goodfriend & Associates, Mr. P. B. Ostergaard, Mr. L.S. Goodfriend.

The broad objective of this program is to develop and compile satisfactory engineering data on the proper use of lead-asbestos pads to isolate buildings from railroad and industrial vibrations.

During the period of this report work was performed in the following areas:

1. Review of existing data on lead-asbestos vibration-isolation pads.
2. Preparation of the pads for static testing, and the preparation of the test site for the dynamic tests.
3. Conduct of the static tests.

An electronic speed limit switch operated from the tachometer signal is now being designed to provide an automatic speed limit control so that excessive speeds are not reached when the unbalance weights are selected for the low speed test points. Unbalanced forces up to 100 can be generated by this machine at any speed within its range by inserting suitable weights in each disc. The frequency range correspond to the rpm range is 16.7 to 167 cps. This range corresponds to the range from the lower limit of bearing to the point where building vibrations begin to be highly damped by the internal construction of the building.

The force generator is now being assembled, and dynamic tests will begin shortly.

The buildings on which field tests are to be conducted are not as yet available for tests because of construction delays. Railroad vibration measurements are under way at several locations. Data are also available from previous tests on railroad yard and main line track vibration. This includes measurements at a major railroad yard in the metropolitan New York area.

Arrangements are currently being negotiated to measure the vibration from printing presses and other heavy machinery. There has been considerable difficulty in finding locations where interfering vibrations from adjacent equipment do not mask out the vibrations from the machines under study at a particular location. An examination of other materials for fillers in lead encased vibration-isolation pads was also carried out. Outside of cork, which is currently used without a protective wrapping, no other material will carry the static loads which even lightly loaded lead-asbestos pads will carry. The sheet material isolators commonly used today seldom carry loads greater than 50 psi and many cannot be loaded over 10 psi. The present view is that lead-asbestos pads of multi-layer construction promise the most effective application for lead in a vibration-isolation pad for both railroad and machinery vibration-isolation.

3. LM-8 - Fundamental Investigation of Lead Powder Metallurgy,
Rensselaer Polytechnic Institute, Mt. D. E. Jensen
Professor F.V. Lenel

The over-all aim of this fundamental research program is to explore the basic mechanism of dispersion hardening techniques in an effort to develop methods for producing stronger and more creep-resistant wrought lead products through particulate metallurgy.

During the first year of the investigation a lead alloy with 5 weight percent copper, distributed in a very fine dispersion, was studied. This alloy was produced by atomizing a homogeneous liquid lead-copper alloy and compacting and extruding the resultant powder.

In the second year, a series of lead-copper alloys with copper contents from 0.5 to 8.1% were investigated in detail, and an analysis was made of the various factors which determine the strength of dispersion strengthened lead-copper alloys. Powders which had been reduced in

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1. Review of existing data on lead-asbestos vibration-isolation pads.
2. Preparation of the pads for static testing, and the preparation of the test site for the dynamic tests.
3. Conduct of the static tests.

4. Construction of the force generator for the dynamic tests.
5. Initiation of the field test program on railroad vibrations.
6. Initiation of the field test program on heavy high speed machinery including printing presses, rolling mills, and ball and rod mills.

Static tests have been run on six lead-asbestos pads of two types. One set of three pads was of conventional construction with burned lead edges. The second set of pads were assembled by extending the lead sheet over the edge and bringing the flat edges together before burning the edges of the two sheets together. These are referred to as having tapered edges.

This purpose of the tapered edges was to remove the effect of the $1/4$ " to $3/8$ " solid lead rim on the small sizes of pads which can be tested in a static load machine. Since large size pads are used under building columns and they are usually loaded only within an area that just clears the lead rim, it was deemed important to check this effect on the pads tested in this program. These steps were also taken to help determine the pad size and method of testing of pads in the dynamic tests.

The static tests indicate that the lead-asbestos pads with tapered edges had load-deflection curves similar to those established in a previous program. It is to be noted that the data for all three pads in a set are quite consistent. Using static deflection data one might be led to conclude that the lead pads would have a resonant frequency of 6.2 to 6.9 cps. However, it is more likely that the actual static deflection is on the order of 0.070" to 0.080" which would indicate a natural frequency of 8.3 to 8.9 cps. Unfortunately, the slope at 1000 psi is not linear and is much steeper than at low loads. Therefore, one must use the slope as a guide to the natural frequency. From the slope it can be shown that the natural frequency should be about 30 cps which is in closer agreement with preliminary field data and the data reported in a previous report for high loadings.

The dynamic force generator design was analyzed, and a suitable design of counter-rotating-disc machine selected and the machine work and assembly effected. The type of machine consists of two $3-13/16$ " diameter x $3/4$ " thick steel discs, each having two sets of seven of diametrically opposed holes through the discs. The two discs are driven in opposite directions by two hardened steel shafts. One shaft is driven directly by a DC motor which is variable in speed from 1000 rpm to 10,000 rpm. The second shaft is gear driven from the motor drive shaft by means of two special hardened steel gears $4-1/2$ " in diameter. These gears are close coupled on the shaft to their respective balancing discs. Bearing, shaft diameter and disc and gear locations have been selected to minimize extraneous vibration from the shaft. The gears were originally designed to operate as part of a 90,000 rpm turbine, and no special protection is required except for lubrication. The motor is driven by an electrical variable speed drive which provides continuous speed variation within the range of the machine. The speed is indicated by means of a precise electrical tachometer coupled to the gear driven shaft.

An electronic speed limit switch operated from the tachometer signal is now being designed to provide an automatic speed limit control so that excessive speeds are not reached when the unbalance weights are selected for the low speed test points. Unbalanced forces up to 100 can be generated by this machine at any speed within its range by inserting suitable weights in each disc. The frequency range correspond to the rpm range is 16.7 to 167 cps. This range corresponds to the range from the lower limit of hearing to the point where building vibrations begin to be highly damped by the internal construction of the building.

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During the first year of the investigation a lead alloy with 5 weight percent copper, distributed in a very fine dispersion, was studied. This alloy was produced by atomizing a homogeneous liquid lead-copper alloy and compacting and extruding the resultant powder.

In the second year, a series of lead-copper alloys with copper contents from 0.5 to 8.1% were investigated in detail, and an analysis was made of the various factors which determine the strength of dispersion strengthened lead-copper alloys. Powders which had been reduced in

hydrogen prior to compacting and extruding showed a linear relationship between tensile strength and volume percent copper in the alloy. The tensile strength of the lead -0.5% copper alloy was 3100 psi, while that of the lead -8.1% copper alloy was 6320 psi.

The tensile strength of the reduced lead-copper alloy was found to be inversely proportional to the square root of the spacing between copper particles. The spacing decreases with increasing copper content while the diameters of the dispersed particles increase with increasing copper content.

In tests made on various lead base alloys to determine creep resistance, extensive room temperature creep data were obtained on lead-copper and lead-aluminum alloys at lower stresses. It was found that the creep rate in lead-aluminum alloys is less than 1% per year at stresses as high as 2500 psi. The creep resistance of lead-copper alloy extrusions at room temperature was inferior to that of the lead-aluminum alloys. The lead-aluminum alloys were also creep tested at 100°C and were found to have excellent creep resistance with creep rates of less than 1% per year at stresses up to 2500 psi.

A summary of the results of this research program to date includes the following:

- (1) Investigations of the steady-state creep rates of a lead-5% copper alloy at room temperature showed that the creep rate increased from 0.47% per year at 1100 psi to 3.64% per year at 2500 psi for the -325 mesh powder extrusions. The series B lead-5% copper powder which was used for producing extrusions for room temperature creep tests had a somewhat coarser spacing between copper particles than the series A lead-5% copper powder used for the tensile tests and elevated temperature creep tests (1.85 microns as compared to 1.25 microns). The copper particles in the series B powder extrusions were distributed in bands rather than uniformly, which may be responsible for the large scatter obtained in the curve for steady-state creep rate versus creep stress. The creep rate in a lead-copper alloy powder having the structure of series A is expected to be superior to the creep rates found for series B powder extrusions.
- (2) Tests on the steady-state creep rate of lead-5% copper at 53°C (127°F) showed that at low stresses the creep rate is proportional to the stress and at high stresses the creep rate is proportional to the fourth power of the stress.
- (3) The tensile properties of a very coarse (-20 to +100 mesh) lead-5% copper powder were determined. The as-received powder extrusions had a tensile strength of 3965 psi and 10% elongation while the reduced powder extrusions had a tensile strength of 740 psi and 18.2% elongation. The tensile specimens of this coarse alloy failed along the surface of individual powder particles, indicating that the coarse particles are not properly "cold welded" during compacting.

(4) The steady-state creep rate of the lead-0.55 aluminum alloy increased from 0.13% per year at 2000 psi to 9.96% per year at 3450 psi. The steady-state creep rate of the lead-1.7 aluminum alloy increased from 0.15% per year at 1100 psi to 8.43% per year at 3450 psi. The results show the superior creep resistance of the lead-aluminum alloys over the lead-copper alloys. The lead-0.55% aluminum is slightly more creep resistant than the lead-1.7% aluminum at stresses in the range of 2000-3000 psi.

(5) The elevated temperature (100°C) steady-state creep rates for the lead-0.55 aluminum are remarkably low, increasing from 0.18% per year at 420 psi to 0.93% per year at 1600 psi. It is evident that at elevated temperatures the lead-aluminum powder extrusions have considerably higher creep resistance than the lead-copper powder extrusions. At a stress of 815 psi the creep rate is 0.53% per year for the lead-0.55 aluminum at 100°C and about 200% per year for the lead-5 copper alloy at 91°C.

(6) For the lead-aluminum alloys creep tests at high stresses, failure without much elongation occurred at both room and elevated temperatures. At 3000 psi and room temperature the lead-0.55 aluminum alloy had an elongation of 0.27% in 700 hours when failure occurred, while at 2500 psi the elongation was 0.36% in 1000 hours without failure. At a temperature of 100°C the lead-0.55 aluminum alloy had elongated 0.15% in 600 hours with an applied stress of 1600 psi when the specimen failed, while at 815 psi the specimen elongated 0.46% in 1000 hours without failure.

(7) The tensile tests of the lead-5 copper-6 antimony alloy gave a tensile strength of 5490 psi and an elongation of 29.7% for a strain rate of 2" per minute, and a tensile strength of 4690 psi with an elongation of 32.8% for a strain rate of 0.2" per minute.

4. LM-9 - Investigation of Metal Fiber Reinforced Lead, Armour Research Foundation, Mr. S. W. McGee, Mr. C. R. Simcoe.

The first two years of this program were devoted to extensive investigations of metal fiber reinforced lead. Methods of infiltrating fiber metal skeletons with lead were developed and the strengthening effect of a coherent metal fiber skeleton incorporated into lead or its alloys was investigated. These studies, which were primarily of a fundamental nature, have been completed with the development of two promising product applications.

The present phase of the program is directed toward bringing each of these product applications to the point of demonstrated feasibility as salable products. The product applications consist of improved lead-base sleeve bearing materials and a unique metal fiber reinforced lead-base soldering tape for use in metals joining.

The procedure being followed in expediting this program consists of the following steps:

- (1) Studies of mechanical properties and environmental effects for several variations of each product.

(2) Perfection of laboratory scale manufacturing processes.

(3) Testing under simulated environmental conditions on a cooperative basis with potential users and manufacturers.

Bearing manufacturing and lead tape impregnation techniques have been tentatively established, the properties of lead tape solder joints have been partially evaluated, and the majority of cooperative bearing tests have been set up.

Tests were performed on the shear strength of steel strip lap joints soldered with reinforced lead tape. Three series of AHSI C 1008 steel strip lap joints were soldered with steel fiber reinforced lead tape. All three series of shear test specimens were soldered using an oxyacetylene torch. The first series, comprising nine specimens, was soldered with the 1/32 in. thick steel fiber-lead tape under an experimental flux of 50% $ZnCl_2$ -50% Hg_2Cl_2 flux. The second series, comprising eight specimens, was soldered with the 1/32 in. thick steel fiber-lead tape under the 50% $ZnCl_2$ -50% Hg_2Cl_2 flux. The third series (eight specimens) was soldered with the 1/32 in. steel fiber-lead tape under a commercial, chloride-free, rosin-type flux (Kester soldering flux 1544). The shear strength of the soldered joints was determined on a low-capacity (max. 2000 lb), low-speed tensile test machine.

Results of the shear tests showed that the average shear strength of the joints soldered with the 1/32 in. thick tape (avg. 1680 psi) is much higher than the average shear strength of the joints soldered with the 1/32 in. thick tape (avg. 1100 psi). Another significant finding is that the average shear strength of the joints soldered under a flux containing $ZnCl_2$ (1680 psi) is more than four times greater than the average shear strength of the joints soldered under a chloride-free flux (410 psi). Quite interesting also is the fact that the shear strengths of some of the samples soldered under a $ZnCl_2$ -containing flux exceed even the tensile strength of pure lead (2000 psi). This observation indicates that the lead in the impregnation process or in the subsequent soldering process has dissolved some ingredients which may have increased its mechanical strength.

During the reported period some wettability tests were performed with pure lead on plain carbon steel and galvanized steel surfaces under chloride-free rosin flux. These tests have shown that pure lead does not "wet" plain carbon steel surfaces under a chloride-free rosin flux (wetting angle 90°). However, under exactly the same conditions, pure lead wets galvanized steel surfaces, indicating that small amounts of zinc dissolved by molten lead from the galvanized steel surfaces may considerably improve the wetting of the steel surfaces.

Soldering tests were also performed with lead tape reinforced with copper fibers and the dimensions of the 1008 steel strips, oxide removal, and degreasing procedures were exactly the same as used in the preparation of the steel fiber-lead specimens. Both series of the shear test specimens were soldered using an oxyacetylene torch. The first series comprising nine specimens, was soldered using the experimental 50% $ZnCl_2$ -50% Hg_2Cl_2 flux. The second series comprising six specimens, was soldered under a commercial, chloride-free, rosin-type flux.

The shear test results show that the average shear strength of the copper fiber-lead tape joints obtained under the chloride flux is practically the same as in the joints obtained with steel fiber-lead tape. However, under the chloride free, rosin type flux, the shear strength of the joints soldered with the copper fiber-lead tape is much higher than the shear strength of the joints soldered with steel fiber-lead tape.

Investigation of the tensile strength of steel strip butt joints soldered with overlapped steel fiber-lead tape included two series of specimens. AISI 1008 steel strips were used for these tests and the oxide film was removed from the steel surfaces by grinding. Before soldering, the oxide film from the lead tape shim surfaces was removed with the help of a wire brush, and all surfaces were subsequently degreased with carbon tetrachloride. The tensile strength of these joints was determined on a low-capacity, low-speed tensile test machine. The tensile strength values were obtained in dividing the fracture load by the cross-section of the tape. With the exception of two tests the specimens yielded tensile strength values considerably exceeding the tensile strength of pure lead (1400 psi), indicating that in these joints the tensile strength of the lead is increased considerably by the presence of the steel fibers in the lead tape. The results of the examination of the fractured joints revealed that in all fourteen specimens the fracture took place in the lead tape, just above the gap, and did not produce any signs of shear fracture along the steel strip/lead shim interface.

Further research will involve tests on the comparative merits of different density tapes and efforts will be made to increase the capillary forces between the steel fibers in the tape.

Tests of experimental metal fiber reinforced lead-base sleeve bearings have been arranged at the Technology Center Laboratories of the Association of American Railroads in Chicago. Additional tests are in the process of being arranged with interested commercial bearing manufacturing companies. Tests are to be conducted using fully instrumented dynamometers. Lubrication will be progressively diminished until bearing failure is induced. Both the severity of the non-lubricated condition which the specimens are able to withstand before failure as well as the mode of failure undergone by them will enter into the consideration of improvements derived from metal fiber reinforcement.

5. LM-16 - Lead for Sound Attenuation, Lewis S. Goodfriend & Associates, Mr. P. S. Ostergaard, Mr. L. S. Goodfriend

Work is continuing on the development and evaluation of methods and materials for increasing the use of lead and lead products as sound control components in architectural acoustics and for the sound isolation of industrial equipment.

The scope of this program includes the following broad objectives:

1. To develop additional analytical techniques for predicting the acoustical performance of lead laminated to building construction panels and to reduce as much of the analytical information as possible to a computer punch tape program.

2. To develop additional architectural and industrial areas for the application of lead as a noise control element.

3. To include, as a parallel program to the research and development work, the preparation of technical and popular articles to be used as a part of an over-all promotion program on lead as the architectural and industrial noise control material.

4. To develop data for an acoustical lead manual which will provide practical information and data on the application and uses of lead and lead products in architectural noise control.

During the period of this report, work continued on:

1. Preparation of additional pages for the acoustical lead manual. A new series of panels is being constructed and acoustical tests are forthcoming.

2. Analytical study of building panel types with lead as a laminate to permit the rapid determination of the panel sound isolating capabilities.

3. Application of the information from the analytical study to the proposed computer program.

4. Completion of engineering and scientific papers for presentation to acoustical societies in the United States and in Europe.

Two papers titled "Transmission Loss of Leaded Building Materials" and "Lead as an Architectural Sound Barrier" were presented at a meeting of the Acoustical Society of America. These papers will be submitted to the Journal of the Acoustical Society of America and to the Acoustical Society's popular publication SOUND for publication. Another paper whose title is "Use of Lead in Improving Sound Transmission Loss" has been presented at the Fourth International Congress on Acoustics meeting in Copenhagen, Denmark, in August, 1962.

During the preparation of the papers some new presentation material was developed which indicates more effectively the powerful capabilities of lead as a sound isolating material. The effectiveness of lead as a sound isolating material is demonstrated by comparing the parameters which control its sound attenuation and its ability to influence the sound attenuation of other materials when combined with them.

The table below shows the ratio of the surface weight of a panel in pounds per square foot cubed to the Youngs Modulus of the panel material. This factor, W^3/E is the parameter which controls the sound transmission loss in the plateau region. There is a small contribution made by the damping. However, the major improvement in transmission loss by use of a thin dense material is through this factor W^3/E . It is obvious from the table that lead is more than 40 times better than steel and more than 300 times better than gypsum board, the nearest common building material.

TABLE 7

	$\frac{W}{E}$	$\frac{E}{\eta}$	$\frac{W^3}{E}$
Lead	710 lbs/ft ³	20×10^5 psi	178
Steel	490	300×10^5	3.92
Gypsum Board	48	2×10^5	0.539
Hardboard	67	8.1×10^5	0.371
Plywood	45	7×10^5	0.130

In continuation of the analytical studies program, a large number of equations for bending stiffness have been examined. It has been determined that those given by the Forest Products Laboratories are quite satisfactory for materials laminated with rigid adhesives. They should also provide reasonably satisfactory results using the elastomeric adhesives although the bending stiffness will be somewhat on the high (safe) side. The equations published by members of the Bolt, Beranek & Newman staff in a variety of publications which mainly apply to thick film layers, such as the damping tapes applied by means of elastomeric adhesives, have been found to be inapplicable to the thicker structures such as lead sheet cemented to building materials. The approximations which are required to retain validity of the Bolt, Beranek & Newman equations cannot be made with the lead sheet.

Measurements of the sound isolation properties of sixteen additional building panels are continuing and the findings will be compiled as technical data sheets in the manual. The new series of panels mostly incorporate 2½ lb and 4 lb lead sheet. The types of construction used include gypsum lath and plaster on wood studs with lead on one and two sides, gypsum lath and plaster on metal studs with lead sheet on one and two sides, and gypsum-core panels with two face boards and lead on one side. The choice of the basic constructions being evaluated with the addition of lead is based on current commercial use, acceptability and interest, and the series is designed to determine the optimum placement and weight of lead in the partition systems.

6. PM-26 - Lead Powder Cladding of Steel, Department of Metallurgy, The University of British Columbia, Dr. J. A. Lund

This report summarizes the results of a study of the feasibility of coating steel container stock with lead by a powder-rolling procedure. Objectives were to determine the conditions necessary to obtain a well-bonded coating, and to ascertain the range of coating thicknesses which it may be possible to obtain by this process.

In the evaluation of variables involved, the following factors were found, in preliminary tests, to contribute to quality and properties of lead-coated steel strip produced by the powder rolling method:

1. Surface Condition of the Steel Strip.
2. Characteristics of the Powders.
 - a) particle size and size distribution
 - b) oxide content of the powder.

3. Roll Gap and Thickness of Applied Powder Layer.
(these are inseparably related factors).

4. Roll Speed.

5. Re-rolling Conditions.

- a) temperature of re-rolling.
- b) reduction taken in thickness.
- c) rolling with or without additional applied powder.

Experimental conditions for the coating of steel strip with lead and with lead-zinc mixtures were investigated and the conclusions derived from the evaluation tests are listed below:

1. Strongly adherent lead coatings in the range of 0.0001" to 0.020" thick can be obtained on steel strip by the direct rolling onto prepared strip surfaces of clean lead powder or shot.

2. For best adhesion of the lead coating, the steel surface should be oxidized (e.g. at 1100°F. for 2 minutes in air) and reduced (e.g. for 10 minutes at 1580°F.) prior to coating.

3. Coating thickness is determined largely by the particle size distribution of the lead powder. For coatings 0.0001" thick, powders of mostly -325 mesh particles are required. At the other extreme, lead shot of -10 + 14 mesh size will give coatings in the range of 0.016" thick.

4. Coatings less than a few thousandths of an inch thick are subject to pin-holes. There are indications that the frequency of pin-holes is much reduced by using cleaner powders (i.e. of lower oxide content.)

5. Re-rolling lead-coated strip with additional powders appears to be able to eliminate pin-holes. Re-rolling without powder, even at elevated temperatures, does not eliminate all pin-holes present beforehand.

6. Oxidized powders (containing in excess of about 3 to 4 percent oxide, calculated as PbO) do not give strongly adherent coatings.

7. Rolling conditions are governed by the thickness of the applied powder layer, the particle size of the powder, and factors associated with the design of the rolling mill itself. Optimum conditions must be found by trial.

8. Speed of rolling is important only insofar as appreciable motion of powder on the strip must be prevented prior to roll-compaction. With coarser powders, it is likely that very high speeds are possible in a continuous operation.

9. Well-bonded lead coatings prepared by this process will stand prolonged heating in air without apparent loss of adhesion.

10. The addition of zinc (mechanically mixed as powder) to lead in amounts of 25 percent or more by weight results in the elimination of pin-hole corrosion. Above about 50% zinc, mixed powder coatings are not as strongly adherent as pure lead powder coatings. However, a final heat treatment for 2 minutes at 600°F. results in the very strong bonding of layers containing up to 100% zinc.

11. An excellent test for evaluating the quality of lead-coating adherence to steel consists of a high strain-rate (20 inches/inch/minute) tension test.

12. Rolls must be lubricated frequently (or continuously) for success with this process. A solid phase lubricant was used successfully in the present work.

Based on the results obtained, the program has been extended to study the possibility of obtaining pin-hole free coatings as thin as 0.0001", and to establish the resistance to corrosion by various media of mixed lead-zinc coatings. Work on this phase of the program is now in progress, and the scope of the studies will include the following topics:

- a) to provide as complete a basis as possible for larger-scale production of roll-compacted lead coatings, and
- b) to obtain detailed corrosion and property data for coatings based on mixtures of lead and zinc.

7. IM-31 - Study of Fatigue Cracking in Lead and Lead Alloys,
University of Queensland, Fellow C. W. Brewer, Dr. B. Russell,
Professor F. T. M. White

This program involves the study of lead alloys containing elements of limited solid solubility in lead, and the influence of such alloying elements on the mechanical and fatigue properties of lead in air and in various controlled atmospheres.

The present contract period has been devoted to the design, construction and assembly of -

- (a) a special furnace for the melting of lead under a controlled atmosphere and in which the molten lead will be deoxidized by means of hydrogen.
- (b) a small mechanized rolling mill, with 2" diameter rolls, for the rolling of lead and lead alloys.
- (c) a steel jig to facilitate the rapid shaping of lead specimens (for flexural bending tests) from sheet lead.
- (d) vacuum pumping equipment, assembled for use with a flexural bending fatigue machine, which has been provided with a vacuum chamber surrounding the specimen.

The design, construction and assembly of the principal items of equipment for the production of oxygen-free lead alloys and for the rolling of lead ingots has been completed and tested.

Experimental work carried out during the present contract period includes the following:

- (a) samples of lead have been decarburized by means of hydrogen at 700°C, using a special controlled-atmosphere furnace.
- (b) several oxygen-free lead-lithium alloys have been prepared in the above furnace, after overcoming initial difficulties due to the chemical reactivity and volatility of lithium.
- (c) ingots of lead, $\frac{1}{4}$ " thick, have been rolled to make lead sheet $\frac{7}{32}$ " thick, for the preparation of cantilever fatigue specimens.
- (d) flexural bending fatigue tests have been carried out on (i) lead melted in air, (ii) lead decarburized with hydrogen, and (iii) lead-lithium alloy.
- (e) electrical counting apparatus has been designed for use on a multi-specimen flexural bending machine to record the number of cycles required to fracture each specimen (this is based on the change in electrical resistance which occurs when fracture takes place).
- (f) the literature survey covering the mechanical properties of lead is continuing and, concurrently, the latest theories of solid state physics, in relation to crack formation in metals, are being reviewed.

Fatigue test results obtained with decarburized lead and lead-lithium alloy are set out in the following table.

RESULTS OF FLEXURAL BENDING FATIGUE TESTS ON LEAD ALLOYS

<u>Remarks</u>	<u>Number of cycles to complete fracture</u>
Preliminary melt in air; cast under nitrogen	< 692,000
Pure lead decarburized with hydrogen	< 555,000
Decarburized lead, + 0.05% lithium	> 2,000,000*

* test still in progress at time of report compilation

The limited number of fatigue tests carried out to date have indicated that the presence of a small amount of lithium increases the fatigue life of lead. However, further tests on lead-lithium alloys, and on decarburized lead control specimens, are necessary in order to confirm this.

8. DM-44 - Joining of Lead to Lead and Other Substrates,
American Smelting & Refining Company, Mr. L. T. Jordan,
Mr. H. E. Howe

This program is directed toward the compilation of data on the bonding characteristics of various classes of adhesives as joining media for lead. Methods of joining and organic adhesives are evaluated as to their physical adequacy, their ease of application and their economic feasibility.

The final objective of the project is to publish a manual on "Adhesive bonding of lead to itself and other materials". This manual will be a compilation of two types of data: (1) those available from the manufacturers of the adhesives on the physical, chemical and mechanical properties of the adhesives themselves and (2) those which will describe these same properties of the adhesives as they serve to join or bond lead.

During the first phase of the program, work was performed in the following areas:

1. Surveying the literature on available adhesives and their characteristics.
2. Contacting the manufacturers of adhesives to obtain recommended materials for use with lead.
3. Reviewing the range of stress and temperature to which bonds between lead and other materials may be expected to be subjected.
4. Selecting specific adhesives for testing.
5. Obtaining the desired adhesives from the manufacturers.
6. Reviewing the types of tests commonly used to evaluate the strengths of bonded materials.
7. Determining the effect of testing parameters on the results.

The literature survey has shown us that there are many adhesive formulations available which perform satisfactorily under various service conditions and that a user of lead can by consultation with the adhesive manufacturers obtain recommendations for a particular set of conditions. But these recommendations in the large majority of cases would not be based on tests or experience with lead adherends and special tests are needed to establish a body of data on the bond strength of adhesives with lead.

In an effort to determine desired criteria for the selection of adhesives, first preference was given to good resistance to exposure conditions, viz., water, heat, light, etc. A rating of good to excellent in resistance to water, heat and light were required of adhesive classes to be initially tested. Other criteria used were bond strength and ease of application and curing as well as the extent of present popular commercial use.

A survey of the properties of these adhesives showed that those classified as thermosetting have the highest probability of fulfilling most of the above criteria, and are thus most suitable for the more demanding applications involving lead. Therefore, the first testing was done with the epoxy-based adhesives, since they represent a class of adhesives having high strength and temperature stability combined with ease of application. It is interesting to note that the epoxies were recommended by several adhesive manufacturers in answer to inquiries as to which group they would suggest for lead.

Since one important objective is to present data which can be used for design purposes on bond properties of some of the commercially available adhesive classes with lead as adherends, it is necessary that the mechanical testing data cover types of simple stresses to which the bonds may be subjected. The four basic types of stress encountered in bonding are tensile, shear, cleavage, and peel. The ASTM describes testing procedures for measuring these stresses, and in some cases offers several test designs for a specific property. The lap joint, although not representing any single type of stress, but rather the interaction of several of these stresses, is often selected as the best method of surveying the properties of a group of adhesives for the following reasons: (1) most of the theoretical effort has been devoted to lap joints, (2) most of the data reported in the literature are based on lap joints, (3) lap joints are the most common means of structural joining, and (4) lap joints are easily prepared in the laboratory. Many structural adhesives are rated in manufacturers' literature by their shear strength using an overlap joint and, therefore, the lap joint design will be used extensively in this program.

During the second phase of the program, a large number of lap shear joints were made and tested. Studies were conducted on the effects of temperature, duration of load, and contact with water on the bond strength of the adhesives with lead adherend.

Good checks have been obtained with the manufacturers' reported values for their adhesives, but it is felt that further investigations are required before definite conclusions can be reached.

9. LM-5 - An Investigation of the Conversion of Particulate Lead to Wrought Forms, American Smelting & Refining Company, Mr. E. E. Howe

The results of our fundamental research program LM-5 on lead powder metallurgy have demonstrated that wrought products made from certain particulate lead compositions have properties superior to those of common lead alloys. The objective of the present program is to develop, by means of laboratory testing, technical data which will be valid in commercial production methods. Primary emphasis is placed on the investigation of those problems the solution of which will shorten the lap between the initial development of a superior lead alloy and its commercial application.

Work during the first phase of this program is concerned with the compacting, extruding and testing of specimens made from a 5% Cu-Pb powder.

Since there are three sources of dispersed particles in the copper-lead powder products, viz., (1) copper, (2) PbO (soluble), (3) surface oxides, the contribution of each phase to the strength and ductility is important knowledge. Previous investigations have shown that corroding lead powder with 0.6% oxygen present had a tensile strength of 4000 psi, with an elongation of 16%. Creep tests on these specimens showed excellent resistance at 30°C. In view of these high results with lead free of copper and very low in soluble oxides, it was decided to use as a basis for comparison with the copper-lead alloys the properties of the particulate lead products. This comparison would give an indication of the contribution to strength of surface oxide vs. copper and soluble PbO dispersions. The effect of the surface oxide was studied by subjecting the powders to various degrees of surface oxidation; followed by compacting, extruding, and testing. This would test the equipment and provide a basis for the evaluation of the contribution of the copper in relation to the surface oxide.

It was noted that the tensile properties of the corroding lead powder specimens were superior to those of the cast and rolled corroding lead. The higher tensile strength and lower percent elongation is undoubtedly due to the fine lead oxide dispersion in the lead matrix. As the amount of oxygen increases, the tensile strength increases and the ductility decreases.

Upon receiving the lead-copper powder, the material was chemically and spectrographically analyzed, and was screened into several size fractions and stored. Measurements of mesh sizes of the powder showed the range produced on commercial equipment as +100, +325, and -325. Comparative tests on various powder sizes are expected to establish a sensible balance between improved properties gained by going to finer powder sizes and the increased cost of these powders.

TABLE I

Room Temperature Tensile Properties of Various Size Fractions
of Lead-Copper Powder Alloy

<u>Alloy</u>	<u>Mesh Size</u>	<u>Tensile Strength</u>	<u>% Elongation</u>	<u>% O₂</u>
95 Pb-5 Cu	-60 +80	4090	20	0.44
95 Pb-5 Cu	-100 +150	4870	16	0.69
95 Pb-5 Cu	-200 +325	4880	17	0.47
95 Pb-5 Cu	-325	5740	17	0.62

The data in Table I clearly indicate that higher strengths occur in the very fine particle fractions. This is probably due to a combination of fine oxide strengthening and the presence of a greater amount of fine copper particles in this fraction. It is interesting to note, however, that high tensile properties were obtained with the large size fractions. This indicates that the cheaper coarse fraction should still be considered along with fine fractions.

To test the effect of duration of load on the strength of the alloys, two common testing procedures were used: 1) measuring stress to fracture and 2) measuring strain vs. time at a specific load fracture (creep).

Stress-to-rupture tests were conducted on a fine fraction (-325 mesh) and a coarse fraction (-100 +150 mesh) of the lead-5% copper alloy powder. The results showed an increase in strength of the dispersion hardened alloys over the arsenical and chemical lead, but the ductility was lower.

The creep tests at 30°C are being conducted in a constant temperature room, but since the creep specimens have been in test for only a short period of time, steady-state creep rates cannot be reliably given at this time.

Elevated temperature creep testing at 100°C in an apparatus recently constructed in the laboratory is under way, however, no conclusive results can be reported at this time.

10. IM-46 - Metallic Lead as a Lubricant, Ethyl Corporation,
Dr. W. L. Ferilstein

The objective of this research program is to survey the utility of metallic lead as a lubricant or lubricant additive. This is being accomplished by measuring the effect of lead in various forms on friction and wear in sliding systems under carefully controlled experimental conditions.

Tests and studies are continuing on the frictional properties of lead films and lubricants containing metallic lead and the findings of this research will be reported in the near future.

11. IM-67 - Development of the D.M. Process, The Broken Hill
Associated Smelters Pty. Ltd., Mr. A. L. J. Oakley,
Mr. R. D. Semmens

The D.M. Process is the result of a technological development which provides a means for the continuous casting of thin lead sheet directly from molten metal. Material as thin as .010 inches has been successfully cast and the quality of the sheet is surprisingly good. Different thicknesses can be cast, within a reasonable range, without requiring changes in tooling. The Broken Hill Associated Smelters Pty. Ltd. has operated intermittently a D.M. Continuous Casting machine for some time and has produced considerable quantities of light weight sheet. This sheet has been used principally for trial installations as a roofing membrane and for sound insulation.

Stated in simple terms, the D.M. Continuous Casting machine is a complete and integrated installation for the conversion of molten lead directly into sheet form. The basic operations consist of:

1. Melting the pig lead.
2. Casting the sheet on the surface of a water-cooled drum.
3. Coiling the finished sheet into reels ready for sale.

Lead ingot is charged into the melting tank to which heat is supplied by the oil burner. The molten lead is pumped up to the roll bath. A rotating water-cooled drum is lowered into the bath of molten lead. A thin layer of the lead adheres to the surface of the drum and, as the drum rotates, the layer of lead can be peeled off as a sheet of lead. After passing the tension rollers, the lead sheet is trimmed to the specified width and wound onto a reel. The process can be continued as long as desired, and a variety of thicknesses can be obtained by adjusting the speed of the operation and varying the depth of immersion of the casting drum.

The machine produces lead sheet in "as cast" condition from a minimum of .010 inches to a maximum of .064 inches thick at speeds ranging from 30 to 100 feet per minute. The representative output is 70 feet per minute at .032 inch thickness, which is equivalent to 12,000 lbs per hour for 18" wide sheet.

Materials which can be successfully cast by the IM process include various lead alloys as well as market lead. The lead alloys tend to form a heavier sheet than market lead, the tendency being to all appearances proportional to the freezing range of the alloy, with an apparent maximum acceptable freezing range of about 7° to 10° C (12° to 18° F).

Lead alloys which have been cast by the IM process include the following:

<u>Lead</u>	<u>Antimony</u>	<u>Copper</u>	<u>Tin</u>
99.9%	0.9%	x	x
99.7%	0.2%	x	x
90.0	10.0	x	x
99.6%	0.1	0.06	x
99.9%	x	0.06	x
38.0	x	x	62.0

The IM Continuous Casting machine is automatic in operation, apart from stopping and starting, and one man can operate the machine effectively. The need for extra help is governed by the available facilities for the changing of reels and the handling of lead pig.

Many of the factors governing sheet production by this method have been evaluated. However, the parameters of the process, in respect to such features as sheet gauge, uniformity of gauge, sheet surface finish, and sheet composition have not been determined. With growing interest in the use of lead for sound insulation, it has been expedient to concentrate on the production of sheet for trial installations. However, as the study of lead in this field of use has progressed, it became apparent that sheet of more varied properties will be required. For example, it appears that there may be a demand for D.M. sheet in gauges outside the range of 1 to 4 lbs./sq.ft. in which experience has previously been gained. Likewise, in other applications, it is desirable to know the limitations on the production of sheet in the known and potential industrial alloys of lead. It is reasonable to expect that the melting range of such alloys would be a dominant factor, and there are indications that if this range exceeds about 5°C. a coherent sheet cannot be formed.

For some applications, it may well be important to ensure that a particular surface finish should be provided on the sheet. While some of the factors governing sheet surface have been examined, a more detailed and systematic study is required before this feature can be brought under full control.

To develop the full potentialities of the D.M. Continuous Casting Process, this program is concerned with investigations of the following features:

1. Practical limitations of sheet gauge within acceptable levels of gauge uniformity and surface finish.
2. Limiting values of lead alloy properties, especially liquidus-solidus range, for casting by the D.M. Process.
3. Controlling factors with respect to sheet finish for lead and alloys over the range of practicable gauges.

The object is to develop the process to cover as wide a range of gauge as possible, in particular with a view of providing sheet in the gauges and surface conditions which may be required for sound attenuation purposes.

The effects of variations in the following factors are being studied and their influence upon the sheet building process will be determined:-

Casting roll depth of immersion;
Roll speed;
Roll diameter;
Roll finish;
Lead temperature and distribution in roll tank;
Lead circulation rate;
Water temperature and flow.

This work is carried out initially with B.N.A.S. market lead but will then be extended to cover a range of lead alloys including antimonial lead, lead-tin, solders, copper-lead, tellurium-lead etc.

B. CHEMICAL PROGRAMS

1. IC-18 - A Fundamental Study of Organolead Chemistry,
Organisch Chemisch Instituut, T.N.O., Utrecht, Netherlands,
Dr. O.J.M. van der Kerk

Research on the exploration and synthesis of new organolead compounds continued with the preparation and study of tri- and diorganolead salts for possible new applications. A number of new salts are described. The reaction product of lead chloride and butylmagnesium bromide, thought to consist mainly of tetrabutyllead (an essential intermediate in the preparation of di- and tributyllead salts), proved to be nearly completely hexabutyllead.

In the work on the reaction of lead chloride and phenylmagnesium bromide, diphenyllead, an unstable intermediate, was observed to hydrolyze easily into lead oxide and benzene. This raises considerable doubt about the identity of the compound described as diphenyllead in the literature.

Trimethyllead hydride was prepared and obtained in solution, and some reactions with it were undertaken.

The preparation of hexaphenyllead from lead chloride and phenylmagnesium bromide was much improved by the use of an excess of lead chloride and by a careful adjustment of the reaction temperatures in the several phases of the process.

Experiments on the stabilization of PVC by organolead compounds indicated that certain organolead compounds can be successfully applied as heat-stabilizers for PVC. The effect is clear both with suspension PVC and with emulsion PVC.

The most interesting compounds found thus far are hexaphenyllead and tributyllead acetate. These compounds probably can compete with stabilizers based on barium-cadmium or in some cases even with dibutyltin dilaurate, and are more effective than inorganic lead stabilizers.

In further research, the preparation of hexaphenyllead was investigated more closely, in particular the conditions which allow for the simultaneous formation of tetraphenyllead. It was shown by separate experiments that the parent Grignard compound does not catalyze the transformation of hexaphenyllead into tetraphenyllead; neither does lead chloride inhibit the transformation.

The solubility was determined of a number of organolead compounds in water. These figures will contribute to the understanding of biological activity data.

Preliminary reports on insecticidal activity of organolead compounds showed that against clothes-moths the lower trialkyllead acetates have a similar activity as DDT.

In some further antifouling screening experiments of a slightly different set-up the algistatic activity again was found to be very interesting. Furthermore, the antifouling program was continued with a more extensive investigation of the most promising compounds under actual service conditions.

The properties of triphenylleadlithium were investigated in greater detail to determine the usefulness of this compound as an intermediate. It proved to be a compound stable under nitrogen at room temperature, however eagerly reacting with oxygen to yield hexaphenyldilead and triphenyllead hydroxide. A reaction with benzylchloride yielded nearly quantitatively benzyltriphenyllead. Bromination led only partly to the triphenyllead bromide to be expected.

The synthesis of the red organolead compound (Ph_3Pb_2) was improved by using diphenyllead as the starting product instead of triphenyllead-lithium. The formation comprises a simultaneous hydrolysis and oxidation. The compound appeared to be more stable against hydrochloric acid than against pure water. Partial iodination of the red compound yielded about three moles of triphenyllead iodide per mole of Ph_3Pb_2 pointing to a branched structure of $\text{Ph}_{10}\text{Pb}_3$ wherein the triphenyllead groups are already present.

A time-saving method was developed for the synthesis of tributyllead acetate. For this purpose crude hexabutyllead was converted directly into tributyllead acetate by shaking a solution in acetone with acetic acid and hydrogen peroxide.

Other organolead salts were again prepared for evaluation purposes.

Organolead compounds were distributed for investigations on catalysis or esterification, wood preservation, and antifouling.

2. IC-26 - Organolead Chemistry, Quartermaster Research and Engineering Command, Dr. A. W. Krebs, Dr. Malcolm C. Henry, Dr. Torsten Hasselstrom, Dr. S. David Bailey

During the period of this report, the program of synthesizing new organolead compounds has continued to center around those containing both lead and sulphur atoms. As the testing program became more intensive, the need for sufficient quantities of these new compounds necessitated resynthesizing all of the compounds made to date.

The testing program has been extended and the following organizations have received samples of all organolead compounds previously synthesized and will continue to receive all new compounds on a continuing basis.

- a. Worcester Foundation for Experimental Biology
Shrewsbury, Mass.
- b. U. S. Department of Agriculture
Pesticides Branch
Beltsville, Maryland
- c. U. S. Fish and Wildlife Service
Denver, Colorado
- d. Ethyl Corporation
Detroit, Michigan

e. National Institutes of Health
Drug Development Branch
Cancer Chemotherapy National Service Center
Bethesda, Maryland

Preliminary results from The Worcester Foundation for Experimental Biology have been received. Methods, interpretations, implications, etc., of these tests are discussed in a new book edited by R. I. Dorfman, "Experimental and Biological Test Methods," Academic Press, 1962.

In addition to resynthesizing all new organolead compounds, some efforts were devoted to studying the reaction between tetraphenyllead and thiophenols. Only small amounts of products could be isolated. Increasing the temperature of these reactions could not be employed since the expected products are known to decompose at higher temperatures. This reaction appears not to be very satisfactory for the synthesis of organolead-sulphur compounds of this type and will not be further investigated.

Bis-thioacetyl diphenyllead, $(C_6H_5)_2Pb[SC(O)CH_3]_2$, was synthesized by the reaction of diphenyllead dichloride with lead (II) thioacetate. This cream-colored compound was synthesized in order to compare with the monosubstituted compound, thioacetyl triphenyllead, $(C_6H_5)_3Pb[SC(O)CH_3]$ which in preliminary tests at the Worcester Foundation for Experimental Biology was found to be active.

A manuscript entitled "Synthesis of Organolead-Sulfur Compounds" was prepared and is to be submitted to the Journal of Organic Chemistry. This manuscript describes the important results of this program's efforts over the past months.

Much work has been devoted to the investigation of reactions of hexaphenyldilead which has recently attracted attention because of its interesting biocidal properties. More detailed knowledge about the types of reactions it will undergo appeared worthwhile, particularly in view of the fact that few reactions have been carried out on this compound in the past.

It was decided to study intensively the reactions of hexaphenyldilead with five different compounds judiciously selected so as to learn as much about this compound as possible and to clear up several conflicting results appearing in the literature. The reactants selected were 1,2-dibromoethane, acetic acid, thioacetic acid, sulfur and tetracyanoethylene.

A considerable amount of basic information about hexaphenyldilead has been compiled and should be made available to the scientific community at large. As a result of this work, a manuscript is in the process of being prepared. The information on hexaphenyldilead should be of value when useful applications of this interesting chemical are forthcoming.

3. LC-34 - Anticorrosive Properties of Lead Pigments in Water Reducible Ferrous Metal Primers, The Eagle Picher Company, Mr. H. R. Harner, Mr. M. J. Hughes.

The objective of this program is the development of water miscible primers for ferrous metals which will utilize the powerful anticorrosive properties of lead compounds in stable paints with satisfactory working properties.

Work continued on the testing of several lead-organic preparations for possible anticorrosive properties in heat curing systems; and the evaluation of stir-in additions of finely divided metallic lead in water reducible heat cured systems.

Previous reports covered tests on the anticorrosive properties of a number of lead preparations among which were lead-phenol and lead-naphthol reaction products. These materials were somewhat effective and had interesting properties. Hence a repeat group of preparations of a slightly broader array of organic hydroxyl compounds were made using a precipitation from solution method rather than the direct reaction between litharge and the aromatic or condensed ring hydroxyl compound. These products proved to be excessively reactive in the paint formulations and gelling prevented their testing. Using the previous direct method a number of preparations were made from which paints suitable for testing were obtained.

The use of finely divided metallic lead in both available forms- as a powder and as a leaf- was evaluated in two types of water reducible heat curing formulations. Although its addition to the control formulation containing no lead pigment produced improved protection, the results were not equal in protection to that obtained with an active corrosion inhibitive pigment, in this case, basic lead-silico-chromate.

A major problem is that of developing an air dry vehicle of such characteristics as to resist blistering in the salt fog cabinet for a very minimum of 250 hours (and preferably very much longer). This blistering resistance is easily accomplished with heat cured formulations. The problem may be described as developing a vehicle which by a suitable choice of solvents or chemical agents will develop the desirable film characteristics upon air drying that are obtained by heat curing.

It appears probable that some of the experimental air drying vehicle combinations would need less "treatment" than others to produce a continuous film, and yet in their air dried state would fail in the salt fog cabinet very quickly. The attempt will be made to obtain significant data by force drying the air drying formulations at several temperatures and correlating any improvement in salt fog resistance with the temperature increase which produced it. The hypothesis is that vehicles whose salt fog resistance can be much improved by a small rise in drying temperature may also be more easily improved by chemical or solvent modifications than vehicles that do not show such improvement when the drying temperature is raised.

Based on these considerations, investigations were continued on:

- (1) the development of a heat curing water reducible anticorrosive lead pigment primer for ferrous surfaces with practical storage stability and application properties;
- (2) the development of an air dry water reducible maintenance type anticorrosive lead pigment primer with good durability and application properties.

Several heat cured water thinned paints with both different vehicles and pigmentation were used as base formulations for the testing of several anticorrosive pigments. Comparisons of the results of the several vehicles can only be made in a qualitative manner since complete series of paints were not tested. The following comments are justified with respect to the specific tests performed:

Calcium and zinc molybdate pigments were without significant anticorrosive properties in Aroclon 304/Dylox K-33.

Aroclon 324, and 7117-18 vehicle, when used at 35 PVR gave significantly better rust protection than Aroclon 304/Dylox K-33 at 32.3 PVR.

The Aroclon 304/Dylox K-33 combination appears to have greater storage stability with basic lead silico chromate than either Aroclon 324 or 7117-18.

The Tung Oil vehicle Z-126-A appears to have some good film properties but to be sensitive and requires further study.

Lead phenolate gave very good rust inhibition in Aroclon 304/Dylox K-33, and four phenolic type compounds (both alpha and beta naphtholate, xylenolate, and a co-precipitated phenolate-silicate) gave good inhibition in Aroclon 324.

Temperatures in excess of 225°F. are apparently needed to alter the film characteristics of an air drying water thinned anticorrosive primer.

Exposure tests on steel emphasize that for durability the anticorrosive primer should be protected by an appropriate top coat.

The film thickness of the primer is directly related to the rust prevention it will give but a normal film of primer and a suitable top coat is more resistant than an equivalent thickness of primer alone.

In the course of this work a number of heat curing water reducible experimental paints have shown excellent corrosion resistance on salt fog tests. These experimental paints in most instances had other properties that would prevent them from being considered as practical formulations. A group of paints have been made which concern formulation variables with several vehicles and inhibitive pigments. Both solvent and water thinned proprietary paints used in the automotive field are included as controls.

A new experimental air drying vehicle was tested with basic lead silicobromate and the results obtained are very promising. Further testing will be done.

Areas for future studies of lead compounds as rust inhibitive additions to water thinned primers are outlined along the lines of controlling the basicity and solubility of the effective compounds through the use of mixtures of compounds or double salts.

4. IC-49 - Lead Compounds as Lubricants and Lubricant Additives, Ethyl Corporation, Mr. E. Balda, Dr. V. L. Ferilstein

This research is concerned with the applicability of lead compounds as lubricant additives. One compound in particular shows excellent stability over a relatively wide range of temperature and is approximately ten times more efficient than available commercial additive compounds. Several of these compounds were developed as part of a fundamental research effort which the industry is undertaking on the synthesis of organo-lead compounds. Interestingly enough, one of the compounds studied behaves as an anti-lubricant.

The success achieved to date points the way to commercial development of these additive compounds for lubricant formulations.

5. IC-50 - The Use of Lead Pigments in Air Drying Water Reducible Paints for Wood, the Eagle-Picher Company, Mr. H. Harner

The objective of this project is the development of suitable paint formulations containing lead pigments in water based vehicles, that can be applied directly to wood. The critical problems are those of obtaining satisfactory drying on woods such as Western Red Cedar without staining from the water soluble components of the wood.

The first part of the work performed during this report period involved the gathering of data on the relative staining characteristics of several lead pigments in three water reducible vehicles. An important part of this work was the further developing and use of a laboratory method of evaluating staining which would be capable of reproducible results.

Two series of staining tests have been made. The complex nature of the staining problem is apparent when the variety of results obtained with each vehicle and pigment is considered. In the formulations and vehicles tested, the 85% basic lead silicate was consistent in reducing staining, though the improvement was not the same in each vehicle. Some of the lead pigments showed non-staining properties in only one vehicle. Basic lead carbonate and lead silico-titanate apparently have no anti-staining properties in any of these three vehicles.

In the course of further research, the work was concerned with:

1. developing a method of measuring and reporting the degree of staining shown by a series of water reducible paint systems on Western Red Cedar;
2. investigating the staining, drying, and resultant film properties of such primers containing lead pigments.

The stains produced in a water reducible paint film by the water extracted colored components of the wood vary a great deal in both color and the amount of staining. Black and white photographs of a series of panels do not necessarily give the correct relative information on their staining because the color of the stain falls mainly in the yellow through red end of the spectrum. The use of filters and panchromatic film emphasizes some stains and minimizes others.

Measuring the light reflected in the blue-green portion of the spectrum, which is strongly absorbed by the yellow brown stain gave numerical values, which if reported as per cent change in reflection, were in reasonable agreement with visual comparisons of the test panels. Both a General Electric Recording Spectrophotometer (operated as a reflection meter at the single wave length, 480 mμ), and a Photovolt Apparent Daylight Reflectance Meter (using a green filter) gave satisfactory results. The greater sensitivity of the spectrophotometer and the resulting wider numerical range of value makes it the preferred instrument when available.

The preparation of wood panels for exposure testing showed that the length of time that the water reducible primer was permitted to dry before the top coat was applied had a very real effect on both staining and the integrity of the paint system. Large differences in behavior were observed among the six vehicles tested. The presence of a lead pigment (8% Basic Lead Silicate) caused further variations. The lead pigment acted to reduce staining but did not completely eliminate it in all vehicles. Allowing the primer to dry for 14 days before topcoating reduced the staining and produced films free from visible defects.

Several series of panels have been prepared and exposed. These contain comparisons of lead compounds, vehicles, and topcoat formulations. The work in progress is primarily concerned with following up the exposure tests now on the test fence. Additional vehicles will be tested as they become available, and as time permits.

6. LC-61 - Lead in Plastics, DeBell & Richardson, Inc.

This recently initiated program is concerned with an exploratory review of the plastics industry, in an attempt to determine areas where lead can be used to advantage for the improvement of properties and the development of worthwhile lead-plastics combinations.

Emphasis will be placed on the following proposed work:

1. Prepare flexible sheets of plasticized polyvinyl chloride and of cured butyl rubber with a maximum content of finely powdered (a) lead and, (b) lead sulfide, to determine the possible extent of loading and the physical characteristics thus obtained. Try to establish whether there would be acoustic advantage in a lead foam sheet. Consider sound insulating wall constructions.
2. Investigate possible electrical uses, especially in cable and radiation shielding.

3. Review fungicidal experience and attempt to relate it to needs in the plastics industry.

4. Review and correlate the chemical means of introducing lead into or on long linear molecules by condensation, by vinyl derivatives, by analogues of silicone technique, by forming lead polymeric salts and otherwise.

The findings of this program will be evaluated and promising areas will then be considered for further research.

7. LC-69 - Variation of Atmospheric Lead Concentration and Type With Particle Size, Stanford Research Institute, Mr. E. Robinson

This program involves an investigation of the chemical composition and size range of particulate lead which may occur in the atmosphere.

This is a new project designed to accumulate fundamental information in the field of atmospheric chemistry.

8. Lead in Ceramic Materials - Fellowship Program

- a. IC-11 - High Emission Lead Compounds, New York University,
Fellow A. Machonis, Professor E. Miller, Professor I. Odoff

The infrared absorption-emission characteristics of lead compounds were investigated in this fellowship project in an effort to determine the relationships between the bulk characteristics of the material and its optical properties.

This program has been concluded and a final report is being prepared.

- b. IC-12 - Lead Glasses for Fast Firing Bodies, Clemson Agricultural College,
Fellow R. G. Coleman, Professor G. C. Robinson

This program was inactive during the 1961-1962 academic year due to lack of a suitable fellowship candidate, but has now been reestablished. The fellow assigned to this research is Mr. R. G. Coleman and work on the project has begun with the 1962-1963 academic year.

An outline of specific procedures to be followed in this work is in preparation and will be reported shortly. In broad terms, two topics are being considered for investigation. The first is a study of the particle size distribution of the glass. Efforts will be made to determine whether the control of particle size distribution of the glass can be used to permit evolution of gaseous constituents from the body before the sealing over of the glass layer.

The second topic involves investigations as to how fast cooling can modify the requirements for the thermal expansion of the glass compared to the thermal expansion of the body. There is reason to think that lead compounds may have considerable merit as constituents in fast cooling glasses.

- c. IC-14 - Phase Relationship and Physical Properties of Selected Ceramics Systems, Pennsylvania State University, Fellow J. F. Argyle,
Professor F. A. Hummel

Work continued on a study of the fundamentals of preparation of high frequency dielectric materials by crystallization of glasses containing considerable amounts of lead oxide. Relative to this objective the $PbO-MgO-SiO_2$ system is being investigated with special attention to phase relationships and liquid immiscibility.

During the period of this report samples of ternary compositions were weighed out using lead carbonate, barium carbonate and silicic acid. On heating these three components together, samples became dark grey in color and X-ray determinations showed that the greyness was due to finely divided elemental lead, indicating some kind of oxidation-reduction process between lead and barium oxides or carbonates. Because of this, future batches were made in one of two ways.

A. The lead and barium carbonates were reacted separately with silicic acid and the lead and barium silicates formed were then mixed together and given the required heat treatments.

B. Ternary batches were mixed using already prepared lead silicates, barium silicates and lead-barium silicates.

Both of these methods were successful in eliminating the formation of elemental lead.

Partial subsolidus phase relations were determined for the system $PbO-BaO-SiO_2$, and two ternary compounds, $PbO.BaO.2SiO_2$ and $3PbO.BaO.2SiO_2$ were found. Solid solution was found along the $PbO-SiO_2$ - $PbO.BaO.2SiO_2$ join and a small area of two liquid separation was detected in the ternary system.

Further investigations determined the phase relationships and liquidus temperatures (where possible) for the system $PbO-SiO_2 - BaO-SiO_2$. One compound, $PbO.BaO.2SiO_2$, was found which takes both PbO and BaO into solid solution. Solid solution is more extensive on the PbO -rich side of $PbO.BaO.2SiO_2$.

Glass-formation is limited to regions around $PbO-SiO_2$ and $BaO-SiO_2$ and does not extend into the center of the system.

This fellowship program has been extended through the 1962-1963 academic year.

d. LC-19 - Low Temperature Lead Enamels Containing Molybdenum and Bismuth Oxides, University of Illinois, Fellow R. B. Amin, Professor R. L. Cook, Professor A. I. Andrews

An extensive study on the use of molybdenum oxide as an opacifier in low firing temperature lead bearing enamels has now been completed and a thesis describing the work has been received. The thesis has been prepared by Mr. R. B. Amin in partial fulfillment of the requirements for a doctorate degree and is abstracted below.

The low temperature enamels having opacity comparable to the conventional white enamels and firing temperature as low as $1200^\circ F$ are difficult to achieve. Conventional opacifiers when used in the frit batch are needed in large amounts so as to produce enough opacity which in turn increases the firing temperature. Many low temperature white enamels, in which the opacity is obtained by the addition of opacifiers in the mill, face the problem of mottiness. These enamels are also characterized by poor acid resistance and gloss.

A satisfactory white enamel must have high reflectance, high opacity and good whiteness. These properties are obtained by the crystallization of a second phase, an opacifier, which gives rise to light scattering in a glassy matrix. The crystalline material used as an opacifier for the low temperature enamel should be such that it can be easily crystallized into a large number of small crystals in the lead boro-silicate enamel glass matrix.

The purpose of this investigation was to study the crystallization characteristics of lead molybdate in low temperature enamels based on lead boro-silicate glasses. An attempt has been made to study the effects of concentration of various enamel constituents on the crystallization of lead

molybdate, and to evaluate the feasibility of a lead molybdate opacified low temperature enamel having a firing temperature in the range of 1100° to 1200° F.

A literature survey was first made of existing data on nucleation and crystallization in glasses to obtain a better understanding and control of opacification in enamels. The rate of nucleation and the rate of growth and their dependence on firing temperature, firing time and the composition of enamel frit were studied to determine the processes that take place and the variables that must be controlled in order to obtain good results.

A number of enamel frit compositions were prepared and a systematic compositional evaluation was carried out in order to study the effects of SiO_2 , PbO , BaO and B_2O_3 content on the crystallization characteristics of lead molybdate in low temperature enamels. Variations in the base composition were made. The components ZnO , P_2O_5 and MnO_2 were kept constant each being 5.0 percent. Two different series of compositions, the first containing 30.0 percent SiO_2 and the second containing 25.0 percent SiO_2 , were formulated. In the first series, the PbO content was varied from 20.0 to 35.0 percent, the BaO content from 15.0 to 20.0 percent, and the B_2O_3 content from 5.0 to 15.0 percent. In the second series PbO , BaO and B_2O_3 contents ranged from 25.0 to 40.0 percent, 15.0 to 20.0 percent and 5.0 to 15.0 percent respectively.

X-ray analysis and spectrophotometer curves were used to study the effects of various oxides on the crystallization of lead molybdate. Further studies included differential thermal analysis (DTA) to detect the crystal growth taking place in the frit, and microscopic analysis by the thin film method technique to determine the temperature range of crystal growth.

Since the microscopic investigation of the heat treated thin film of enamel glass was not able to provide enough information, an electron microscope study was undertaken in order to know about the crystal habit and size of the crystals present in the enamel glass.

The Thesis summarizes the results of this research project as follows:

1. Lead molybdate crystallizes in the low temperature enamel glass matrix into a large number of small crystals and provides to the enamel a high reflectance value of 75 to 80 percent. The opacity obtained is comparable to the white enamels in which conventional opacifiers such as titania, zirconia, and antimony oxide are used.
2. The observation of melt condition, and the results of X-ray diffraction analysis of many of the frits showed that the nucleation and crystal growth rate curves for lead molybdate are partially overlapping. Because of the partial overlap of the nucleation and crystal growth rate curves some lead molybdate was already crystallized in the frit and further crystallization occurred on heat treatment of the frit.
3. The various enamel constituents have marked influence on the crystallization of lead molybdate;

a. A sodium oxide content of more than 15.0 percent in these enamels increases the solubility of lead molybdate to a considerable extent in the firing range of the enamel. Increased solubility of lead molybdate adversely affects the opacity.

b. Certain minimum amounts of glass formers SiO_2 and B_2O_3 , depending upon other constituents present, are necessary for the crystallization of lead molybdate.

c. Sodium silicofluoride addition up to 8.24 percent, increased the temperature of maximum amount of lead molybdate crystallized in the frit. Also the amount of crystal content at the maximum was increased with increase in sodium silicofluoride addition. Composition with no sodium silicofluoride had very small amounts of lead molybdate crystallized in the firing process of the enamel and the opacity was very low.

d. Molybdenum trioxide concentration from 1.0 to 5.0 percent increased the reflectance value of the enamel very rapidly. An enamel with 5.0 percent molybdenum trioxide gave an average reflectance value of 75 percent in the visible spectrum for an application of 25 grams per square foot. The theoretical amount of lead molybdate which can be crystallized in this frit was 12.75 percent. According to quantitative X-ray diffraction analysis the maximum amount of lead molybdate crystallized upon heat treatment was 12.0 percent at 1150°F . Increase in molybdenum trioxide concentration above 5.0 percent showed further increase in reflectance values but the increment was not too high.

e. Lithia substitution of 2.5 percent for soda lowered the temperature of maximum crystal content by 75°F . The firing temperature of the enamel was also lowered by lithia substitution.

f. Potassium oxide substitution of 5.0 and 7.5 percent for soda lowered the increase in lead molybdate crystal content in the frit upon reheating. The reflectance value in the shorter wavelength region of the visible spectrum was increased with K_2O substitution. This was thought to be due to the smaller size of the lead molybdate crystals. The larger size of K^+ ions might have retarded the crystal growth.

4. Differential thermal analysis of two frits showed the crystal growth exotherm. The temperatures of the exotherms were close to the temperatures at which maximum amount of lead molybdate crystal content was observed on heat treatment of the frit. No conclusive evidence of nucleation was observed in the DTA of the two frits.

5. Microscopic observation of heat treated thin films of enamel glass showed the presence of very small crystals. The temperature range in which the crystals appeared in the thin film was lower than the temperature range in which further crystallization was observed in the frit upon heat treatment. This was due to the high surface to volume ratio of the film.

6. Electron microscope study of the lead molybdate crystals present in the enamel showed that most of the crystals were needle-shaped and some were irregularly shaped. The size of the crystals ranged from 0.05 microns

to 0.2 microns. The small size of the crystals gave an explanation for the Rayleigh Scattering observed in the spectrophotometer curve.

This program has been extended through the 1962-1963 academic year.

- e. LC-21 - Development of Lead Fluxed Ceramic Bodies, Rutgers, The State University, Fellow Paul Whelan, Professor J. H. Koenig

Work during this period continued in the area of lead-fluxed tile bodies. Conventional commercial tile bodies are being used involving the following general types: Clay-talc; talc-pyrophyllite, low and high wollastonite bodies. The results on the raw bodies using up to 10% of the lead flux have been encouraging. A limited amount of work with reacted bodies has shown marked improvements in physical properties and the possibility of reducing firing temperatures.

This program has been extended through the 1962-1963 academic year and Mr. Paul Whelan has been assigned to this research for the continuation of the project.

- f. LC-22 - Fundamental Behavior of Lead in Glasses, Alfred University, Fellow Michel Renault, Dr. C. H. Greene

This fellowship program involves the study of the effect of lead and other constituents on the physical properties of various glasses.

Work is continuing on the construction of equipment for melting lead glasses, and apparatus are being constructed for the measurements of thermal expansion from liquid nitrogen temperatures to the yield point of the glass. Primary attention will be given to the $PbO-K_2O-SiO_2$ glass system.

During the period of this report, a cylindrical platinum-rhodium crucible for melting lead glasses in a closed container (to avoid loss of lead oxide and potash by volatilization) was designed on the basis of model experiments with glucose solutions. The glass in this melting crucible will be stirred by tipping about a horizontal axis. The crucible will be heated by high frequency currents induced by a water-cooled copper coil.

Equipment for drawing rods from melts in the platinum crucible has been designed and constructed. A viscosimeter for measuring the viscosity of the lead glass melts at high temperatures has been designed.

A series of preliminary melts covering the $PbO-K_2O-SiO_2$ system have been made in clay crucibles to study the melting behavior of the glasses in this system before making more refined melts in the platinum equipment. The lead oxide to be employed in the melts of lead glasses has been analyzed in several ways and found to be almost pure Pb_2O_3 . Potash carbonate is being analyzed for these melts. Especially pure silica sand has been acid washed and analyzed by evaporation with hydrofluoric and sulfuric acids. Operation of three dilatometers from $-190^\circ C$ up to the softening point of lead glass is also being studied.

- g. LC-23 - Study of Ferroelectrics Containing Lead Compounds, University of California, Professor S. Navits

This fellowship program has been extended through the 1962-1963 academic

year and will involve research on the magnetic properties of leaded ferro-electric compounds.

A graduate fellow for this research has not been appointed at this time, but it is hoped that the project will be commenced this fall.

A paper on the previous work on "Phase Relations and Structures in the System $PbO-Pb_2O_3$ " by Mr. A. J. Mountvalla has been published in the Journal of The American Ceramic Society, Vol. 45, No. 6. June 1962.

b. LC-37 - Polymorphs of Lead Oxide, Pennsylvania State University, Professor R. Roy, Fellow David A. Grisafe

Work is continuing on the study of lead oxides and hydroxides under conditions of high temperature and pressure. The purpose of this research is to obtain a better understanding of their thermodynamic behavior through the study of conditions of preparation and stability of various lead oxides and their polymorphs.

A thesis on the work performed during the 1960-1961 academic year on the phase relations in the system lead-oxygen has been prepared by Mr. W.B. White in partial fulfillment of the requirements for his doctorate degree. A copy of the thesis has been received and is abstracted below:

The primary objectives of this thesis were to (1) determine unequivocally the phases present in the lead-oxygen system and fit the various observations in the literature into this pattern, (2) determine the stability ranges of the lead oxides as functions of temperature and oxygen pressure, and (3) measure certain physical properties to further characterize the oxides and interpret their behavior.

The starting materials used in this study were as follows:

PbO:	Pure massicot by X-ray.
PbO:	Mixed litharge and massicot.
PbO:	Litharge prepared hydrothermally at 350°C and 1000 bars pressure.
Pb ₂ O ₃ :	Chemical stock. Pure Pb ₂ O ₃ by X-ray.
Pb ₂ O ₃ :	Prepared by decomposing PbO ₂ in a sealed tube at 500°C and 1000 bars pressure.
Pb ₁₂ O ₁₉ :	Prepared by decomposing PbO ₂ in open foils at 500°C and 166 bars oxygen pressure.
PbO ₂ :	Chemical Stock. Pure PbO ₂ by X-ray.

All starting materials were checked for crystallographic purity.

All runs were identified by X-ray diffraction using a Morelco diffractometer with copper K α radiation. The petrographic microscope was of little use because of the dark color and opaque nature of most of the compounds. Many samples were examined under the binocular microscope.

Hydrothermal apparatus, consisting of conventional cold seal pressure vessels were used for all runs with high pressure water. Runs at very high pressures were made in uniaxial high pressure devices of the Bridgman-Bassett design. Oxygen pressure apparatus constructed for this study were

similar to those used by Klingsberg and Roy (1959) in their study of the manganese-oxygen system, and consisted of test-tube bombs of Stellite-25 alloy which would withstand oxygen pressures of 200 bars at temperatures up to 900°C for extended periods.

Summarizing the work performed during 1960-1961, it can be stated that phase relations in the system lead-oxygen were investigated using high oxygen pressure and high hydrostatic pressure techniques. An apparatus was devised for obtaining oxygen pressures from 50 to 20,000 psi over a temperature range of 200 to 900°C. Conventional hydrothermal and uniaxial devices were used for the hydrostatic pressure experiments.

The principal results are:

(1) $Pb_{12}O_{19}$ and Pb_2O_3 were established as valid phases in the system. $Pb_{12}O_{19}$ is stable at lower pressures; Pb_2O_3 is stable only above 1 kilobar, although it may be prepared metastably at lower pressures.

(2) PbO_2 -II was found to be a high pressure polymorph of PbO_2 -I. The univariant equilibrium curve for the reaction is given by the equation:

$$P = 7.98 T + 8000$$

(P is in bars and T is in °C)

(3) The univariant equilibrium curve for the polymorphic transition between litharge and massicot is given by:

$$P = -10.64 T + 5780$$

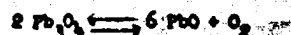
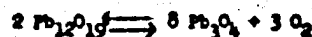
(4) The solid-solid disproportionation reaction



occurs at high pressures. The univariant equilibrium curve is given by:

$$P = -156 T + 69,000$$

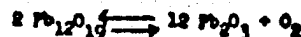
(5) Solid-vapor equilibria for the reactions



were measured over the range of 3 to 1000 bars oxygen pressure.

(6) Eutectic melting between PbO and Pb_3O_4 occurs at 875°C and 124 bars pressure.

(7) The reactions



were observed under equilibrium conditions.

(8) A phase diagram summarizing the present status of the system lead-oxygen was prepared.

During the 1961-1962 academic year, studies of the lead-oxygen system are continuing and investigations have begun of the phase relations in the system PbO-PbCO_3 . More data have been collected on the decarbonation series $\text{PbCO}_2 \rightleftharpoons 3\text{PbO} \cdot 5\text{PbCO}_3$ (I) $\rightleftharpoons \text{PbO} \cdot \text{PbCO}_3$ (II) $\rightleftharpoons 2\text{PbO} \cdot \text{PbCO}_3$ (III) $\rightleftharpoons \text{PbO}$. Preparation of pure intermediate phases for X-ray and optical characterization is progressing.

The major effort has been devoted to the P-T diagram for the PbO-CO_2 system, and the $\text{PbCO}_3 \rightleftharpoons \text{I}$ equilibrium is known up to 40,000 psi. Although essentially complete, a few more runs are required before presentation of the complete diagram. X-ray patterns indicate the presence of a fourth intermediate compound.

The Phase II field terminates at an invariant point in the general neighborhood of 4,000 psi and 540°C . At this point, the univariant curves $\text{I} \rightleftharpoons \text{II}$ and $\text{II} \rightleftharpoons \text{III}$ join to form a univariant curve at slightly higher temperatures and pressures for the reaction $\text{I} \rightleftharpoons \text{III}$. From the latter two new curves appear at a second invariant point around 8,000 psi and 575°C indicating the appearance of the new phase (IV) field and the equilibrium $\text{I} \rightleftharpoons \text{IV}$ and $\text{IV} \rightleftharpoons \text{III}$. Thus, two invariant points occur, one terminating the field of the second oxycarbonate, and the second indicating the appearance of a new compound at CO_2 pressures above 8000 psi.

This fellowship program has been extended through the 1962-1963 academic year.

1. LC-51 - Lead Glasses for Structural Clay Products, Georgia Institute of Technology, Dr. W. E. Moody, Dr. L. Mitchell

This fellowship program remains inactive pending the appointment of a suitable fellow to carry out the research.

C. ELECTROCHEMICAL PROGRAMS

1. LE-29 - Adsorption of Oxygen on Lead, University of Melbourne, Mr. V. B. Fare, Professor J. R. Anderson

The purpose of this research program is to provide fundamental data for the interaction between oxygen and lead under a variety of experimental conditions with a view to interpreting the mechanism of reaction and studying the structure of the reaction products.

During 1960, the effect of temperature on the stability of evaporated films of lead was investigated. The activation energy of sintering calculated from the initial slopes of the surface area vs. temperature curves, was found to be about 2 Kcal/mole. This exceptionally low value was explained on the basis of surface diffusion. The change in the rate of sintering due to the chemisorption of oxygen was attributed to the decrease in mobility of lead atoms due to the barrier created by adsorbed oxygen.

Although a parabolic rate law has been established for the oxidation of lead at temperatures approaching the melting point and above the melting point, there is a lack of data at lower temperatures and therefore in the work during 1961 the temperature range -183°C to 275°C was studied.

The temperature range investigated can broadly be classified into two regions corresponding to the division into protective and non-protective oxide layer behavior. Adsorption of oxygen was studied at -183 , -78 , 20 , 100 , 230 , and 275°C and protective behavior was observed at all temperatures up to 100°C . In all cases up to 100°C there was an initial very fast oxygen uptake, generally followed by a slower process which fitted a logarithmic law for the growth of the oxide layer. At 230 and 275°C the oxidation kinetics were complex; an exponential law was observed initially, followed by an apparent linear law. The latter may represent the transition between exponential and parabolic growth. In both regions the apparent activation energies are low - with an upper limit of about 6 Kcal mole $^{-1}$ - and in both regions the rate of oxygen uptake is approximately dependent on the first power of oxygen pressure, suggesting that oxygen molecules are involved in the rate determining step.

The oxide layers which were obtained above room temperature were identified by electron diffraction as orthorhombic lead oxide.

It was found that the initial adsorption of oxygen at 21°C resulted in a decrease in the work function of the lead - apparently the adsorbed oxide ions are buried below the average metal surface. As the surface coverages increased the surface potential slowly attained a small negative value typical of the electronegative adsorbate.

Since previous research involved primarily studies of dry oxygen reactions with a lead surface, the present work was extended to study oxidation in the presence of water vapor. The oxidation of lead in presence of water vapor and of carbon dioxide has been studied by a few

workers (eg. T. Markovic, 1955; Rolf Uggla, 1949) but without any conclusive results. Attempts have therefore been made to investigate the effect of these substances on the oxidation rate of lead films and to determine the final products formed.

Known amounts of oxygen and water vapor (obtained from distilled water from which dissolved gases had been removed by boiling) were mixed together and passed into the adsorption vessel. After a fixed time interval, a small amount of this mixture was taken into the McLeod gauge through a liquid air trap which froze out the water vapor and the oxygen pressure was measured. The pressure of H_2O is most of the experiments was about 10^{-5} mm. of Hg, and it was found that oxidation at $20^\circ C$, $100^\circ C$ and $230^\circ C$ was not affected at all by the pressure of water vapor. The oxidation products obtained at $100^\circ C$ were examined by electron diffraction to detect the presence of hydroxide formed during the oxidation, but only the pattern of orthorhombic PbO was observed.

The total number of oxygen molecules required to form a protective layer is slightly less than the number required in the absence of carbon dioxide. However, this difference decreases as the temperature increases. The activation energy calculated from the slopes of the curve at a point where the same number of molecules of oxygen is adsorbed is about 5.8 K. Cal/mol, which is similar to the figure obtained previously for oxygen alone. The total number of carbon dioxide molecules incorporated was found to be negligible, and the activation energy for the oxidation remains substantially the same as in the absence of carbon dioxide.

There also appeared to be a correlation between the rate of oxidation and the type of conductivity of PbO which is known to change with temperature, pressure and the presence of monovalent and trivalent impurities. Investigations were therefore made to study the effect of the monovalent impurity thallium on the rate of oxidation.

Films with various percentages of thallium were prepared by co-evaporation of lead and thallium at different rates and the rate of oxidation was studied. Samples were analyzed for thallium using atomic absorption spectrometry. The same type of exponential oxidation law was found to be obeyed as was previously found for pure lead. The diagram showed the dependence of oxidation rate on thallium content at two different temperatures $20^\circ C$ and $100^\circ C$ and two different film thicknesses. There are two distinct regions at room temperature. Below about 1 percent thallium there is marked decrease in the rate which is followed by a rather slow decrease varying linearly with increasing thallium content in the range 1% - 20% thallium. The rate was found to decrease more sharply as the film thickness increased. At $100^\circ C$ the rate decreased linearly throughout the composition range studied. Here again the rate decreased more sharply as the film thickness increased.

Further work will consist of a study of the oxidation rate using the n-type dope Bi^{3+} . However it seems essential to a better understanding of the oxidation mechanism that the defect properties of PbO be studied in greater detail, particularly with reference to the relative ionic mobilities together, if possible, with an elucidation of the exact type of non-stoichiometry present.

2. LE-35 - Electrochemical Behavior of Lead in Various Media Including Cyclic Conditions, University of Cambridge, England, Dr. J. M. Costa, Dr. T. P. Soar

This program involves the study of the behavior of lead battery electrodes in various media and under conditions of pulsed charges having variable timing and wave characteristics. The object of this study is to explore the fundamental mechanisms and reactions involved, thereby throwing more light on the behavior of lead and its compounds when used in electric storage batteries.

Anodic corrosion of battery electrodes under conditions of alternating current superimposed on direct current has received very little attention, despite its importance in technical fields where incompletely smoothed direct current is used. The present work consists of a preliminary study of pure lead in sulphuric acid under direct current and combined d.c. plus a.c. conditions. Rather high direct current densities were used in an attempt to simulate the conditions during too rapid charging that are known to be destructive to lead accumulator grids.

All experiments were performed for 20 hours at room temperature, 17-18°C. Corrosion was determined by weighing the electrodes before and after each experiment. The oxide film, adherent to the metal, was then dissolved with a little 1:1 hydrochloric acid, and the electrode was weighed again to determine the quantity of adherent oxide.

Experiments were carried out at direct current densities of 25, 50, 75, 100 and 150 mA/cm². The superimposed alternating current was from 0 to 2 mA/cm². Oxygen evolution, greater at the higher current densities, occurred in all experiments. During the first few seconds of each experiment the anodes took on a brown coloration as oxide formed on them. Much more oxide was nonadherent and fell to the bottom of the cell.

The results of this research indicate that the superimposition of up to 1% of a.c. on lead anodes operating in 28% aqueous sulphuric acid at 25-150 mA/cm² produces a small increase in the fraction of the PbO₂ formed that is adherent, and a very small decrease in the total attack on the metal. This is satisfactory from the practical aspect, for it indicates that charging batteries with incompletely smoothed direct current with a few percent alternating current ripple at the current densities under investigation certainly does no great harm to the anode grids, and may even be slightly less harmful than charging with pure d.c.

3. LE-36 - High Speed Plating of Lead, Graham, Savage & Associates, Inc. Mr. E. L. Pinkerton, Dr. A. K. Graham

This program is directed toward the development of low cost electroplating techniques for the deposition of lead coatings on steel sheets. The objective of the research is to create economically competitive materials which will find application in containers for nonfood products in architectural components and in radiation shielding. The necessary thicknesses of lead plating are being determined by corrosion tests which form part of the program.

An abstract report of the work performed during 1961 includes the following features:

1. A cell designed for the rapid screening of addition agents and the evaluation of plating variables was used in all this work.
2. The fluoborate bath was selected by test over all other available lead solutions.
3. Over 230 compounds were evaluated as possible addition agents.
4. Eleven agents were selected as superior on the basis of limiting current density, grain refinement (visually), stability in the bath for a long period and under electrolysis, and cost.
5. The so-called ferroxyl porosity test was selected from those reported in the literature, and, after careful standardization, was used to study the effect of processing variables on porosity of deposits ranging from 2 to 0.05 mil thick. One addition agent (hydroquinone) was used in the bath in all this preliminary work. An optimum and a sub-optimum cycle with respect to reduction of porosity of the lead coating were developed.
6. The effect of increased bath temperature on porosity is bad for the bath containing no agent, but beneficial for the bath with hydroquinone. This may be related to the effect of increased temperature on grain size - in the former case the deposit is visibly coarsened, but not in the latter.
7. The optimum and sub-optimum cycles were used to prepare 0.05 mil (50 millionths) deposits from baths containing the eleven chosen agents. The optimum cycle in all cases produced low-porosity deposits; the other produced low to high porosity deposits, depending on the agent.
8. Twenty-five samples were prepared for hardness testing and metallographic examination, representing plating and addition agent variables.

During the period of this report, active laboratory work has been temporarily halted while details of the tests for lead-coated can stock and lead-coated steel for architectural applications have been worked out and approved.

An outline for atmospheric exposure tests of lead-coated steel for architectural applications has been prepared. The object of this proposed evaluation is to determine the effect of the preferred lead plating bath, including the preferred addition agent and operating conditions for high-speed lead plating with certain additional variations as follows:

- 1) With and without treatments designed to reduce the over-all porosity of the coating.
- 2) With and without a strike undercoat of tin, copper, and zinc for lead coatings from 0.25 to 2.0 mil in thickness.

It is proposed to evaluate lead coatings at thicknesses of 0.05 and 0.10 mil with and without a strike undercoat of tin, copper, and zinc.

The strike coatings are to vary in thickness from 0.01 to 0.05 mil. The value of the strike coatings as a means of improving the wettability of the can stock during soldering will be one of the variables to be determined. Four water-base paints and one shellac will be evaluated.

It has been ascertained that the American Society for Testing and Materials will cooperate with the LIA-Expanded Research Program by making their test sites at Kure Beach, State College, and New York City available, provided the test data will be subsequently published. This is a standard procedure with A.S.T.M. and should impose no serious limitation.

The recommended grades of water-base paint and of shellac for the corrosion tests for lead-coated can stock have been purchased.

As soon as the steel will be received, it will be cut into the required sizes for the various test programs discussed above. These test samples will be protected against rust and held for use as required in the laboratory program.

Three papers, which were prepared for publication in lieu of patents, have been completely edited and revised in accordance with reviewers' suggestions. One paper, entitled "Porosity Testing of Electrodeposited Lead Coatings", has been sent to the American Electroplaters' Society for publication in Plating magazine. The other two papers, entitled "A Cell for High Speed Plating Evaluation" and "Evaluation of Addition Agents for High Speed Lead Plating" have been sent to Dr. F. A. Lowenbels, Chairman of the Symposium on High Speed Plating for the educational program of the 1963 Convention of the American Electroplaters' Society. It is anticipated that subject to minor modifications required by the Publications Committee these will be accepted and published within the next year.

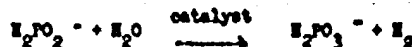
4. LE-47 - Chemical Reduction Plating, Eltex Research Corporation,
Mr. Thomas Wolf, Dr. E. Kroll

The primary purpose of this applied research program is to develop methods of applying adherent coatings of metallic lead onto a variety of metal and nonmetal surfaces by means of chemical deposition.

Prior work has shown the feasibility of depositing a displacement coat of lead over steel from a lead EDTA/hydrazine bath. The corrosion resistance of steel panels, plated with lead by the displacement method, was tested in a humidity cabinet. A maximum protection of 650 hours was found for a panel plated for 30 minutes. The approximate thickness of this coating was 0.2 mils.

The reduction of lead salts from aqueous systems was studied. No metallic lead was detected in the precipitates from these systems.

The reaction



is catalysed by palladium or nickel and is an essential part of several

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electroless metal plating processes. The evolution of hydrogen from hypophosphite solutions containing nickel or palladium was completely inhibited by the addition of lead salts at a slightly acid pH.

The plating of lead over lead was attempted with negative results. The plating of lead over electroless nickel resulted in a very small deposit.

In additional work on the plating of steel panels for test purposes, different thicknesses of lead were plated on two types of steel. The panels have been submitted for evaluation.

Panel plated in four different baths were compared for porosity. In these tests, sodium hypophosphite was compared to hydrazine hydrate, 1% non-chelated lead compared to 3% and 10%; also the use of a surface active agent was studied. The presence of the surface active agent was very detrimental to both the rate of plating and to the adherence of the final metallic film. Large variations were found between panels plated for similar lengths of time in identical baths.

The plating of lead over nickel was compared for various pH values. Only very small deposits were obtained at pH 5.5 to 13.

A process for improving corrosion resistance by sealing pores in the lead coating with electroless nickel was attempted. Considerable decrease in porosity was obtained.

The findings obtained from this research may be summarized as follows:

1. The panels for environmental testing have been prepared from the optimum displacement bath. Thicknesses of 0.05, 0.20 and 0.50 mils of lead were plated on cold rolled steel and on polished steel coupons. These panels have been forwarded for testing.
2. Minimum porosity was found for a bath containing 57 g/l hydrazine hydrate and 0.18 g/l (1%) nonchelated lead. However, this bath plates slowly and after 1-2 hours blisters begin to appear. Therefore, for greater thicknesses of lead plate, 3% nonchelated baths are better. That containing 57 g/l hydrazine hydrate is preferred over that containing 171 g/l sodium hypophosphite, mainly on account of the lower concentration of reducing agent.
3. The addition of a surface active agent substantially reduces the plating rate and gives a nonadherent lead film.
4. The quantity of lead plated by a chemical reduction process (over nickel) at all pH values is too small to be of practical importance.
5. A method of substantially reducing corrosion in the lead films by sealing the pores with nickel by a chemical reduction process has been conceived. The method was found to be effective in reducing the porosity of the lead coating.

Corrosion testing and evaluation of the lead coated steel samples are proceeding and the results will be reported shortly.

III. ZINC RESEARCH PROGRAMS

A. METALLURGICAL PROGRAMS

1. ZM-2 - Holding Power of Galvanized Fasteners, Purdue University, Mr. J. F. Benft, Professor S. K. Buddarth

Investigations are continuing in this program which is being carried out on a cooperative basis with the Purdue University Wood Research Laboratory.

Scientific devices for nail driving and for nail pulling have been devised and constructed to eliminate variables in these processes and to accurately record the forces involved.

Nails are being driven into wood under controlled conditions, and withdrawal resistance is measured after various artificially induced cycles of moisture content. Tests results will then be compared with those of ungalvanized nails and evaluated as to the relative importance of different factors. Moisture cycling is now underway.

Consideration is given to the fact that many types of zinc coated nails are being marketed and that different woods can affect the performance and life of the driven nails. However, the present scope of the program is restricted to a study of only the major variables which affect the withdrawal resistance of galvanized nails. Hot dip galvanized nails are used in all the tests and the only wood varieties being studied are fir and oak.

2. ZM-3 - Improvement of Zinc Lithographic Plates, Lithographic Technical Foundation

The current phase of this program is concerned with providing technical information and field services on the LTV Zinc Wipe-On Process, to firms interested in utilizing the LTV process on a commercial basis and to organizations desiring to produce the chemicals. A manual is also being prepared offering a detailed description of the process, instructions on proper operation, and a list of the chemicals used, complete with necessary formulas.

A number of inquiries have been received relating to technical information and license agreements on the LTV process and great interest in zinc lithographic plates is manifest in countries outside the United States. All letters are being given individual attention and samples for evaluation are being made available to interested users.

3. ZM-5 - Development of Improved Zinc Die Casting Alloys, The New Jersey Zinc Company, Mr. O. L. Werley, Mr. E. A. Anderson

During the period of this report the effects of adding $TiCr_2$, $TiMn_2$, ZrV_2 , Co_2Si , Al_2O_3 , $AlMn$ or Al_2Co_2 to base alloys of appropriate Al content have received attention. All alloys were gravity cast in a steel mold. Alloys containing $TiCr_2$ and $TiMn_2$ also were die cast. The introduction of an intermetallic compound did not result in significant improvement in the properties of the base alloy.

The study of hot chamber zinc die casting alloys has discovered an alloy which may have commercial possibilities. The alloy (presently designated AZ35 by the H.J. Zinc Company), contains 12 Al, 0.75 Cu and 0.02 Mg, the remainder being Special High Grade zinc. It compares favorably with Zamak-2 (4 Al-3 Cu-0.03 Mg) in tensile strength and hardness but unlike Zamak-2 it does not lose ductility or undergo dimensional expansion during normal use. Preliminary die casting tests have indicated good fluidity but have revealed a strong tendency to form shrinkage voids in or near the surface.

The present report supplies the available information on the alloy as a guide to those who may wish to make practical die casting tests on commercial shapes.

Comparison With Zamak Alloys

Table 1 compares the properties of AZ35 with those of Zamak-2, -3 and -5.

Table 1 - Properties of AZ35, Zamak-2, Zamak-3 and Zamak-5

Alloy Designation	AZ35	Zamak-2	Zamak-3	Zamak-5
Al - per cent (nominal)	12	4	4	4
Cu - " "	0.75	3	0	1
Mg - " "	0.02	0.03	0.03	0.03
Tensile Strength-psi				
as cast	51400	52100	41000	47600
10 days 95°C	42900	49400	34300	37700
Elongation-% in 2"				
as cast	4	8	10	7
10 days 95°C	8	3	15	17
Brinell Hardness				
as cast	101	100	82	91
10 days 95°C	81	88	62	73
Impact Strength-ft.lb.				
as cast	18	35	44	48
10 days 95°C	14	2	40	27
Dimensional Change in./6in.				
10 days 95°C	-0.0025	+0.0032	-0.0027	-0.0037
Beam Creep-days/%				
25000 psi	15.5	**	4	31.1
Impact Strength				
40°C (104°F)	17	n.d.	n.d.	n.d.
30°C (86°F)	19	35	44	47
20°C (68°F)	14	32	44	48
10°C (50°F)	13	30	27	46
0°C (32°F)	5	27	8	42
Coef. Thermal Expansion 20 to 100°C	0.0000271	0.0000272	0.0000272	0.0000272
Melting Point °C	432	380	387	388
" " °F	810	716	729	730

* Dry heat aging

** Note test creep tests on Zamak-2 are unreliable because the alloy ages during test.

n.d. - no determination

It will be noted in this table that AZ35 compares favorably with Zamak-2 in strength and hardness and is superior in retention of ductility and dimensions. Initial impact strength is lower but is adequate.

Die Casting Experience

The test data were obtained on standard 1/4 in. diameter round tension specimens and 1/4 in. x 1/4 in. x 6 in. impact bars. A gate thickness of 0.020 in. was found to be about optimum for the impact bars while an arbitrarily chosen 0.050 in. gate was used for the tension specimens. Both test bar cavities were equipped with substantial overflow wells. It may be noted that Zamak-3 was cast with great difficulty with these gates. It is evident that AZ35 can be cast with a thinner gate than that required for the Zamak alloys.

In most cases the metal temperature was held at 480°C. (896°F) with a die temperature of 210°C (410°F). Pressure on the metal was about 1500 psi. All casting was done in a hot chamber machine.

Preliminary castability tests were made in an available die which produces a 3in. x 3in. x 0.155in. flat plate often used in finishing studies. The die is gated across a 3 in. edge and contains substantial overflow well space.

Initially the gate was 0.020 in. thick. Successive increases to 0.060 in. and 0.080 in. were made during the test. Castings made with a metal temperature of 475°C (887°F) were found to show rug marks until the die temperature reached about 200°C (392°F). At 220°C (428°F) and above shrinkage pits, cracks and voids developed. The changes in gate thickness had no significant effect on this.

Shrinkage pits are known to develop in the Zamak alloys wherever heavy sections and high local die temperatures result in slow solidification. The cause lies in the inability of the first frozen skin to withstand the shrinkage stresses which develop as the remaining metal cools. It is probable that the same mechanism operates in AZ35 but the effects are increased as the result of the wide circa 45°C (81°F) spread between first and final freezing points. The spread in Zamak-3 is about 4°C (7°F).

It appears that best results with AZ35 will be obtained in shapes where, due to section size and control of die temperature, rapid freezing can be obtained. This is confirmed by the relatively minor incidence of shrinkage pits or voids in the test bars where rapid freezing did take place.

Alloy Composition

While no attempt has been made thus far to define operating limits of composition for AZ35, some information is available from the project program. The following suggested compositions, while by no means final, should approximate the ultimate ranges:

Aluminum

11 min. - 13 max.

Available data reveal little difference in strength or stability in this range.

Copper

0.5 min. - 1.25 max.

While longer exposures might reveal small aging effects at 1.25 cu, none of consequence were found in the ten-day test at 95°C.

Magnesium

0.01 min. - 0.03 max.

The tensile strength and hardness of AZ435 depend, to a considerable extent, on the Mg content. Accordingly, Mg should be held as high as casting properties and ductility needs permit.

Impurities

If the magnesium content can be held at 0.02 per cent or higher, it is probable, but not proven, that AZ435 will remain free of intergranular corrosion when Pb, Cd and Sn are at the maxima presently specified by A.S.T.M. Until complete information is at hand, it would be wise to hold impurity contents as low as possible.

Suggested Basis for Commercial Trial

Casting Shape

It would be wise to conduct the first trials with shapes of low mass which will permit rapid freezing. Heavier sections could follow later.

Metal Temperature

475 ± 10°C (887 ± 18°F)

Die Temperature

To be found by trial - should be lowest which will give a reasonably satisfactory surface. For engineering uses, some fine run marks may be accepted.

Gate

It is suggested that a 0.020 in. thick gate be used at the outset. Increase in gate thickness should be made in small steps.

The alloy also exhibits good mechanical properties when gravity cast and can therefore be considered for use in sand, plaster, permanent mold and slush casting.

The following properties were determined on 1/4" x 1/4" x 6" test bars gravity cast in a warm steel mold:

Tensile Strength-psi	48000 - 55000
Impact Strength*- ft.lb	20 - 30
Brinell Hardness	119 - 124

*Charpy test on unnotched bar.

The melting point (completely liquid) is 432°C (810°F) and the freezing point (completely solid) is 380°C (717°F). The liquid alloy is very fluid and should have good ability to reproduce mold detail.

Like other zinc alloys AZ-430 has a relatively high shrinkage. The coefficient of linear thermal expansion in the range 20 to 100°C (68 to 212°F) is 0.0000271 per degree Centigrade or 0.0000151 per degree Fahrenheit. This compares with $0.0000117/^{\circ}\text{C}$ and $0.0000065/^{\circ}\text{F}$ for iron. Because the range from solidification to room temperature is so much greater for iron, the patternmakers shrinkage allowance ($0.15''$ per foot) for AZ-430 is not much larger than that for cast iron ($0.125''$ per foot).

Where solid castings are involved, gating and risers must be designed to feed the solidification shrinkage of the main casting. It is suggested that sand molds be used as dry as possible and that plaster and metal mold be preheated to about 200°C (392°F). A metal temperature of about 480°C (896°F) seems best for first trials but should be adjusted to optimum on the basis of experience.

In alloys of this type good control must be exercised over the amounts of such impurities as lead, tin and cadmium which may be present. Until specific data on safe impurity limits are available, the limits set forth in ASTM Specification B - 86 for zinc die castings should be observed.

It is felt that the properties of the alloy described herein are of sufficient significance that industry in general will find interest in evaluating the application of this alloy to the manufacturing operations. The Expanded Research Program will be very pleased to work with those organizations desiring to explore the application of this alloy and will assist wherever possible in applying the results of this research.

4. EN-9 - An Investigation of the Zinc-Aluminum System,
Department of Mining & Metallurgy, University of Alberta,
Mr. G. R. Goldak, Professor W. V. Youdelis, Professor
J. Gordon Parr

This fundamental research program involves investigations of the phase relationships and transformation kinetics of the Zn-Al binary system in an effort to determine the influence of various factors on the physical and metallurgical properties of the Zn-Al alloys.

The immediate objective of this research program is to determine the precise nature of the Zn-Al phase diagram about the immiscibility loop. The experimental work involves precise X-ray diffraction measurements of lattice parameters at temperature in solid specimens. The alloys used are of high purity, prepared by levitation melting in an inert atmosphere.

A high-temperature specimen housing equipped with a new type of specimen ocillator has been built. The specimen holder is now driven by a thin stainless steel cable which passes through the copper terminal posts, around two miniature ball bearing pulleys to a central drive pulley. The oscillation of the drive pulley thus moves the specimen back and forth through the X-ray beam. The great advantage of the cable drive is that no torques are applied to the high temperature bearing on which the specimen is mounted. The unit has now functioned nearly continuously for about

three months. Completely reliable operation of this apparatus has been obtained, and the determination of lattice parameters is routine. A paper on the specimen oscillator is being prepared for publication.

Approximately 45 parameters have been measured at temperatures between 270°C and 400°C, and the alloys are now being chemically analyzed. Lattice parameter versus temperature curves have been constructed from the data. When the analyses are available these curves will be converted into lattice parameter versus composition isotherms. These isotherms will indicate the nature of the phase diagram in the region studied. The data obtained are being compiled and studied to determine whether a peritectic reaction does or does not occur in this system.

5. D4-17 - Fundamental Investigation of Zinc Powder Metallurgy,
Rensselaer Polytechnic Institute, Mr. C. J. Barton, Professor
F. V. Lenel

The broad objective of this fundamental research program is to develop, by means of powder metallurgy techniques, zinc base alloys having superior creep and strength properties than those of alloys produced by conventional fusion metallurgy. Theoretical investigations are directed toward obtaining a better understanding of the basic mechanisms which underlie metallurgical improvements in dispersion strengthened alloys.

Investigations performed during the period of this report included the following work:

1. The relationship between log creep rate vs log stress was accurately determined for Zn-1% Cu - 0.15% Ti. It was found that the slope of this line is much steeper than that indicated by short time tests.

2. Room temperature creep tests were made on Zn-Cu-Ti alloy powder specimens that were annealed at 212°F for 50 hours and 300°F for 24 hours. The results indicate that these annealing treatments do not materially decrease the high room temperature creep strength of the powder extrusions.

3. Construction of elevated temperature creep testing equipment has been completed and testing at 100°C has begun on three Zn-Cu-Ti specimens and stresses of 3000, 4000 and 5000 psi have been applied.

4. Investigation of the poor mechanical properties of Zn-0.14% Fe powder extrusions has been continued in an attempt to understand the behavior. Porosity was found even when compacts were hot pressed prior to extrusion.

In further investigations an attempt was made to correlate the differences in creep properties with the differences in microstructure and the following Zn-Cu-Ti specimens were evaluated:

1. extrusions from cast billets and powder compacts.
2. extrusions made at slow speeds and fast speeds.
3. wires as-extruded and after elevated temperature creep testing.

Relatively long time room temperature creep tests of the alloy containing 1% Cu and 0.15% Ti indicated that the creep rate of the powder extrusions is superior to the extrusions from cast billets even at the very high creep rate of 10^{-4} days/percent. The extrapolated figures are a stress of 10,000 psi for the cast material and 20,000 psi for the alloy powder.

Creep tests on a number of annealed specimens revealed that (1) heat treatments such as 50 hours at 212°F and 24 hours at 300°F in air do not appreciably deteriorate creep properties and (2) heat treatments in boiling water provide a corrosive atmosphere for the alloy powder extrusions.

Creep tests at 212°F on Zn - 1% Cu - 0.15% Ti alloy powder extrusions indicated that lower stresses are required to cause a given creep rate at 212°F than 77°F. In order to obtain a room temperature inverse creep rate of approximately 250 days/percent, a powder extrusion has to be stressed at 32,000 psi, while at 212°F a stress of only 5000 psi is required; however, the creep behavior of the powder extrusions at 212°F is still quite superior to that of strip from cast ingots even though the latter were tested at the lower temperature of 176°F.

Preliminary room temperature creep testing was conducted on two new powders: Zn-1% Cu-0.45% Ti and Zn-0.29% Cr- 0.17% Ti. Extrusions were made and tested at 16,000 psi; a period of transient creep was observed following which no further creep took place.

6. ZM-30 - Rolled Zinc in Architecture, Cooperative Program

Service tests and field investigations of zinc-copper-titanium alloy gutters and downspouts are being continued in order to establish representative data on the behavior of zinc alloys under various exposure conditions.

It has been decided to standardize the methods used for the physical testing of rolled zinc alloys, so that technical data obtained from different manufacturers are directly comparable. This is particularly important in the case of the zinc-copper-titanium alloy which has superior properties of creep resistance, coefficient of expansion, and tensile strength, and finds ready application in building and other markets.

Discussions are proceeding on the standardization of testing procedures and laboratory work will be initiated in areas where additional data are necessary.

7. ZM-31 - Effects of Steel Metallurgy and Bath Composition on Galvanized Coating Properties, Mines Branch, Canadian Department of Mines and Technical Surveys through the Galvanizing Subcommittee of the Canadian Zinc Research & Development Committee, Mr. R. Palmer, Mr. J. J. Sebisty, Dr. J. O. Edwards

The first phase of this program was associated primarily with a study of the effects of steel metallurgy on the structure and properties of galvanized coatings. The second phase of the program involves an investigation of the influence of zinc bath composition on the properties of galvanized coatings.

This phase of the project represents an extension of two earlier studies made at these laboratories on the influence of bath additions on the structure and properties of experimental galvanized coatings. Fifteen alloying elements not normally encountered in galvanizing practice are under investigation; these are being added individually in various concentrations to iron-saturated zinc baths, with and without 0.15% Al plus 0.3% Pb. Some variation from these standard aluminum and lead compositions has been included.

The first part of this report describes the galvanizing preparation and surface examination of coatings containing additions of chromium, manganese, zirconium, titanium and thorium. Further work with uranium and metallographic studies on various zinc-base master alloys prepared to date are also covered.

Of the various alloying additions in this series, only zirconium exhibited any significant effect on bath composition. This was reflected in a consistently rising iron content during the course of dipping from which it is concluded that 0.3% and higher concentrations of zirconium promoted steel attack, even with up to 0.15% Al present in the bath.

Oxidation of the galvanizing baths was excessive with all except chromium additions. In order to avoid coating deterioration from oxide drag-out in the "aluminum-free" series of tests, it was necessary to add 0.005% Al to the affected baths. In this series, the three concentrations of uranium and thorium, as well as the two lower concentrations of manganese and zirconium, all tended to produce fine-grain coatings that were generally smooth or slightly roughened to a fine-pebble texture. In contrast, the 1% Mn addition provided dull coatings marred by pimple defects, and in the case of 0.5% Zr, the surface was roughened to a coarse sandpaper-like texture. This latter effect appeared to be related to pick-up of reaction products or intermetallic compounds on withdrawal of the panels from the bath. Chromium was the only addition to provide an increase in spangle grain-size and was also associated with some loss in zinc fluidity at 0.2%. With respect to titanium, satisfactory coatings could not be produced at concentrations in excess of 0.01%.

In the high-aluminum series of tests, the influence of uranium and thorium on coating surface appearance was minor to negligible. With 10 sec immersion, both manganese and chromium at the higher levels resulted in some reduction in spangle size and variable degrees of spangle contrast and coating brightness. However, at 60 sec, the coatings altered significantly and were characterized by moderately large, well-defined, contrasting spangles. Neutralization of the inhibiting effect of aluminum and considerable development of iron-zinc alloy over the entire steel surface was indicated. The lower zirconium concentrations and the two intermediate titanium additions appeared to provide comparable effects. Increasing the content of either titanium or zirconium to still higher levels caused marked coating deterioration varying from gross wrinkling of the surface with titanium to severe roughness in the case of zirconium.

The following portion of this report describes the stripping tests and metallographic studies made on coatings previously prepared with thorium, zirconium, manganese, chromium, titanium and silicon. The extra series of

uranium- and magnesium- containing coatings are also covered, as well as surface appearance and other effects relating to the silicon- and magnesium-containing coatings. Steel weight loss, ductility and adherence tests for the entire series of coatings prepared to date have been completed and results of these are also described.

Thorium appeared to have no effect on coating formation. Uranium was similarly ineffective except at higher concentrations (0.2% to 0.4%) in aluminum-containing baths. These produced moderate increases in iron content and thickness of the coatings but these changes were not reflected in the microstructures.

Additions of 0.10% and 0.30% Zr in aluminum-free baths were instrumental in modifying growth of the iron-zinc phases, thereby reducing the outer zinc layer and total coating thickness by approximately 25%. On the other hand, 0.5% Zr contributed to pronounced intermetallic compound formation that resulted in thick non-uniform coatings. When 0.15% Al was present, its inhibiting effect was progressively reduced by increase in the zirconium content of the bath. Growth of the continuous-type of iron-zinc alloy formation was promoted and coating weight was significantly increased.

Manganese at 0.5% and 1% in aluminum-free baths tended to retard steel attack and iron-zinc alloy growth. As a result, thinner coatings were produced despite the presence of finely-distributed intermetallic compounds in the outer zinc layer which would be expected to increase its thickness and of the coating as a whole. In the high-aluminum baths, the above additions of manganese produced neutralization of aluminum similar to that found with zirconium. Correspondingly thick coatings were obtained.

Chromium in aluminum-free baths duplicated the reduction in steel attack and iron-zinc alloy growth in the same manner as manganese, nickel and vanadium. The maximum decrease in coating weight achieved was 40% with 0.2% Cr and 60 sec immersion. Its behavior in the aluminum-containing baths was also similar to that found with the above elements and heavy coatings resulted because of pronounced iron-zinc alloy formation.

Titanium up to 0.05% was also effective in reducing iron-zinc alloy growth and coating weight in the aluminum-free baths. At still higher levels, pronounced and unusual compound formations were observed. These contributed to very thick coatings and very unsatisfactory surface appearance as described in the last progress report. The same compounds were found in the high-aluminum coatings with titanium at 0.05% and above. Neutralization of the aluminum addition was again evident so that the thickness and iron content of the coatings was increased markedly.

The behavior of silicon was of interest because of its effectiveness in scavenging iron from the bath, with or without aluminum present. As a result, silicon retention was low, but even at 0.01% to 0.02% in aluminum-free baths it tended to reduce the thickness of the outer zinc layer significantly. A somewhat similar effect was found when aluminum was also present at and above 0.15%.

In the extra galvanizing tests made, it was confirmed that the influence of magnesium was principally restricted to alteration in the surface appearance of the coatings. In combination with 0.005% Al, 0.05% Mg produced a metallic, spangle-free silvery finish that gradually deteriorated to a dull, matte grey finish as magnesium was increased. Grain size was also significantly reduced. As far as coating weight and microstructure were concerned, the effect of low magnesium (0.05%) was negligible. However, at and above 0.2%, marked fissuring of the outer zinc layer was produced and eutectic formation in this layer could also be observed. The amount of eutectic appeared to be dependent on the aluminum concentration.

In general, the steel weight loss tests reflected the iron content determinations. However, discrepancies between the two sets of values, such as found in previous investigations, were evident. In the aluminum-free series of tests, the steel weight loss was invariably lower, but in the aluminum-containing series, this trend was reversed and the differences were much more pronounced. Work in the concluding stages of this project has been scheduled to investigate these anomalies further.

According to the performance standards set up, the entire aluminum-free series of coatings, as well as the high-aluminum coatings which contained appreciable iron-zinc alloy growth, were classified as having poor ductility and adherence. In contrast, the remaining high-aluminum coatings were all rated good to excellent in these tests.

Metallographic measurements and coating tests outstanding on all the experimental panels prepared so far is continuing. Galvanizing preparation of panels using the remaining three addition elements, lithium, phosphorus and mischmetal has also been scheduled.

8. DM-34 - An Investigation of Resistance Spot Welding of Galvanized Carbon Steel, The Budd Company, Mr. H. H. Freytag, Mr. J. J. McKinney, Mr. H. D. Van Sciver, II.

Systematic investigations of the various factors which affect the spot welding of galvanized steel are continuing in an effort to establish recommended welding practices which will consistently produce quality welds at economical production rates.

During the period of this report, the research was directed toward the investigation of the following features:

- 1) The significance of the weld zone resistance signal as it relates to weld quality.
- 2) The effect of a zinc coating on the formation and the subsequent deterioration of a spot weld.
- 3) The effects of natural aging on the weldability of galvanized steel.
- 4) The merits of a new dispersion hardened electrode material.

- 5) Whether or not electrode forces other than those recommended in the previous report would result in better performance during extended welding.

Extensive tests were performed to provide sufficient data for evaluation and a summary of the conclusions reached is presented below:

1) The average weld zone resistance recorded during the formation of a spot weld has been shown to be dependent to a large extent on the size of the resultant weld in extended welding runs. Based on this finding it may be possible to design a nondestructive weld quality evaluation system and then an automatic feed-back weld quality control system. However, one weak spot in this application is the insensitive response of the change in weld resistance to a change in weld quality.

2) The lack of a high interface contact resistance along with the highly thermally conductive electrode-to-work contact are responsible for the higher welding currents required for galvanized steel as compared to uncoated steel.

3) Weld quality deterioration in galvanized steel cannot be blamed primarily on an increase in electrode wear due to the presence of zinc. Testing has shown that the same amount of electrode wear does not result in the same effects on weld quality of galvanized and of uncoated steel. However, the presence of zinc does affect the general deterioration of the face of the electrode, causing pitting and crater formations. In this respect it may contribute to accelerated wear (increase in contact diameter) in subsequent welding runs if only the sides of the electrodes are dressed to restore the original contact face diameter.

4) It has been concluded that weld failure is caused by a change in the electrode face contact area. A change in this area for galvanized steel is more critical than for uncoated steel for the following reasons:

- a. A larger electrode contact area increases heat losses from the weld zone. However, this is not countered in galvanized steel as in uncoated carbon steel with an increase in heat generation at the electrode-to-work surface because force density changes have a greater effect on uncoated steel than on galvanized steel.
- b. A change in current density has a greater effect on the heat generated in the base metal (major factor in galvanized steel) than at the interface contact (major factor in uncoated steel).

5) Changes in the weldability of galvanized steel occur with storage time under normally dry conditions. No attempt was made to determine the degree of these changes as a function of time.

6) Test results indicate that, at the present time, internally oxidized copper-beryllium oxide electrodes (a new dispersion hardened material) does not offer any advantages over presently commercially available welding electrodes.

7) Changes in electrode force with corresponding changes in welding current do not have major effects on weld quality. Higher forces than

those recommended have resulted in less consistent welds in extended welding tests. The use of lower forces is not particularly objectionable in automotive production and may be employed where necessary.

9. ZN-40 - A Study of Alternate Zinc Cladding Processes,
Department of Metallurgy, The University of British Columbia,
Professor W. M. Armstrong.

The objective of this program was to evaluate the feasibility of producing adherent zinc coatings on steel sheet by direct powder rolling and to study the effects of operating variables on the process. Alternate methods of coating steel with zinc were investigated with a view to improve the application of heavier coatings, coating of only one side, zinc coatings providing increased cathodic protection, and zinc alloy coatings having higher inherent corrosion resistance.

This high-spot investigation is now concluded and much fundamental information has been developed. A final report on this project has been received and is abstracted below.

Zinc powders of various types, particle sizes and compositions were roll-coated on the surface of annealed low-carbon steel strip. The surface of the steel was treated by abrasion sand blasting, pickling and oxidation - reduction treatments prior to roll coating. Roll force was measured by force washers in the mill housings and was used to control the mill settings. Weight of coating was varied from 0.25 to 0.51 oz/sq.ft. (one side only).

Coatings were evaluated by bend testing, re-flattening and re-bending and by a nonstandard high speed tensile test.

Adherent coatings were produced by rolling -200 mesh powder on a steel surface which had been oxidized for 2 minutes at 1000-1100°F. and reduced in cracked ammonia for 10-15 minutes at 1700°F. All other methods of surface preparation produced patchy coatings which were poorly bonded to the steel base.

Adherence of coatings was improved still further by reheating roll-coated sheets for about 2 minutes at 600°F.

Adherent coatings of mixed lead and zinc powders were obtained which were much more resistant to corrosion than coatings containing lead powder alone. Mixtures containing from 25-75% zinc were used successfully although the high-zinc coatings required heat treatment at 600°F before strong bonding was obtained.

The steel used as base material for most of the test work in this investigation was cold rolled and annealed rimmed steel, 0.0179 inch thick.

Various types of zinc powders were used, and screen sizes ranged from +200 mesh to -325 mesh. -200 mesh zinc powder was used for most of the tests.

The following variables were investigated;

1. Surface Condition of Steel Sheet

All sheets were degreased in toluene prior to application of surface treatment and the following methods of surface treatment were used.

- A. Hand alundod with abrasive mesh cloth.
- B. As-received surface (degreased only).
- C. Heated in cracked ammonia atmosphere for 30 minutes at 1290-1300°F.
- D. Heavily blasted with coarse alumina powder.
- E. Very lightly blasted with alumina.
- F. Pickled in 10% H₂SO₄ at 150°F followed by dip in cold concentrated HCl followed by alkaline rinses and dried.
- G. Oxidized in air at various temperatures in electric muffle furnace and reduced in cracked ammonia at various temperatures and times.
- H. Oxidized in moist air (water added to furnace atmosphere) at various temperatures and reduced as in G.
- I. Pickled in 50% HCl at room temperature for 5 minutes, rinsed in water and dried with ethyl alcohol.

2. Powder Applications

In most cases powder was applied dry and without additives. Initially, powder was shaken through a cloth sheet until a layer of the desired thickness had been built up. More uniform results were obtained by shaking a Tyler screen containing zinc powder over the steel strip and this method was used for the majority of the tests.

In a few tests, zinc powder was cleaned with a solution of diethylenetriamine sulphate (DETA-SO₂) and the cleaned powder was applied to strip while still wet with the solution.

3. Characteristics of the zinc powder

- a) particle size and distribution.
- b) oxide content.

4. Roll Pressure and Roll Gap

Related very closely to thickness of applied powder layer.

5. Roll Speed

6. Heat treatment after roll-coating

The tests used for the evaluation of coatings were as follows:

Coating Weight was evaluated by thickness measurements and by chemical methods according to A.S.T.M. specifications A-93-50T and A.S.T.M. A90-33.

The Preco test (A.S.T.M. A239-41) was used to check coating uniformity.

Bend Tests were used for all test strips according to A.S.T.M. specifications A-93-50T. Many of the better coatings were subjected to flattening and re-bending through 180 degrees. Bend test specimens were cut from coated strips at different angles to the direction of rolling to check for directional effects.

Olsen Cup Tests were tried but were not sufficiently sensitive to show differences in adherence of coatings.

High Speed Tensile Test

Tensile tests on coated strips 1" x 5" were pulled to failure at a high rate of cross-head travel (20 inches/minute). The best coatings did not flake or peel in regions of severe deformation or "necking".

Although this test is not standard it was found to give the most sensitive indication of small differences in coating adherence.

Experimental procedures used for the coating of test strip with zinc powder and with lead-zinc mixtures showed that:

Adherent zinc coatings could not be produced by direct powder rolling on any of the surfaces described previously as type, A, B, C, D, E, F, H, J.

Adherent coatings were produced on surfaces prepared by a type of treatment but with a narrow range of oxidation and reduction temperatures. Best results were obtained when the steel surface was oxidized at 1000-1100° F for 2 minutes and then reduced in cracked ammonia for 10-15 minutes at 1600° F.

Coatings produced in this way gave good results in bend tests and bend-and-flatten tests but were generally less adherent than commercial galvanized coatings in the high-speed tensile tests.

Bonding was improved greatly by reheating and coated sheets for about 2 minutes at 600° F in air.

Hot re-rolling of the coated sheet also gave promising results but facilities did not permit an accurate evaluation of this method of treatment.

The best coatings were obtained with -200 mesh powder. Finer powders produced patterned coatings, but these may have been caused by vibration of the short lengths of strip used for these tests.

Rolling speed was not an important variable within the range available.

Coating weights from 0.25 to 0.89 oz. per square foot were produced by varying roll gap and roll pressure.

Adherent coatings of mixed lead and zinc powders were produced which were more resistant to corrosion than coatings containing lead powders alone. Mixtures containing from 25 to 75% zinc were used successfully.

although the high-zinc coatings required heat treatment at 600° after coating to improve the bonding.

Summarizing the results of this research program, the following conclusions have been reached:

The feasibility of obtaining adherent zinc coatings on one side of steel strip by direct powder rolling has been demonstrated by this investigation.

Thin uniform coatings were made with good reproducibility over the range of 0.25 - 0.89 oz. per square foot.

The good adherence and corrosion resistance of mixed-powder coatings suggests that further work in this field may be justified.

Further work is necessary to develop a method for the simultaneous coating of both sides of the strip by powder rolling.

The coating process developed by these investigations should be readily adaptable to existing types of process equipment.

It should be possible to produce similar coatings in cold strip mills of standard design.

Surface preparation could be carried out in a furnace line of the type used in the Sendzimir galvanizing process.

It seems probable also that if the zinc powder could be spread and rolled on the freshly reduced sheet surface while it was at a temperature of about 600° the heat treatment after coating would not be necessary.

10. 24-5 - An Investigation of Some Properties of Molten Zinc and Zinc Alloys, Mines Branch, Canadian Department of Mines and Technical Surveys through the Galvanizing Subcommittee of the Canadian Zinc Research & Development Committee, Mr. J. W. Meier, Dr. D. W. G. White, Dr. E. E. Thresh, Dr. J. O. Edwards

The purpose of this fundamental research program is the study of the effect of temperature and composition upon the viscosity, surface tension and density of molten zinc and some of its alloys.

The determination of liquid metal densities has been completed for pure zinc, fourteen binary zinc-aluminum and five binary zinc-lead alloy compositions. In both alloy systems, a linear relationship between density and temperature was found. In preparation for work on further zinc alloys, a new graphite pycnometer has been made.

Viscosity results are now available for all the binary zinc-aluminum alloy compositions examined up to 5% Al. All experimental data have been gathered for the other alloys up to 15% Al and await computer processing. The most recent viscosity results show a gratifyingly small scatter and a marked linearity, which supports their validity in that they do not confirm anomalies in the regions of the liquidus and solid solubility limit reported by other workers.

After a major refit of the surface tension apparatus, experimental work has resumed. Surface tension measurements have been obtained on various pure zincs, all of which are the order of 750 dynes/cm at 435°C. While these results are much below some previously obtained and those reported by Pelzel, it is now believed that, because of certain experimental difficulties, these previous determinations were in error. Confidence in the present results is encouraged by their consistency within individual determinations and as a group.

Steady progress has been made in all fields during the period, and experimental work is proceeding smoothly. The Mines Branch professional staff have spent some time in preparing papers on "Theory and Experiment for the Precision Measurement of Surface Tension and Viscosity" for presentation at the Liquid Metals session of the National Metal Congress, to be held at New York City in October, 1962. While this work is outside the limits of the sponsored program, it has entailed a thorough study of the broader aspects of the problem, which are of direct benefit to the program.

11. 2M-56 - Study of Flow in Die Casting Dies, Case Institute of Technology, Professor J. F. Wallace

This newly initiated research program is being conducted at the Case Institute of Technology under the cooperative sponsorship of the American Foundrymen's Society Training and Research Institute, the Expanded Research Program and the Die Casting Research Foundation.

The objective of the work and final purpose of the investigation is the establishment of basic principles governing flow of metal in the gating and die cavity of pressure die castings. It is believed that a better understanding of these principles will lead to:

1. Improved density of die castings with minimum porosity and gas entrapment.
2. Improved physical properties through improvement in density and metallurgical structure.
3. Improved surface characteristics for subsequent finishing and/or machining operations.
4. Reduction in rejection rate of defective die castings.
5. Better guides for die design to minimize the time between initiation of die design and the production of satisfactory die castings.
6. Minimization of die wear and erosion.

It has long been recognized that the characteristics of metal flow and gate design in die casting have pronounced effects on the properties and performance of the resulting die castings. These effects become evident in the density of the die casting, the amount of entrapped gas, its metallurgical structure, surface finish and final strength. Likewise, the mechanics of the die casting operation are affected, such as tooling wear, erosion, and scrap losses. Much work has been done in the past to resolve the phenomena involved in pressure die casting, however, a careful review of the literature leaves much of the problem unresolved.

A Joint Research Committee, composed of representatives of the three sponsoring organizations, carried out preliminary work to determine new methods of studying the flow of metal in die casting dies. From this came the recommendation that a simulated die casting injection system be employed using (1) transparent dies, transparent replaceable gate and runner sections for studying variations (2) water with or without colored dye injection, (3) high-speed movies, (black and white and color) supplemented with time-delayed still photographs to record the flow patterns and plunger positions simultaneously, and (4) correlation checks with actual die castings made employing the identical sections, gates and runners used in the simulated tests.

The systems designed and work performed in this investigation will be broken down into two major areas. Experiments will be conducted with simulated water studies and zinc alloy die casting in each area. These two areas are described below.

I. Injection Chamber and Gate Runner Design

- a) Determine the influence of volume of air to metal ratio in the injection cylinder on air entrapment in runner and die casting.
- b) Establish optimum runner cross section design for minimum turbulence and air entrapment.
- c) Determine influence of runner geometry, including the effects of sharp bends in runners and the effectiveness of different methods for fanning the runners down to join the gate opening.
- d) Compare single runners, manifold runners and multiple separate runners.

II. Gate Orifice Design and Location

- a) Study the effect of gate orifice design, both with respect to length and thickness, and nozzle design to produce different stream patterns.
- b) Determine the "reach" and directional characteristics of the metal stream leaving the gate orifice as influenced by gate and runner.
- c) Compare single gate opening vs. multiple gates.
- d) Determine influence of coring on metal flow in cavity.
- e) Determine influence of injection pressure and velocity on pattern of flow in the runner and through the gate orifices.
- f) Determine the optimum ratio of runner size to gate orifice area.
- g) Study effect of die surface on metal flow.
- h) Study effect of overflows on metal flow in die cavity.

The results of the water analogue studies will be evaluated by visual and photographic means. The die castings will be inspected for their surface appearance and plating classification and by radiographic and metallographic examination.

12. ZM-57 - An Investigation of the Properties of Galvanized Steel at Elevated Temperatures, Mines Branch, Canadian Department of Mines & Technical Surveys through the Galvanizing Subcommittee of the Canadian Zinc Research & Development Committee, Mr. D. Watt, Mr. J. J. Sebisty, Dr. J. O. Edwards

This investigation involves study of the behavior of hot-dip and electroplated zinc coatings during long-term heating in air at various temperatures up to 400°C (750°F). The effect of continuous exposure as well as alternate heating and cooling on structural modification and/or deterioration of the coatings and on mechanical properties of the base steel is being studied.

This report period was devoted largely to exposure tests on Cook-Mortman and Sendzimir galvanized sheet. Evaluation of the elevated temperature effects on samples treated to date was continued. Short-term exposures were made using some experimental coatings galvanized in previous phases of this project and additional tests on laboratory-prepared and commercial electroplated coatings were also attempted.

Thermal cycling tests on the galvanized materials have been confined to temperatures at and below 300°C (570°F). After relatively short periods of exposure, favorably oriented grains in the outer zinc layer were deformed to produce a wrinkled surface. A secondary stage involved development of parallel cleavage cracks, generally restricted to the deformed grains. This was accompanied by well-defined cracking along the grain boundaries.

Other observations and available test data applicable to both continuously exposed and thermally cycled samples may be summarized as follows:

At 200°C (390°F), both the Cook-Mortman and Sendzimir sheet showed little evidence of deterioration even after twenty weeks. Projecting pimples, indicative of local iron-zinc alloy growth, were very small and scattered.

At 250°C (480°F), scattered pimples visible to the naked eye were observed on both grades of sheet after two weeks. The number and size of the growths steadily increased with time but were relatively small and widely spaced even after twenty weeks. Mechanical properties of the steel base exhibited no change for up to ten weeks exposure.

At 300°C (570°F), an exposure of one day produced pimples over the entire surface of panels of Cook-Mortman material and within three days a frosted appearance developed. General pimpling on Sendzimir panels was less pronounced and the characteristic matte finish was not developed.

At the still higher temperature of 355°C (635°F), the deterioration of the Cook-Mortman coating described above was duplicated but at an accelerated rate. General pimpling over the whole panel surface and development of the matte finish was more or less complete after one and

a half weeks and there was little further change up to twelve weeks. The outer zinc layer remaining could be readily peeled away after two weeks exposure.

Exposure of the Bendisair sheet at 335°C (635°F), also exaggerated the effects seen at the lower temperature of 300°C (570°F).

Exploratory heating tests on 1-mil commercial electroplated coating resulted in gross blistering and the same effect occurred with high-purity, laboratory-prepared coatings of various thicknesses. However, additional samples of the latter prepared by a novel technique behaved satisfactorily and without evidence of blistering on exposure to the same heat treatments.

Preliminary evaluation of the results of tensile tests on the steel base after stripping of the heat-treated Cook-Mortenson and Bendisair type coatings has revealed the following:

Cook-Mortenson sheet exposed at 200°C (390°F) and 250°C (480°F) showed a tendency to lowering of the tensile strength after about fourteen weeks, but this effect was minor. At 300°C (570°F) both tensile and yield strengths declined steadily with time of exposure, although elongation appeared to be unaffected. This behavior was more exaggerated at 335°C (635°F) and an unusual effect observed in this case was an abrupt and appreciable reduction in tensile strength and elongation after four weeks exposure. To what extent this is a real effect is not known.

The Bendisair sheet gave much better resistance to exposure and no significant changes in the tensile properties of the steel base were evident at or below 300°C (570°F). At the higher temperature of 335°C (635°F), a progressive reduction in tensile and yield strengths was noted, but this was much less pronounced than with the Cook-Mortenson grade.

Stripping tests on the above materials heated at or below 335°C (635°F) revealed well-defined trends in the case of the iron content determinations only. The Bendisair material again behaved differently in that only at 335°C (635°F) was any significant increase apparent.

Inspection of panels of both grades of sheet exposed at 365°C (690°F) and 400°C (750°F) revealed rapid deterioration of the coatings at a very early stage. Cook-Mortenson samples developed numerous small pimples over the entire surface within two hours at 365°C (690°F) and the surface was transformed to a dull gray finish within sixteen hours. Little or no further change in appearance was observed even after four weeks. The outer zinc layer could be peeled away after three days. Bendisair sheet exposed at this same temperature retained the characteristic feature of nucleating pimple growths at relatively widely scattered sites. Peeling of the outer zinc layer was possible after two weeks. At the higher temperature of 400°C (750°F), the various effects described above for each material were reproduced at a somewhat more exaggerated rate.

X-ray fluorescence and diffraction techniques, as well as microhardness measurements, have been applied in attempts to identify the iron-zinc alloy phase or phases present in the pimple growths occurring in the Bendisair coating. The results have been inconclusive and further tests are being made.

13. 24-64 - Joining of Zinc Base Products, American Smelting & Refining Company, Mr. L. T. Jordan, Mr. E. E. Howe

This program is directed toward the compilation of data on the bonding characteristics of various classes of adhesives as joining media for zinc. Methods of joining and organic adhesives are evaluated as to their physical adequacy, their ease of application and their economic feasibility.

The final objective of the project is to publish a manual on "Adhesive bonding of zinc to itself and other materials". This manual will be a compilation of two types of data: (1) those available from the manufacturers of the adhesives on the physical, chemical and mechanical properties of the adhesives themselves and (2) those which will describe these same properties of the adhesives as they serve to join or bond zinc.

During the first phase of the program, work was performed in the following areas:

1. Surveying the literature on available adhesives and their characteristics.
2. Contacting the manufacturers of adhesives to obtain recommended materials for use with zinc.
3. Reviewing the range of stress and temperature to which bonds between zinc and other materials may be expected to be subjected.
4. Selecting specific adhesives for testing.
5. Obtaining the desired adhesives from the manufacturers.
6. Reviewing the types of tests commonly used to evaluate the strengths of bonded materials.
7. Determining the effect of testing parameters on the results.

The literature survey has shown us that there are many adhesive formulations available which perform satisfactorily under various service conditions and that a user of zinc can by consultation with the adhesive manufacturers obtain recommendations for a particular set of conditions. But these recommendations in the large majority of cases would not be based on tests or experience with zinc adherends and special tests are needed to establish a body of data on the bond strength of adhesives with zinc.

In an effort to determine desired criteria for the selection of adhesives, first preference was given to good resistance to exposure conditions, viz., water, heat, light, etc. A rating of good to excellent in resistance to water, heat and light were required of adhesive classes to be initially tested. Other criteria used were bond strength and ease of application and curing as well as the extent of present popular commercial use.

A survey of the properties of these adhesives showed that those classified as thermosetting have the highest probability of fulfilling most of the above criteria, and are thus most suitable for the more demanding applications involving zinc. Therefore, the first testing was done with the epoxy-based adhesives, since they represent a class of adhesives having high strength and temperature stability combined with ease of application. It is interesting to note that the epoxies were recommended by several adhesive manufacturers in answer to inquiries as to which group they would suggest for zinc.

Since one important objective is to present data which can be used for design purposes on bond properties of some of the commercially available adhesive classes with zinc as adherends, it is necessary that the mechanical testing data cover types of simple stresses to which the bonds may be subjected. The four basic types of stress encountered in bonding are tensile, shear, cleavage, and peel. The ASTM describes testing procedures for measuring these stresses, and in some cases offers several test designs for a specific property. The lap joint, although not representing any single type of stress, but rather the interaction of several of these stresses, is often selected as the best method of surveying the properties of a group of adhesives for the following reasons: (1) most of the theoretical effort has been devoted to lap joints, (2) most of the data reported in the literature are based on lap joints, (3) lap joints are the most common means of structural joining, and (4) lap joints are easily prepared in the laboratory. Many structural adhesives are rated in manufacturers' literature by their shear strength using an overlap joint and, therefore, the lap joint design will be used extensively in this program.

During the second phase of the program, a large number of lap shear joints were made and tested. Studies were conducted on the effects of temperature, duration of load, and contact with water on the bond strength of the adhesives with zinc adherend.

Good checks have been obtained with the manufacturers' reported values for their adhesives, but it is felt that further investigations are required before definite conclusions can be reached.

3. CHEMICAL PROGRAM

1. ZC-42 - Fundamental Investigation of Zinc Chemicals, Quartermaster Research & Engineering Command, Dr. J. O. Moltes, Dr. M. C. Henry

This fundamental research program is concerned with the chemistry of organozinc compounds and the synthesis of new zinc organic chemicals.

The preparation of a variety of zinc-containing compounds and polymers was continued and much attention was devoted to the synthesis of zinc containing polymers. Reactions studied involved poly-coordination of zinc ion with appropriate bis-bidentate ligands and inorganic condensations involving zinc bromide and IVth group organometallic compounds containing SiO_2 and GeO_2 groups. A series of bipyridyl and O-phenanthrolyl complexes of inorganic zinc salt has now been obtained analytically pure. A study of substitution reactions of zinc bis-acetylacetonate was started.

The ability of the zinc ion to complex or coordinate with many different types of organic molecules makes it possible to synthesize a variety of interesting compounds with as yet undetermined properties.

Compounds have been and will be submitted on a continuous basis to evaluation and testing groups for application possibilities. These are as follows:

U. S. Department of Agriculture
Pesticides Branch
Bethesda, Maryland

U. S. Fish & Wildlife Laboratories
Denver, Colorado

National Institutes of Health
Drug Development Branch
Cancer Chemotherapy National
Service Center
Bethesda, Maryland

During the period of this report emphasis was also directed towards the synthesis of molecules containing zinc-sulfur bonds. Attention was given to chelation and polymerization reactions of some of these new compounds and several attempts were made to synthesize halogenated zinc acetylacetonates. Direct bromination of zinc acetylacetonate as well as an alternate procedure, reaction of zinc carbonate with haloacetylacetone, gave inconclusive results.

The coordination polymers obtained from bis-potassium manganate and zinc acetate were found to have low thermal stability. Decomposition products include carbon disulfide and carbonyl sulfide.

A number of zinc salts of thiocacids have been synthesized and their ability to coordinate with nitrogen bases were studied. A series of interesting chelate compounds as well as some new coordination polymers have been obtained.

In future work investigations will be directed to the zinc-thioacid coordination compounds and polymers. Chelate formation of diphenylzinc, diethylzinc and ethylzinc chloride will be studied.

2. ZC-69 - Zinc in Agriculture, C. E. Kline & Company, Mr. E. Wolf, Mr. Chas. E. Kline

An extensive literature survey has been completed on the problem of zinc deficiency in the soil of various countries throughout the world.

The survey includes a review of the factors which cause zinc deficiency, the areas of known zinc deficiency, and a summary of the test methods and corrective treatments successfully used by others to diagnose and treat zinc deficiency in crops.

The information obtained has been compiled into a preliminary draft copy of a brochure on zinc in agriculture. The report is now in the hands of the American Zinc Institute, which will utilize the information as a basis for the preparation of a descriptive and illustrated brochure for general distribution.

3. Zinc in Ceramic Materials - Fellowship Program

a. ZC-41 - Phase Relationships & Physical Property Measurements of Zinc Oxide Systems, The Pennsylvania State University, Mr. J. J. Brown, Professor F. A. Rummel

Work is continuing on fundamental studies of ternary systems which include zinc oxide and other metallic and submetallic oxides. Phase equilibrium relationships of the binary ties in this system are being worked out and efforts are being made to examine the luminescence potential of the phases present.

During the period of this report the phase equilibrium relations in the $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$ system were determined in order to establish the existence of any solid solution regions which might serve as host lattices for phosphor preparations. It was shown previously that Cd^{2+} and Zn^{2+} would isomorphously replace each other in $\text{Zn}_2(\text{PO}_4)_2$ and $\text{Cd}_2(\text{PO}_4)_2$ and that the resulting solid solutions were suitable host lattices for manganese-activated phosphors. It is therefore reasonable to believe that solid solution also exists in the $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$ system and that phosphors could be prepared.

THE SYSTEM $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$

In the phase equilibrium diagram for the system $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$, Ratnack and Rummel have shown that $\text{Zn}_2\text{P}_2\text{O}_7$ has a rapid reversible inversion at 137°C . In the present investigation it was found that the high temperature β form could be stabilized by the addition of more than 6 mole percent $\text{Cd}_2\text{P}_2\text{O}_7$.

It was established that β - $\text{Zn}_2\text{P}_2\text{O}_7$ is soluble in $\text{Cd}_2\text{P}_2\text{O}_7$ to about 30 mole percent $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{Cd}_2\text{P}_2\text{O}_7$ is soluble in β - $\text{Zn}_2\text{P}_2\text{O}_7$ to about 25 mole percent $\text{Cd}_2\text{P}_2\text{O}_7$. The X-ray diffraction patterns for β - $\text{Zn}_2\text{P}_2\text{O}_7$, β - $\text{Zn}_2\text{P}_2\text{O}_7$, and $\text{Cd}_2\text{P}_2\text{O}_7$ are quite similar. Therefore, it is reasonable to assume that the structures of the three materials are closely related. The eutectic temperature and composition are 947°C and 29 mole percent $\text{Cd}_2\text{P}_2\text{O}_7$ respectively.

The entire $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$ system is glass forming. The refractive indices vary almost linearly from $\text{Zn}_2\text{P}_2\text{O}_7$ (1.615) to $\text{Cd}_2\text{P}_2\text{O}_7$ (1.692). As the content of $\text{Cd}_2\text{P}_2\text{O}_7$ increases, it becomes increasingly difficult to form glasses.

Another phase of this investigation was to examine the phase equilibrium relationships in the binary systems ZnO - CaO , ZnO - SrO , and ZnO - BaO and subsequently measure the thermal expansion of the compounds.

Compositions were prepared by reacting appropriate proportions of ZnO , CaCO_3 , SrCO_3 , and/or BaCO_3 at 1000°C in air. Identification of the phases in these preparations by standard X-ray diffraction procedures showed that SrZnO_2 and BaZnO_2 were the only compounds present in the systems ZnO - SrO and ZnO - BaO respectively. No compounds were found in the ZnO - CaO system. It was impossible to obtain bar specimens of SrZnO_2 and BaZnO_2 suitable for thermal expansion measurements because both compounds hydrated rapidly when exposed to air.

The phase relationships in the ZnO - CaO system are of the simple eutectic type. The solidus temperature was determined to be about 1550°C ; however, substantial vaporization made it possible to determine the liquidus boundary.

The probable phase relationships in the ZnO-SrO system were constructed from differential thermal analysis (D.T.A.) data. SrZnO, apparently melts incongruently at 1275 $\pm$ 10 $^{\circ}$ C. The eutectic temperature and composition are 1240 $\pm$ 10 $^{\circ}$ C and 35 to 40 mole % ZnO respectively.

The ZnO-BaO phase relationships are very similar to those in the ZnO-SrO system. BaZnO₂ melts incongruently at 1230 $\pm$ 10 $^{\circ}$ C and the eutectic temperature and composition are respectively 1175 $\pm$ 10 $^{\circ}$ C and 30 to 40 mole % ZnO.

In both the ZnO-SrO and ZnO-BaO systems, compositions containing less than 40 mole % ZnO rapidly hydrated after reaction when exposed to air.

This fellowship program has been extended through the 1962-1963 academic year.

b. 2C-45 - Fundamental Study of Zinc Compounds in Glasses, Rutgers, The State University, Fellow G. A. Chase, Professor C. J. Phillips

Work was continued on the development of new glasses containing zinc compounds in their compositions. It is anticipated that these glasses will find wider application in markets for products in the electronic field; for chemical ware, and for the manufacture of fibrous glass; as frits, to develop low-loss glass phases in ceramic dielectric bodies; as constituents in ceramic dielectric bodies; as constituents in ceramic dielectric and other bodies after devitrification.

The procedure outlined in previous reports has been continued. All systems include one or more group VI oxides (O, S, Se, Te) to which ZnO or other zinc compounds have been added. Other oxides of fundamental interest are gradually being added.

The systems which have been screened for glass formation and the work done to date can be summarized as follows:

System	Data Previously reported	Additional work reported here	New work first reported here
1. TeO ₂ + SeO ₂	X		
2. TeO ₂ + ZnO	X	X	
3. TeO ₂ + SeO ₂ + ZnO	X	X	
4. TeO ₂ + SeO ₂	X		
5. TeO ₂ + SeO ₂ + ZnO	X		
6. TeO ₂ + As ₂ O ₃	X		
7. TeO ₂ + As ₂ O ₃ + ZnO	X	X	
8. TeO ₂ + Sb ₂ O ₃	X		
9. TeO ₂ + Sb ₂ O ₃ + ZnO	X		
10. Sb ₂ O ₃ + As ₂ O ₃ + ZnO	X		
11. TeO ₂ + PbO + ZnO	X	X	
12. TeO ₂ + SeO ₂ + Bi ₂ O ₃	X	X	
13. TeO ₂ + SeO ₂ + ZnSeO ₃	X		
14. TeO ₂ + PbO + ZnCl ₂	X		X
15. TeO ₂ + ZrO ₂ + ZnO			X
16. TeO ₂ + V ₂ O ₅ + ZnO			X

- | | |
|---|---|
| 17. $\text{TeO}_2 + \text{B}_2\text{O}_3 + \text{ZnO}$ | X |
| 18. $\text{B}_2\text{O}_3 + \text{H}_2\text{O}_3 + \text{ZnO}$ | X |
| 19. $\text{TeO}_2 + \text{P}_2\text{O}_5 + \text{ZnO}$ | X |
| 20. $\text{B}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{ZnO}$ | X |
| 21. $\text{B}_2\text{O}_3 + \text{As}_2\text{O}_3 + \text{ZnO}$ | X |

Further work done in the system $\text{TeO}_2\text{-ZnCl}_2\text{-PbO}$ showed that as the amount of ZnCl_2 is increased the melting temperature decreases very greatly. However, when ZnCl_2 exceeds 40% (by wt.) large crystalline centers of devitrification occur marking the limit of solubility of ZnCl_2 in the glass. On the basis of the low melting tendency of these glasses, the coefficient of thermal expansion will be measured on several compositions to determine their possible value as solid-state device encapsulation glasses.

Additional melts produced a number of glass formations which seemed to have interesting electrical properties.

This fellowship has been extended through the 1962-1963 academic year.

c. 2C-47 - Physical & Chemical Properties of ZnO Glasses for Vitreous Enamelling, Department of Glass Technology, University of Sheffield, (England), Mr. Anthony E. T. Lam, Professor R. W. Douglas

Investigations were continued on the phase relationship of the $\text{Li}_2\text{O-ZnO-SiO}_2\text{-TiO}_2$ system over a wide range of composition.

Specimens in the form of a cone and weighing 0.2 g were used to study the limits of glass formation. The specimens were held at a temperature slightly higher than the liquidus temperature until a clear melt was obtained. The specimens were then withdrawn from the furnace rapidly and quenched in air. A petrological microscope was used to examine for crystals.

The glass forming region limits were established and cristobolite, lithium metasilicate, lithium silicate, zinc ortho silicate and an unknown crystal were identified as primary phase crystals. From the results obtained in the present investigation and the information from previous work on the $\text{Li}_2\text{O-SiO}_2$ system and ZnO-SiO_2 system, it is likely that these five crystals and the high temperature form of silica, cristobolite, are the only primary phase crystals in this system with more than 50% SiO_2 .

Some difficulties were encountered in the identification of the unknown crystal A, but the composition of the unknown crystal A is now tentatively found to be $\text{Li}_2\text{O.ZnO.SiO}_2$. More data on the liquidus temperature have been collected at composition near the expected boundary lines between the adjacent primary phase crystals fields. The compositions of the eutectic point and the peritectic points have not yet been found.

In future work, compositions near to $\text{Li}_2\text{O.ZnO.SiO}_2$ will be investigated to determine whether the crystal A forms any solid solution with SiO_2 , ZnO , Li_2O , or compounds of them. Also the shifting of the peaks, if any, will be investigated to assist the interpretation of results. However, the compositions are expected to have very high liquidus temperatures and sintering technique with repeated grinding and remaking may have to be used.

Phase equilibria relationship of the composition near the eutectic point and the peritectic points will be investigated so that the phase diagram may be established.

A hot stage microscope will be constructed to study the mechanism of crystallization.

This fellowship program has been extended through the 1962-1963 academic year.

d. EC-58. - Investigation of the Behavior of Zinc Compounds Under High Pressures, The Pennsylvania State University, Fellow C.E. Bates, Professor R. Roy

High temperature-high pressure investigations of the polymorphs of ZnO are continuing in an effort to obtain a better understanding of the reasons for the great variety of physical properties of ZnO and to develop new uses for ZnO.

The predicted high pressure polymorph of ZnO with the NaCl structure has been synthesized, crystal growth studies on ZnO have been started, and work is progressing on the complex zinc hydroxide problem.

Uniaxial high pressure anvils of a new style were then tried which enabled runs to be made up to 120,000 bars. With the use of saturated NH_4Cl solution as a mineralizer, it was found that ZnO does indeed have a high pressure polymorph which forms in the 105 kbar pressure range from 120 to 300°C. NH_4Cl is the only mineralizer so far tried which will facilitate the conversion. Na_2CO_3 , even at 113 kbar and 325°C, gave no conversion.

Work was also begun on the growth of ZnO crystals under hydrothermal conditions, though in the P-T region so far studied (up to 16,000 p.s.i. and 567°C) increase in crystal size of the ZnO occurs only in the presence of impurities.

Studies on $\text{Zn}(\text{OH})_2$ showed that in view of the apparent complexity of the $\text{Zn}(\text{OH})_2$ polymorphs, the true phase relations can only be determined by eliminating any possibility of complex formation with the reagents used to prepare the zinc hydroxide. Even controlled crystallization of $\text{Zn}(\text{OH})_2$ from an ammoniacal solution in a closed system has given only limited amounts of crystals and further work is still required.

High pressure studies on willemite are continuing. So far it has not been possible to convert willemite into a high pressure polymorph even with H_2O or NH_4Cl as mineralizers.

Two indirect methods are being tried. The first utilizes the mineral benmorphyte $\text{Zn}_2(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$, which dehydrates under high pressure and temperature to a $\text{Zn}_2\text{Si}_2\text{O}_7$ composition. X-ray examination of the initial runs has shown only willemite and benmorphyte in the end products. However, a run at 275°C and 105 kbars produced a sample whose X-ray pattern was completely devoid of detectable reflections. Hence, it would appear that this is the threshold level for the postulated structural transition.

The second method utilizes gels so that the existing structure of willemite need not be first broken down before rearrangement to the Olivine structure can take place. Using the method described by Roy (1956), gels of composition $2\text{ZnO}:\text{SiO}_2$ are now being prepared.

An attempt was also made to obtain a high pressure form of ZnS . Phosphorescent grade ZnS was used. Its X-ray diffraction pattern showed it to be a mixture of 90% sphalerite, 10% wurtzite.

The only effect of pressure on this ZnS was to remove all trace of the wurtzite from the X-ray patterns of the high pressure runs. No change in the X-ray pattern of the sphalerite could be detected even up to 113 kbars and 198°C. H_2O saturated NH_4Cl and saturated Na_2S solution were added as mineralizers but no conversion to a NaCl structure could be detected.

Crystal growth studies on ZnO showed that it was possible to prepare crystals of ZnO up to 5 millimeters long and 1 millimeter in diameter by hydrothermal techniques at 16,000 psi and 570°C. Saturated NaOH solution has been used as a catalyst. Both blue and green tinted crystals have been prepared but their true compositions have not yet been determined. It may be that leakage of NaOH from the gold containing tube produced, Co, Fe, Mo or Ni ions by reaction with the stellite bomb.

This fellowship program has been extended through the 1962-1963 academic year.

e. 2C-63 - Zinc Ferrites, The Pennsylvania State University,
Mr. S. Young, Professor V. R. Ruessem

Manganese silicate ferrites are investigated in this fellowship program and a study is made of the factors which affect the magnetic properties of silicate ferrites.

During the period of this report standards of known composition were diluted in borax glass (sodium borate) to a ratio of 100 parts of glass to 1 part of sample, melted together in a platinum crucible, then poured onto a hot plate to form small glass discs. The composition of these samples before their dilution in the borax glass are shown below.

COMPOSITION OF STANDARD SAMPLES

Sample	Mole Percent		
	Fe_2O_3	MnO_2	ZnO
I	80%	10%	10%
II	60%	20%	20%
III	40%	30%	30%
IV	20%	40%	40%
V	0%	50%	50%

The glass discs made from these samples were subjected to X-ray fluorescence analysis. Graphs were drawn up plotting the X-ray emission of the cations versus the mole percentage composition of oxide present in the original sample.

Due probably to inhomogeneous mixing in the glass, the borax glass disc method of X-ray fluorescence standardization was not completely satisfactory and a new method of standardization is being investigated.

In addition, fired samples are being prepared in the composition range of Mn-Zn-ferrites of greatest technical interest. The problem of zinc loss will be studied on these compositions.

f. ZC-71 Zinc Oxide in Structural Clay Bodies, Ohio State University, Fellow Donald Branson, Dr. William B. Shock

This fellowship program has been recently initiated at the Ohio State University for the 1962-1963 academic year. The study is being conducted by Fellow Donald Branson, who is a graduate student in Ceramic Engineering, and work on the project has already begun.

The proposed research will involve investigations to determine the influence of ZnO on the mechanical and physical properties of structural clays and to explore the mechanisms responsible. Samples will be prepared and tested as to flexure, porosity, saturation coefficient, modulus of elasticity and thermal expansion, and microscope and X-ray techniques will be employed to study the firing behavior and other parameters.

Basic studies will be predicated on the use of pure zinc oxide, so that its effects per se on the properties of structural clay bodies can be properly delineated. Following this, the use of roasted ore will also be investigated to study the effects of impurities on the structural clay and to establish limits on impurities. If the feasibility of using roasted ore in structural clays can be proven, it would constitute a great economic advantage to the use of zinc oxide in structural clay bodies.

g. ZC-72 Zinc Oxide in Sewer Pipe Glazes, Clemson Agricultural College, Fellow E. M. Boet III, Professor G. O. Robinson

This fellowship program has recently been established at Clemson Agricultural College and work on the project has begun with the 1962-1963 academic year. The fellow assigned to this research is Mr. Edwin M. Boet III who finished Clemson College with an excellent scholastic record and is now continuing his post-graduate work.

Two possibilities for the incorporation of zinc in glazes for sewer pipe have been proposed for investigation. One approach would be to study whether addition of zinc oxide to lead-fluxed glazes (developed on a previous LIA fellowship) could increase the durability and resistance to corrosion of the glaze and could modify the thermal expansion to give better fit of the glaze to the body. This approach would also investigate the effect of small additions of zinc oxide on reducing the viscosity of sewer pipe glazes to provide better coverage of the glaze and a lower maturing temperature.

The second possibility would be to investigate the use of zinc borosilicate as the primary flux in a glaze prepared from natural sewer pipe raw materials and the prepared zinc borosilicate. This approach offers a good chance of developing new information by providing a method of introducing B_2O_3 into the glaze (borax cannot be used in an unfritted glaze directly).

An effort will be made to pursue both lines of endeavor simultaneously in this fellowship project.

C. ELECTROCHEMICAL PROGRAMS

1. EX-11A - Wet Storage Staining of Galvanized Sheet, Armour Research Foundation

The broad objective of this research program is the discovery of organic coatings which may be applied to a galvanized metal surface by spraying, brushing, dipping, or other appropriate means, to produce a water-repellent, self-healing, corrosion-preventive coating. It is anticipated that such a material will be based on oils, waxes, and wetting agents, and will have greater affinity for the zinc surface than does water, thus preventing corrosion through the exclusion of moisture.

Galvanized steel products suffer a type of corrosion known as "wet storage stain" during shipping and storage. Many protective treatments have been developed, most of which utilize some form of chromate as an inhibitor.

In evaluating the requirements for an effective wet storage stain protective treatment, the following features were given considerations:

1. Low Cost - Allowable cost will depend on the product, but should be in the order of cents per ton for strip.
2. Degree of Protection - An ideal treatment will last indefinitely and will not be easily destroyed during handling.
3. Ease of Application - As pointed out above, a protective treatment should not require excessive time for application, nor should it require a great deal of space in a processing line. Dipping or spraying is preferred.
4. No Color - The appearance of the galvanized product should be essentially unchanged; if some change occurs, it should be pleasing.
5. Easily Removed - If removal is required for painting or other manufacturing processes, the treatment should be readily stripped by conventional cleaning or degreasing methods.
6. Soldering - The treatment must not impair solderability (and should preferably not need to be removed before soldering).
7. Welding - The welding properties of galvanized steel should not be made worse by the treatment.
8. Painting - Again, an ideal protective treatment would not interfere with painting, but should certainly not have an adverse effect if removed prior to painting.
9. Slipping Properties - The treatment should not cause stacked sheets to slide on each other, since this would be quite dangerous during handling of heavy loads. On the other hand, where material is supplied in coils, this requirement is probably of no importance. In fact, a degree of lubricity might be highly desirable in certain operations, such as deep drawing of auto body sections.

The basic requirement of any method for preventing wet storage stain is that the conversion of zinc to voluminous corrosion products be halted. This is accomplished in the case of inhibitor-type treatments by the formation of an isolating film at the zinc surface. It could also be accomplished by storing the material in a moisture-free enclosure or by applying a heavy coating of a protective organic material, such as paint.

There is another principle, however, which can be used to produce effective isolation of a zinc surface from an aqueous environment. When certain organic compounds are brought into contact with zinc, they tend to wet the surface preferentially, in some cases actually displacing water or aqueous media which are already present. This principle is the basis for the "powderless etching" of zinc printing plates. Certain blends of oils, solvents, and wetting agents creep over the surface of the plate, displacing nitric acid from the zinc and thereby controlling the etching rate.

It is precisely this principle which was suggested as the basis for a wet storage stain treatment. In view of the very effective way in which attack of zinc by nitric acid can be controlled, it was postulated that it should be even easier to find a composition which would displace pure water from a zinc surface.

Furthermore, a water-displacing film would not need to be heavy, since its protective action is by "preferential wetting" as opposed to "covering power".

Even more attractive is the fact that simple oils and waxes are among the least costly organic materials available.

Laboratory indications are that two low cost, wax-like compounds with excellent wet storage stain inhibiting characteristics have been discovered, however, field tests are continuing to determine their adequacy under service conditions.

Summarizing the findings of this program the following results were observed:

A. The concept of a "water-excluding" and "creeping" film has been shown to be sound. Furthermore, coatings have been discovered which have either, neither, or both of these properties.

B. The water-repellent action appears to be derived from certain chemical additives which promote the ability of an oil phase to wet the zinc surface. In this sense, they are "wetting agents"; this term must not be confused, however, with the usual meaning associated with "detergents", where the wetting action of the water is enhanced--causing displacement of the oil phase.

C. The creeping action of an organic film is related closely to its viscosity as well as to the presence of wetting agents. A very protective coating, for example, may show no creeping action whatever if it is composed largely of highly viscous waxes and oils.

D. Excellent protection against wet storage stain may be obtained from a number of low-cost, easily sprayed coating compositions.

E. The material costs for the coatings developed in this program are low. It is estimated that galvanized steel sheet can be treated at a cost of \$0.10 to \$0.20 per ton, and possibly much less.

F. The organic coatings recommended for protection against wet storage stains do not interfere with soldering, welding, or painting and are easily removed by conventional degreasing methods, where necessary.

EX-115 - Wet Storage Staining of Galvanized Sheet, The British Non-Ferrous Metals Research Association, Mr. H.S. Campbell

This program constitutes another promising approach towards a solution to the problem of wet storage staining of galvanized sheet. The primary objective of this research is the study of gas phase treatments for the deposition of insoluble protective films which would be strongly adherent to the galvanized surface.

In an effort to correlate the structure and composition of protective films with their resistance to white rusting under wet storage conditions, work during this report period was divided into two main sections. Firstly, the views of the producers and users of galvanized sheet have been sought on the incidence of white rusting, the efficacy of chromating and other preventive treatments available and the effect of these treatments, and of white rusting, on weldability and paintability of the steel. Secondly, a start has been made on the main part of the research, an attempt to produce a white-rust resistant coating on galvanized steel.

As a result of inquiries amongst manufacturers and users of galvanized steel little information about paint adherence has been found, but divergence of opinion on weldability has come to light. Some claim that chromating adversely affects weldability, others that it does not. Experimental tests performed in this program have established that satisfactory welds can be made through the thickest of chromate coatings, but there are indications that chromating might have an effect if the welding conditions were of marginal acceptability. No information has been obtained on possible effects of chromate or white rust films on electrode life.

Galvanized steel is reported to have a higher resistance to white rusting when it is naturally weathered or stored in dry conditions before exposure to wet storage. For this reason, the possibility is being investigated of producing artificially and at an accelerated rate the type of protective film formed naturally during weathering or dry storage. The nature of the films on galvanized steel - whether freshly produced, after dry storage or after weathering - is not known, and experiments are in progress to determine the nature of these films. The effect of the aluminum present in continuously galvanized strip will also be taken into account.

Previous research has shown that the rate of corrosion of zinc is reduced in atmospheres with high carbon dioxide content. This may be due to the formation of corrosion products in a more protective form. It was therefore reasoned that zinc carbonate would theoretically form a good protective layer on zinc because of its physical hardness and insolubility in water. However although zinc carbonate is formed when galvanized steel is used in supply waters of high free carbon dioxide content it does not adhere to the metal surface.

Since alloy layer formation is a factor which has an effect on whether or not a protective film is formed initial experiments are being carried out on solid specimens of pure zinc and zinc containing 0.1% aluminum. This aluminum content is of the same order as that in the coating of continuously galvanized strip. If these initial experiments suggest a process by which a protective film may be successfully produced, attempts will be made to adapt this process to conditions which are compatible with continuous strip production and to produce zinc carbonate by a gas phase reaction. In this case the probability is good that the zinc carbonate film thus formed will adhere to the metal surface.

Data on this equilibrium $\text{ZnO} + \text{CO}_2 \rightleftharpoons \text{ZnCO}_3$ are not readily available but it has been reported that zinc carbonate decomposes between 300 to 500°C in air and that the partial pressure of carbon dioxide is equilibrium with zinc oxide and zinc carbonate is 1 atmosphere at 395°C. In order to provide more working information on this equilibrium, the weight loss of zinc carbonate and weight gain of zinc oxide after heating at different temperatures in carbon dioxide atmospheres are being measured. Other factors to be taken into account are the presence of oxygen and the presence of water vapor in the atmosphere.

Another approach that is being tried is the possibility of producing a protective film of Gehlitzite ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$) on galvanized coatings containing aluminum.

Some experimental work has been directed towards finding the most satisfactory method of testing for susceptibility to white rusting, a stack test simulating service conditions being preferred to tests by complete immersion.

Future work will include:

- (1) Experimental investigations to determine the feasibility of the production of a protective coating of zinc carbonate or of Gehlitzite on galvanized steel.
- (2) Evaluation of the best method of testing for susceptibility to white rusting.
- (3) Consideration of any further information which may come to light on the effects of protective films on fabrication processes and on paint adhesion.

2. 22-12 - New Finishes for Zinc Die Castings. Battelle Memorial Institute, Messrs. W. H. Saffranek, H. N. Miller, R. W. Hardy and C. L. Faust

This program of research on superior finishes for zinc die castings has as its chief objective the development of procedures for improving the durability of electroplated zinc die castings.

A survey of practices employed for painting electroplated die castings revealed distinct differences from plant to plant which might account for inconsistent paint adherence on exterior automotive hardware. Recent changes in practices at one plant, which effected a large improvement in adherence, include (1) more thorough and complete rinsing after chromium plating and (2) thorough drying with blasts of cold air. Practices in other plants, which include similar rinsing procedures, but which also include the use of heated air, evidently are not as successful. Heating the chromium plate tends to passivate it. Thus, it appears that activating treatments are better than passivating treatments for parts that cannot be painted for many hours or several days after plating. This hypothesis will be checked during future laboratory work on procedures for conditioning chromium surfaces prior to painting.

Research aimed at establishing the optimum condition of chromium plate for paint receptivity was initiated with a study of procedures appropriate for maintaining the chromium in a relatively active state. The results of these experiments were compared with others based on passivating procedures. A series of experiments included treatments for reactivating passive chromium. In all cases, the results of evaluating paint adherence are correlated with electrode potential data in order to pinpoint, insofar as possible, the optimum chromium surface condition for painting.

In exposure tests to establish outdoor-weathering data, electroplated panels were corroded in decreasing degree at the following sites:

- (1) New York Harbor tug boats, 2-1/2 months of weathering
- (2) Wrightsville Beach Harbor (splash zone), 3 months
- (3) Eure Beach - 600-ft lot, 3 months
- (4) Truck trailers, front, above cab level, 4 months
- (5) Detroit, Chrysler Engineering roof, 4-1/2 months
- (6) Truck trailers, side, below bed, 4 months.

Results to date confirmed previous data with respect to (a) the effectiveness of microcracked chromium plate containing at least 750 cracks/inch for protecting zinc die casting from corrosion and (b) the failure of crackfree chromium to withstand mobile conditions of exposure. A distinct effect was observed for the 30-second cathodic treatment in sodium dichromate solution for inhibiting pitting in a composite of duplex nickel and 0.01 mil of low-temperature chromium and for reducing stain on a composite of bright nickel and microcracked chromium.

A survey of die castings on 1960 models showed much better durability for parts plated with any one of three composites. By comparison with parts plated with the outmoded composite of copper bright nickel, and conventional (0.01 mil) chromium. The three more protective composites were as follows:

- (a) Copper, bright nickel, and dual, microcracked chromium (0.02 mil, or more)
- (b) Copper duplex nickel, and conventional (0.01 mil) chromium
- (c) Copper, duplex nickel, and crackfree chromium (0.02 mil, or more).

Composite (a) appeared to be the most effective of the plating systems utilized for 1960 model parts.

Cleaning and conditioning treatments for preparing zinc die castings for painting were selected after checking their influence on the electrode potential of the chromium. The selection includes activating and passivating treatments.

Cyclic cathodic and anodic electrocleaning effectively cleaned 3-month aged chromium that was covered with a layer of dust. When this cleaning treatment was followed by cathodic charging at room temperature, the chromium was decreased in potential to between 0 and -40 millivolts. Cathodic treatment in sodium dichromate solution or immersion in hot chromic acid further increased the activity of aged and cleaned chromium to -80 and -105 millivolts, respectively which is in the vicinity of the potential of freshly deposited chromium. The most effective passivating treatment for aged chromium was anodic treatment in sulfuric-phosphoric acid solution. The average equilibrium potential was 365 millivolts.

Alkaline spray cleaning plus cathodic cleaning did not completely remove the dust and film layer from aged chromium but was the next most effective and practical cleaning procedure for aged chromium. Magnesium oxide scrubbing was as effective as cyclic electrocleaning in removing dust and film from aged chromium but was considered impractical from a production point of view because of the need for manual operations. Unsuccessful cleaning techniques included cathodic cleaning in a proprietary cleaner, emulsion cleaning, vapor degreasing, and various combinations of these procedures.

In future work, panels plated with copper, nickel, and chromium and aged 3 months will be subjected to one of several candidate conditioning procedures and painted in preparation for paint-adherence tests. Research on silicon coatings, recessed in April will be resumed shortly.

3. ZZ-13 - Zinc Anode Installation for Marine Tankers, Cooperative Program

Observations are continuing on the effectiveness of zinc anodes for the protection of cargo tanks when in ballast with sea water. The results show that a well designed installation of zinc anodes provides long term economical protection to marine tankers against corrosion and the use of zinc anodes is increasing.

A technical paper entitled, "The performance of Zinc Anodes in the Cathodic Protection of a Cargo Tank of a 45,000 Ton Tanker", by A. R. Cook of the Expanded Research Program and B. C. Lattin of Ebasco Services, Inc., has been presented at a meeting of The National Association of Corrosion Engineers. Anode and reference cell locations are given and graphs are shown of recorded potential vs. time functions. The paper will be published in the November 1962 issue of MATERIAL PROTECTION.

4. ZZ-20 - Surface Characteristics of Zinc in Aqueous Media. Case Institute of Technology, Messrs. D.M. Geehan, R. Arun, S. Shalman, T. Steiner, Dr. R. C. Weast.

The investigations concerned with the cause of embellment of the zinc potential in dilute, aqueous systems have been completed and a thesis describing the work has been received. The thesis has been prepared by Mr. David M. Geehan in partial fulfillment of the requirements for his Doctorate Degree and is abstracted below.

An investigation of the electrode behavior of zinc in corrosive aqueous systems was undertaken with the objective of determining the mechanism causing the phenomenon of embellment. The results have been reviewed in the light of electrochemical corrosion theory. The solution variables significantly affecting the overall potential were shown to be oxygen concentration, pH, conductivity, and to a lesser extent, temperature.

The observation of considerable embellment was found to be associated with solutions of relatively low conductivity with indications that the cathodic reaction was predominantly that of oxygen reduction. The distribution of the pitting attack of such environments indicated presence of large cathodic areas with relatively small anodic areas. In such circumstances and with low conducting solutions, the full development of anode and cathode polarization curves is not attained and as seen by the use of an Evans' diagram, the overall potential becomes essentially a measure of the polarized potential of the cathode reaction. In such cases the depolarization of the cathode (e.g. through increase in oxygen pressure), becomes the factor controlling increase in corrosion rate.

Indication of a shift of the controlling cathodic reaction from hydrogen ion discharge to that of oxygen reduction was given by the observation of a maximum in active potential after oxygen was introduced into the solution. These were observed in solutions of pH = 3. The appearance of such maxima was explained as the net effect of the development of a new cathodic reaction and the simultaneous decrease of the previous cathodic reaction. Such maxima were not observed in solutions of a pH greater than 5, indicating that the attack of mild acids on

pure zinc is insufficient to affect overall potential until oxygen is introduced, whereupon oxygen reduction immediately controls the cathodic reaction.

The effect of temperature in the systems studies was much more subtle than the effects of pH and oxygen pressure. Zinc is commonly considered to exhibit potentials cathodic to steel only above 60°C in aerated solutions. Ennoblements were observed well into the range of steel potential as low as 25°C. The magnitude of such ennoblements were not greatly different from those at higher temperatures, and were primarily a function of oxygen pressure in solutions of a given conductivity and pH.

The effect of corrosion films up to 1/8 inch thick (maximum obtained in this research) was found to contribute only a small amount to the overall potential in all of the systems studied. Possible electrode processes by semiconduction through the zinc oxide film are considered unlikely contributors to the overall corrosion reaction, and consequently have little effect on the potential. Apparently the porous nature of the films was such that inhibition of reactions at anode or cathode areas did not occur.

Summarizing the results of experimental evidence and application of electrochemical corrosion theory, the following general conclusions were drawn:

1. In the range of variables studied the potential of corroding zinc in aqueous systems is a function of oxygen pressure, pH, solution conductivity, and, to a lesser extent, temperature.
2. Increasing oxygen concentration in solution causes the zinc to become more noble when the predominant cathodic reaction is oxygen reduction.
3. In solutions where hydrogen ion discharge is initially the predominant cathodic reaction, increase in oxygen concentration brings about more active potentials until oxygen reduction dominates the cathodic reaction, whereupon ennoblement is again observed.
4. Increase in solution conductivity tends to dampen the speed and magnitude of ennoblement, provided the ionic species involved with the conductivity increases do not directly participate in the corrosion reaction.
5. Depolarization of the cathode areas is the process controlling the corrosion rate.
6. In aerated solutions, with oxygen reduction the principal cathodic reaction, corrosion occurs by the action of local cells, with cathodic areas being much larger than anodic areas.
7. Large ennoblements observed in solutions of relatively low conductivity are essentially a measure of the polarized potential of the cathode.

8. In pressurized systems, ennoblement of zinc into the range of steel potential, occurs even at the low temperatures studied (85°C, 40°C), and consequently reversal can be encountered below 60°C. Nothing significant with regard to magnitude of ennoblement was observed at 60°C, a temperature prominently mentioned in the literature as the temperature at which zinc will become cathodic to steel.

9. Investigation of zinc electrode behavior in solutions of relatively low conductivity using an inert gas containing accurately known trace amounts of oxygen, together with highly refined boundary conditions, might establish more clearly the relation between oxygen concentration and temperature on the polarization properties of corroding zinc.

10. The influence of the corrosion films on zinc electrode potential, even though they are known semiconductors, is insignificant compared to the influence of oxygen itself.

This program has been terminated and will no longer be reviewed in future Research Digests.

5. 22-12 - Surface Characteristics of Zinc, British Non-Ferrous Metals Research Association, Mr. R. W. Lucas, Mr. R. J. L. Eborall.

The work described in this report forms part of an investigation of the dependence of the rate of oxidation of zinc on the temperature of the metal, crystallographic orientation of the surface and impurities both in the oxidizing atmosphere and in the metal. Zinc specimens are oxidized at temperatures between room temperature and the melting point (or slightly above) and the nature of the oxide film formed under various experimental conditions is being studied. Work has been carried out on the oxidation of single crystals and polycrystals of pure zinc (99.999%) in pure oxygen at constant temperature and of commercial purity zinc polycrystals under similar conditions. This report describes a completion of experiments with specimens of commercial purity and a series of experiments with specimens of a composition similar to that encountered in the outer layers of galvanized coatings. Further examination of oxide films by electron microscopy has also been carried out and the original apparatus has been modified to facilitate the use of oxidizing atmospheres containing condensable impurities.

The progress of oxidation of flat zinc specimens has been studied by continuous measurement of weight increase during oxidation using a Oulbransen type micro-balance fitted with an automatic recording device which permits continuous recordings of weight increase to be made over periods of 100 hours. After oxidation the surface films formed on the specimens were examined by electron diffraction. Previous reports have been concerned with the oxidation of pure single crystals of different orientations in pure oxygen at 300°C, 340°C and 390°C and pure polycrystals at 300°C. During the present report period, oxidation experiments were made with pure zinc polycrystals at 300°C, 350°C and 390°C and with Prime Western zinc (main impurity approx. 1% lead) at 300°C and 390°C.

The results from the pure polycrystals lay within the range previously encountered for pure single crystals, and electron diffraction showed the oxide to be in the form of fine grained polycrystals. Parallel lines, terminating at grain boundaries, were observed on microscopic examination of oxidized specimens. It was deduced that these were slip lines due to stresses caused by anisotropic expansion and contraction on heating and cooling. Similar markings were observed on a specimen heated to 300°C in an argon filled capsule and air cooled.

Experiments with Prime Western zinc produced straight lines on plots of log weight increases vs. log time. With reference to the $w \propto kt^n$ relation at 300°C, k is slightly smaller and n approximately equal to the corresponding values for pure polycrystals; at 350°C, k is smaller and n is larger. Only zinc oxide has been detected by electron diffraction of the surface film.

Further oxidation experiments were carried out in this report period with a Prime Western specimen at 350°C and with specimens of galvanized coating composition at 300°C and 350°C. The Prime Western specimen confirmed that at 350°C, the oxidation rate for zinc of this purity is substantially the same as that for pure zinc polycrystals. The galvanized coating composition showed a lower oxidation rate than pure zinc at 300°C and 350°C.

Oxide films formed on two of the single crystals of pure zinc have been examined both by shadowed carbon/platinum replication and by stripping the oxide from the metal by mercury amalgamation. Selected area diffraction in transmission has also been carried out on the stripped oxide films.

A selected area diffraction examination of the oxide film as stripped from the metal, produced a ring pattern showing no preferred orientation. The rings were formed from discrete spots. When previously examined by glancing incidence electron diffraction the specimen had produced a pattern showing distinct preferred orientation.

The apparatus has now been modified so that impurities such as water vapor and carbon dioxide can be added to the oxidizing atmosphere. This modification entailed insertion of a large tap between the balance chamber and the cold trap which is surrounded by liquid oxygen.

Future work will include a study of the effect of water vapor and carbon dioxide additions to the oxidizing atmosphere on the oxidation rate of pure zinc, polycrystals over the temperature range previously used. Further examination of oxide films in the electron microscope will also be carried out.

6. 22-35 - Evaluation of Zinc-Rich Paint, National Smelting Co. Ltd., Mr. F. O. Sampson, Mr. D. S. Newton, Dr. J. O. Rigg

This research program is being conducted by the National Smelting Company, Ltd., with cooperation from two other British zinc dust manufacturers, Amalgamated Oxide, Ltd., and Durban Chemicals, Ltd.

The investigations are aimed at three main objectives:

1. The development of satisfactory priming paints for the automobile industry, with special attention to good adhesion and flexibility, compatibility with overlying paint systems and applicability to standard welding procedures.
2. The improvement of paints for priming and maintenance of structural and other types of steelwork.
3. The development of zinc dust paints for the marine field.

Preliminary screening work on a number of paint media pigmented with a zinc dust which was readily available (Dalaville Superfine) was shown that, with alkyd media, storage stability was affected by acid value; high acid value giving serious thickening. Corrosion resistance appeared to be governed by the Pigment Volume Concentration (P.V.C.) of the zinc dust. With chlorinated rubber the level of plasticiser was an important factor.

The tests to evaluate the merits of various available types of paint media in zinc dust paints are now well advanced. A standard fine sized zinc dust has been incorporated into these media by high speed stirring and paint films have been applied to burnished steel sheet (for corrosion tests) and to tinned sheet (for adhesion tests), by spinning. This technique gives uniform films.

Storage tests are incomplete. Corrosion is being assessed primarily by means of a salt droplet test which is showing large differences between different classes of media. Epoxy Esters, as a class, are producing some very promising compositions and merit further examination. Some oleoresinous paints are also good, and so are plasticized compositions based on styrene-butadiene and chlorinated rubber.

The following conclusions may be drawn from the first screening tests:

1. The first seven stoving primers arranged in order of corrosion resistance may be classed as "very good" and the next twelve as acceptable.
2. The tests so far indicate that Epoxy Esters, as a class, show the greatest promise.
3. A certain number of oleoresinous compositions based on Congo Ester and Reduced Phenolic resin with linseed/china wood oil, and a vinyl toluenated alkyd, also fall within the "very good" classification.
4. Within the "acceptable" classification, the only other types of stoving primers are based on phenolic resin modified linseed/china wood oil alkyd types, and 100% phenolic resin modified/wood oil varnish.

5. Pigment Volume Concentration has an important bearing on corrosion resistance, but it is probable that the Pigment Volume giving optimum corrosion resistance is highly dependent on the type of medium employed. Generally, Pigment Volume Concentrations of 58% and 64% give the most satisfactory performance so far.

6. Media which dry by evaporation (styrene butadiene and chlorinated rubber) vary considerably in performance depending on the amount of plasticizer present. Both Pliolite 85 and chlorinated rubber provide satisfactory corrosion resistance and flexibility at high Pigment Volume Concentrations.

Further evaluation of commercially available media in zinc dust primers has continued with the testing of a number of modified epoxy esters, two pot epikotes, two pot polyurethanes and modified epikote resins.

Phenolic, vinyl toluenated, and polyester modified epoxy esters have all shown considerable promise with the first type of modification giving the better results. The two pot epoxy resins (Epikote 1001 and Epikote 828 with Versamid 115) tend to be rather brittle 24 hours after application, but their corrosion resistance is high. The two pot polyurethane media (Desmophen 1100 and Desmodur L) show better flexibility than do the epikotes, whilst their corrosion resistance is comparable to them.

Due to the difficulty in determining the density of both sets of cured resins, these paints have been formulated by weight instead of by volume as in previous tests.

The flexibility and adhesion of the epoxy esters is strongly affected by the level of pigmentation. Only two resins Scopon 1200M (a vinyl toluenated epoxy resin) and Berydolac C954 (a long oil unmodified epoxy ester) gave paints which passed the 1/16" impact indentation test, and these were paints formulated at low P.V.C's.

Summarizing the work performed during the second portion of this report period, the following findings have been established:

1. The modified epoxy esters have excellent corrosion resistance when used as binders for zinc dust paints, the best performance being given by those modified with vinyl toluene and phenolic additives.
2. The flexibility and adhesion of the modified epoxy esters falls off with increasing pigment volume concentration, and above 58% may be questionable except for paints containing the vinyl toluenated ester.
3. The modified epikote resins are obviously unsuitable in their present form due to brittleness, but their corrosion resistance is excellent.

4. Two pot epoxy resins are deficient in flexibility and adhesion within the neutralization ratios examined; their corrosion resistance is high.
5. The polyurethane/isocyanate resins possess good flexibility when used at 8% w/v of zinc dust in the dry film, and at 60% cross linking. Their corrosion resistance is very good, particularly at 8% and 92% w/v zinc in the dry film, but their resistance to impact is poor.
6. Both Bentone 38 and Synthavex show some effect as suspending agents at the 0.8% w/v level on the zinc dust, but more time will be needed to determine their real efficiency.
7. EZ-38 - An Investigation of Electrochemical Finishes for Zinc.
The Consolidated Mining and Smelting Company of Canada Ltd.,
Mr. J. R. Wallington, Mr. R. C. Bell, Dr. M. M. Wright

Work is continuing on improvements of alternate anodic finishes for zinc. The emphasis is placed on the study of properties of anodized films which have been successfully formed on zinc from electrolytes containing additions of vanadate, molybdate or tungstate as a second anion.

The commercialization of the COMECO process for anodizing zinc metal is proceeding satisfactorily. Contact has been established with appliance manufacturers and with segments of the automobile industry to evaluate these coatings in several unique applications.

The process produces a grey-green coating which is hard, smooth and corrosion resistant, and which can be applied on rolled zinc, zinc-base die castings and galvanized steel. The new anodized finish is formed in a near neutral electrolyte of ammonium phosphate-chromate-fluoride solution. The throwing power of the electrolyte is excellent, and a continuous coating is possible even in deeply recessed cavities. Satisfactory coatings approximately 1 mil thick can be produced by using either direct or 60 cycle alternating current, and the coatings form an excellent paint base.

A manual presenting detailed instructions for operating the anodizing process is now available and requests for license agreements to operate under our patents are being considered. Samples for test purposes can be supplied to potential users.

8. EZ-52 - Galvanized Steel Reinforcement Rods for Concrete.
University of California, Professors B. Bresler and I. Cornet

This program is concerned with an investigation of the effect of galvanized coatings on bond strength and corrosion performance of steel reinforcement in conventional concrete and in prestressed concrete structures.

During the first year of work on this program two problems were investigated:

1. The effect of galvanizing on bond strength of steel reinforcement in concrete.
2. The effect of galvanizing on corrosion of steel reinforcement in concrete.

For the first of these problems, a standard bond test procedure of The American Concrete Institute was adopted. Beams 78 x 18 x 8 inches were prepared and tested. The concrete was made with Type 1 cement and had a compressive strength of about 4.2 kpsi. Black and galvanized steel reinforcement were used in the beams, with both plain and deformed bars. Results indicated that there is no significant difference in bond strength between black and galvanized deformed bars. The bond on galvanized plain bars appears to be slightly better than that of black plain bars. The bond of plain bars to concrete depends greatly on surface roughness, and the small difference in bond observed between galvanized plain bars and black plain bars may be due to this factor of roughness.

For the second problem, the effect of galvanizing on corrosion of steel reinforcement in concrete, no established procedure could be used. Exploratory tests were made with a four-inch diameter concrete cylinder through which one reinforcing bar runs. Again the reinforcement included plain and deformed bars, black and galvanized. An EN-A strain gage was attached to the reinforcing bar and the bar was calibrated. The concrete cylinder was cast around the bar and then cured, and the steel bar was then subjected to a working load in a stressing fixture. Some of these reinforced concrete cylinders were then exposed to salt water, others to salt water, and others to salt water with imposed anodic current. Preliminary results showed that black steel reinforcement produced earlier cracking of the concrete cylinders in an aggressive environment (salt water plus imposed anodic current) than did galvanized steel reinforcement, for both plain and deformed bar. There were indications that, at higher loads, the bond in galvanized bar systems may be appreciably better than in black bar systems, when an aggressive environment is present.

A literature survey was made and some 800 abstracts of articles pertinent to this project were accumulated.

Future work will involve completion and analysis of the beam tests, further development and refinement of the corrosion tests, and analysis of the bibliography compiled. Studies will be extended to high tensile strength reinforcement, where crack frequency and width, and corrosion performance, are increasingly important.

The relationship of crack frequency and crack width versus bond and concrete quality will be examined. Concrete permeability and thickness of cover will be considered. The mechanism by which galvanizing protects the bond of steel to concrete in a corrosive environment will be studied.

The effect of galvanizing of prestressed wires in concrete beams will also be explored.

9. FE-66 - Zinc Shot Blasting of Structural Steel, Steel Structures
Painting Council, Mr. J. D. Keane

This program has only recently been initiated and is concerned with the investigation of a process involving the use of zinc for inhibitive blast cleaning of structural steel.

It is common practice to remove mill scale and rust from steel prior to the application of a protective paint coat. However, the freshly cleaned surface after sand blasting is exceedingly active and rusts very rapidly, often becoming unsuitable for painting in a matter of a few hours. Attempts have been made to apply various coatings to the freshly de-scaled stocks, but these constitute an extra coating operation, with consequent delay for application and drying time. Furthermore ordinary coatings are easily damaged during handling and fabrication and in many cases, they must actually be removed before fabrication can be completed.

Preliminary investigations have shown that the shot blasting of steel with zinc particles effectively removes rust and mill scale from steel and, in addition, provides temporary corrosion protection in the interval between cleaning and subsequent painting. Based on these considerations, the work of this program is aimed at establishing the optimum parameters of zinc shot blasting, such as particle size, distribution, choice of alloys, welding characteristics, paintability, and other variables.

Pilot plant work on this program is proceeding satisfactorily and a report on the findings of this research will be available soon.

STANDARD OPERATING PROCEDURE

EXPANDED RESEARCH PROGRAM

American Zinc Institute, Inc. - Lead Industries Association, Inc.

June, 1962

1. INTRODUCTION

The Expanded Research Program (ERP) was established in 1958 by the American Zinc Institute (AZI) and Lead Industries Association (LIA) with the active cooperation of lead and zinc producers in other countries.

The objectives of the ERP are to develop, internationally, new uses of lead and zinc and to support with technical information the efforts of the AZI, LIA and similar organizations in other countries in promoting and extending existing uses of the two metals.

The producers of other materials which compete with lead and zinc continue their large expenditures to promote the sale of their products, and in addition spend substantial sums on research. To meet this competition and to provide funds for the high cost of research, the support of the entire lead and zinc industry is needed. Such cooperative effort reduces the cost to each producer, pools the experience and information of the industry, and speeds the achievement of objectives.

The ERP does not have its own research laboratories. It uses laboratories and research organizations throughout the world. Such organizations may be government controlled, profit or nonprofit, or the research laboratories of members of the industry. The policy of ERP is to negotiate research projects and award them to whichever organization can do the work most efficiently and economically, wherever located and however financed.

2. CONTRIBUTORS TO THE PROGRAM

The ERP is supported by all U. S. producer companies of the AZI and LIA and by a growing number of producers in other countries. (See Appendix A). Each supporting company contributes directly in the proportion that its production of refined lead and slab zinc, or of zinc oxide, bears to the total production of each product contributing to the ERP. Zinc oxide is assessed at one-half of the per ton rate for slab zinc.

After the annual research budget is approved, the rate of contribution for the new budget is established on the following basis. The dollar amount of the budget is divided by the total number of tons produced in the preceding year by all supporting companies. This determines a rate per ton. The staffs of the AZI and LIA allocate this rate to each supporter's individual production figures, which are kept confidential.

The annual budget is now over \$1 million. For 1962, the rate per ton of 2000 pounds to each member is:

20¢ for lead

24¢ for zinc

12¢ for zinc contained in zinc oxide produced from other than metallic zinc.

3. COMMUNICATIONS

ERP works closely with all development and promotional organizations in the free world and provides them with technical information of benefit to their efforts. A list of such organizations is shown in Appendix B. Thus ERP is international in scope, and its technical information is disseminated as widely as possible for the benefit of the whole industry.

4. ORGANIZATION

The Director of Research is responsible for management and administration. He and his staff are located at 292 Madison Avenue in New York City in the same building as AII and LIA.

He reports to an Executive Committee of five members, composed of the President of AII, acting as Chairman of the Executive Committee, the President of LIA, one further representative of either AII or LIA, and two representatives of companies in other countries.

For each metal there is a Technical Steering Committee and an Industry Development Committee. The Director of Research and each Technical Steering Committee work with three subcommittees entitled, Metallurgical, Chemical and Electrochemical, whose responsibilities are respectively: (a) metal as a structural material, (b) paint, pigments, ceramics, organic and inorganic chemicals, and (c) electroplating, accumulators, chemical reduction plating, corrosion and anodes for cathodic protection. The Industry Development Committee may appoint subcommittees as required by the projects under consideration.

Each contributing company is entitled to be represented on each of the committees (except the Executive) by one person. The companies are expected to nominate technically qualified personnel for the technical committees and sales executives for the Industry Development Committees.

The Technical Steering Committees are responsible for over-all technical feasibility and review of the research programs and for recommendation of research policies. Research ideas and projects originate primarily in these committees and their subcommittees.

The Industry Development Committees exercise the commercial and financial judgement of the supporting companies. These Committees guide research policy and review the commercial desirability and sales potential of projects. They make market studies when required, play a vital part in the planning and programming of research and market development, assure close coordination between research and promotion, and may present research ideas. They consider the over-all cost of the projected program to the industry and approve the research budgets.

Research programs and budgets approved by the Technical Steering Committees and the Industry Development Committees are presented by the Director of Research to the Boards of Directors of AZI and LIA. When these Boards act on RDP matters, the members of the RDP Executive Committee from other countries have full voting rights with the U. S. Directors. This procedure is established in AZI and is under consideration by LIA. The two Boards make the final review and decision on each project and determine the total amount of each year's budget.

Experience has shown that the Boards usually adopt the recommendations made by the Technical Steering Committees and the Industry Development Committees.

3. METHOD OF OPERATION

(a) Sources of Research Facilities

Every possible source in the United States and in other countries is utilized including nonprofit research organizations, government laboratories, universities, and industrial research laboratories.

(b) Sources of Ideas for Research

All available sources from within and without the industry are utilized, and the proposed ideas are carefully screened for their technical and commercial feasibility.

(c) Appraisal, Scheduling and Approval of Ideas

Twice a year, each of the technical subcommittees meet in separate sessions to discuss ideas generated by them and by others. Each idea is critically appraised. If accepted, it is assigned to one member of the committee, or RDP staff who is then charged with the responsibility of developing a work statement. This statement contains the information from which a research proposal can be formulated (i.e. a discussion of the problem, the scope of the desired investigation, and the economic incentive). The Director of Research thereafter investigates where the work might be best performed and obtains contract proposals.

In the fall of each year the technical subcommittees meet (usually in New York), review the work statements and the research proposals, and agree on a recommendation for each project and its budget for the following calendar year. Thereafter, the completed budgets of the subcommittees are submitted to the Technical Steering Committee. Final recommendations of these Committees are presented by the Director of Research to the Industry Development Committee who pass on the marketing and financial aspects of each research work statement or proposal.

The Industry Development Committee make their recommendations to the Director of Research who presents the mine projects to the Board of Directors of ARI and the lead projects to the Board of Directors of LIA. The meetings of these Boards are assisted by the representatives of the contributors in other countries and by the Director of Research. The decisions of these Boards are final and the Director of Research immediately begins to implement their recommendations. The final annual budgets approved by these Boards usually include a contingency fund to provide a reserve for unbudgeted research which may become urgent during the coming year. Such urgent programs are subjected to the same screening as the formally budgeted programs.

(d) Selection and Supervision of Contractors

In general, contracts are made for one year or less. For existing contracts on which additional work is desirable, the Director of Research awards a new contract for another year. For new work on which a contract has not yet been negotiated, the Director of Research investigates and negotiates where he feels advisable. Such new contract proposals, when received, are referred to the technical subcommittees who select the proposals they prefer and make recommendations to the Technical Steering Committee. The Director of Research awards the contract to the research facility whose proposal was approved by these Committees.

The Director of Research and his staff make frequent visits to the contractors to check progress, to insure that the work is proceeding as desired, and to stimulate the best effort of the contractors. From time to time members of the technical subcommittees accompany the Director of Research on such visits and contractors are invited to discuss their work at scheduled meetings.

6. REPORTS

(a) Budget

Copies of the final budget and semi-annual financial statements are mailed to all contributing companies.

(b) Research

Each contractor submits to the Director of Research quarterly progress reports which are distributed to each contributor to the ERF. A summary report is similarly distributed each year. The development and trade associations such as those listed in Appendix B receive the final reports, i.e. when a project has been completed. The Director of Research semi-annually issues an abstract-summary of all the research currently under way. This is sent to the participants and to interested laboratories and development organisations throughout the world. When advisable, the Director of Research may send his or the contractors' reports to other interested companies or organisations.

7. DISSEMINATION OF INFORMATION

Information developed by ERF is distributed widely and without restriction to the consuming industries and to contractors, architects and design engineers all over the world. Much of the distribution is done by the development associations who may prepare individual papers to suit conditions in their market.

8. PATENTS

The general policy of ERF is to promote the dissemination of information, to broaden the utilisation of new developments, and to make the patents available license-free to all potential users and contributors. However, the policy is reviewed when each patent is issued.

DEVELOPMENT OF RESEARCH PROGRAMS

Flow Process Chart

Step 1

Development of new research ideas by technical subcommittees and by RFP staff.

Step 2

- (a) Preparation of work statements by subcommittee members and RFP staff.
- (b) Preparation of extension research proposals by existing contractors.

Step 3

Work statements and contractors' extension proposals reviewed and budgets proposed by subcommittees and RFP staff.

Step 4

Research and budget proposals submitted to the Technical Steering Committee for technical review.

Step 5

Final recommendations of Technical Steering Committee presented by Director of Research to Industry Development Committee for review of marketing and financial feasibility.

Step 6

Budgets recommended by Industry Development Committee presented by Director of Research to Board of Directors for final review and approval.

Step 7

Approved budgets presented to Director of Research for execution.

Step 8

- (a) Director of Research submits work statements to potential contractors who will prepare proposals for new research.
- (b) Director of Research awards contracts for approved extension programs on work already under way.

Step 9

Proposals received from potential contractors submitted by Director of Research to technical subcommittees for review and selection.

Step 10

Proposals selected by subcommittees submitted to Technical Steering Committees for review and approval.

Step 11

After approval by Technical Steering Committees, contracts are awarded by Director of Research.

Appendix A

CONTRIBUTORS TO THE EXPANDED RESEARCH PROGRAM OF THE
AMERICAN ZINC INSTITUTE AND LEAD INDUSTRIES ASSOCIATION

American Metal Climax, Inc.
New York City

American Smelting & Refining Co.
New York City

American Zinc Lead & Smelting Co.
New York City

Anaconda Company
New York City

Athletic Mining & Smelting Co.
Fort Smith, Arkansas

Broken Hill Associated Smelters
Proprietary, Ltd.
Australia

Bunker Hill Company
San Francisco, Calif.

Cerro Sales Corp.
New York City

Combined Metals Reduction Co.
Salt Lake City, Utah

Compania Minera Asarco
Mexico City, Mexico

The Consolidated Mining & Smelting Co.
of Canada Ltd.
Montreal, Quebec, Canada

The Consolidated Zinc Corp.
London, England

Eagle-Picher Company
Cincinnati, Ohio

Electrolytic Zinc Co. of Australasia, Ltd.
Australia

Bodeon Bay Mining & Smelting Co.
Winnipeg, Manitoba, Canada

International Smelting & Refining Co.
New York City

Matthiessen & Beggs
LaSalle, Illinois

Meadow Brook Corp.
Spelter, West Va.

Metallurgica Mexicana Pachuca, S.A.
Apartado Postal 251
Matamoros Oriente 416
Monterrey, N.L., Mexico.

Montecatini
Societa Italiana Del Piombo E Dello Zinco
Milano, Italy

Mt. Isa Mines, Ltd.
Australia

National Zinc Co., Inc.
New York City

New Jersey Zinc Co.
New York City

Newmont Mining Corp.
New York, N.Y.

St. Joseph Lead Company
New York City

Mr. Charles Stott, General Manager
Trumbo Mining Corp. Ltd.
P.O. Box 1940, South West Africa.

U.S. Smelting Refining & Mining Co.
Boston, Mass.

Appendix B

LEAD AND ZINC
DEVELOPMENT AND PROMOTIONAL ORGANIZATIONS

Belgium - Centre Belge Hollandais
d'Etudes et de Recherches
pour le Développement des
usages du zinc
31 Rue du Marais
Brussels and
18, Stationsweg, The Hague

Union des Lamineurs Belges de Zinc
31 Rue du Marais
Brussels, Belgium

England - Lead Development Association
34 Berkeley Square
London, W.1 England

Zinc Development Association
34 Berkeley Square
London, W.1 England

France - Centre D'Information du Flomb
22 Rue de la Paix
Paris 2, France

Chambre Syndicale des Fabricants
de Tôles Galvanisées
5 Rue de Madrid
Paris 8e, France

Chambre Syndicale du Zinc et du Cadmium
39 Rue St. Dominique
Paris 7e, France

Tolgalva
21 Rue D'Artois
Paris 8e, France

Zinc et Alliages
34 Rue Collange
Levallois - Perret (Seine)
Paris, France

Germany - Eisenberatung E.V.
Am Wehrbahn 96-100
Post Office Box 8706
Dusseldorf, Germany

Fachvereinigung Metallernbergbau E.V.
Am Wehrbahn 100
Dusseldorf, Germany

Zinkberatung E.V.
Friedrich-Ebert-Strasse 37-39
Dusseldorf, Germany

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Italy - Associazione Italiana Zinostura
via Marco De Marchi, 7,
Milano, Italy

Italian Die Casting Association
18 Via Leopardi
Milano, Italy

Istituto Italiano Del Piombo E Dello Zinco
Via Marco de Marchi, 7
Milano, Italy

Japan - The Japan Mining Industry Association
24, 3-chome Kanda Nishiki-cho
Chiyoda-ku
Tokyo, Japan

The Netherlands -
Stichting Doelmatig Verniemen
Jan van Masekenstraat 93
's-Gravenhage, Holland

THIS AGREEMENT, made as of the day of 19 , between the Lead Industries Association Inc., a nonprofit corporation existing under the laws of the State of New York, and having a post office address at 292 Madison Avenue, New York 17 New York (hereinafter called Sponsor) and a corporation of and having a post office address at (hereinafter called Contractor);

WHEREAS, Sponsor desires the Contractor to conduct research on (hereinafter sometimes referred to as subject research), as set forth in Contractor's proposal identified by Exhibit A, attached hereto and made a part hereof; and Contractor is willing to do such work under the following terms and conditions:

WHEREAS, the parties may wish to renew this Agreement on the basis of proposals for renewal which shall become a part hereof in lieu of Exhibit A in the event the renewal agreement is entered into;

NOW, THEREFORE, in consideration of the premises and mutual covenants and understandings herein contained the parties agree as follows:

I. TERM.

(a) The term of this Agreement shall expire one (1) year from the date of actual beginning of research work which date shall be within three (3) months of the execution date of this agreement. Contractor shall advise Sponsor of the actual date of initiation of research work.

(b) Either party may terminate this agreement at will upon sixty (60) days written notice to the other in which event the term of the agreement shall consist of the period from the initiation of research work to the effective date of such termination.

(c) Contractor shall advise Sponsor in writing as to the desirability of continuing or stopping the research work, at least ninety (90) days prior to the expiration date of the Agreement. If continuation be recommended, the statement shall be accompanied by a formal proposal for renewal outlining in detail the additional work recommended, the time needed and total cost of performing the recommended work. If Sponsor desires to accept the proposal for renewal, it shall notify Contractor in writing. Any renewal agreement shall expire automatically within the time set in the proposal for renewal, unless terminated earlier, provided that in no event shall the term of the renewal agreement be longer than one (1) year from the date of renewal.

(d) All terms and conditions of the present agreement shall apply to any renewal agreement except the proposal for renewal shall apply to the renewal in lieu of proposal, Exhibit A.

II. CONDUCT OF RESEARCH PROGRAM

Contractor shall initiate and conduct the subject research program in accordance with the attached proposal, Exhibit A. Contractor shall expend its best efforts to fulfill the requirements of this Agreement, and shall provide laboratory, supervision, personnel, equipment, and other facilities, as set forth in said proposal, Exhibit A.

III. COSTS

Sponsor shall reimburse Contractor for costs of the subject research program which shall not exceed the total cost stated in this proposal, Exhibit A. Contractor shall render itemized invoices, quarterly, for the costs actually incurred for the previous quarter, and Sponsor shall pay said invoices promptly upon presentation. Contractor shall keep books of account showing costs of the subject research program, which books shall be open to inspection by representatives of Sponsor.

IV. INVENTIONS AND PATENTS

(a) All inventions relating to the subject research which Contractor or any sub-contractor, or their personnel, engaged in this work, conceives or first reduces to practice during the term of this Agreement, or of any renewal thereof, shall become the property of Sponsor. This requirement applies, whether or not the inventions are patentable, and whether or not patent applications are filed on them.

(b) Contractor represents that it has required, or will require, each of its personnel engaged in work on the subject research to agree in writing (1) to disclose promptly to Contractor which, in turn, shall disclose promptly to Sponsor, any such inventions relating to this work, he conceives or first reduces to practice during the term of this agreement, and any renewal thereof, and (2) to assign to Contractor the entire right, title and interest, both for the United States and for countries foreign to the United States, in and to any such inventions, and (3) to execute at any time during such term or thereafter, all applications for patent covering such inventions, as well as any papers that may be necessary or helpful in the prosecution of applications for patents thereon.

(c) Contractor agrees to assign to Sponsor the entire right, title and interest, both for the United States and for countries foreign to the United States, in and to the aforesaid inventions, and at the request of Sponsor, to execute, or obtain the execution of, any and all papers, including applications for patent rights relating thereto, as may be necessary to vest in and secure to Sponsor the rights to be assigned as aforesaid to Sponsor; provided, however, that Sponsor shall bear all expenses incident to the preparation of such papers, and the filing and prosecution of such applications for patent as Sponsor may elect to file on such inventions.

(d) In any subcontract, Contractor shall include appropriate provision to require the subcontractor, and personnel of subcontractor, to assign inventions to Sponsor, which inventions are conceived, or first reduced to practice, by subcontractor or its personnel during the term of the subcontract, or any renewal thereof, and which relate to the subject research. Such provision shall correspond, as closely as possible, to the terms under which Contractor and its personnel are obligated to assign inventions to Sponsor.

V. PUBLICATIONS

Contractor and any subcontractor shall take reasonable precaution to keep results of subject research confidential, shall not disclose such results to unauthorized persons, and shall not publish such research results, unless prior written approval is obtained from Sponsor's Director of Research. In any subcontract, Contractor shall include appropriate provision to require the subcontractor to carry out the obligations of this Article V.

VI. LIAISON

Contractor shall advise of the name of the person who will maintain liaison with Sponsor's Director of Research, and Contractor will maintain such liaison to insure adequate communication as to changes, scope, objectives, acceleration or deceleration of the program. All instructions as to performance, and the program to be undertaken, shall be accepted only from Sponsor's Director of Research. Contractor shall notify Sponsor of any change in assignment of liaison personnel. When requested by Sponsor, Contractor will permit its personnel conducting subject research to meet with representatives of Sponsor's member companies to review over-all effort.

VII. RESEARCH RECORDS

Contractor and any subcontractor shall require their personnel engaged in subject research to keep a daily diary of work done. Contractor and any subcontractor shall maintain complete and detailed records of all work performed relating to subject research, together with their findings and conclusions relating thereto, which records shall be open at all times for inspection by Sponsor. In any subcontract Contractor shall include appropriate provision to require subcontractor to carry out the obligations of this Article VII.

VIII. REPORTS

Subject to the requirements of Article IX relating to inventions:

(a) Contractor shall furnish Sponsor with 75 copies of a formal progress report on subject research, and abstract-summary thereof, at quarterly intervals, or more frequently if the nature of results of the subject research warrants it. Contractor will advise firm date for the quarterly progress reports immediately after date of initiation of research work.

(b) Contractor shall furnish Sponsor with 200 copies of a detailed final or summary report, and abstract-summary thereof, at the close of each contract year and at the completion of the research program.

(c) In preparing such abstract-summaries Contractor agrees to the following requirements:

1. The abstract-summaries of the quarterly reports should be between about 100 and 500 words in length, nominally 300 words. They may contain brief tables but no figures, and must include statements concerning over-all objectives of the program, intermediate objectives during the report period, work accomplished toward these objectives in the report period, including a brief review of the experimental procedure, highlights of the results obtained, and a brief statement of future work to be conducted in the next report period.

2. The abstract-summary of the final or summary report should be between 750 and 1500 words in length, nominally 1000 words. This abstract-summary should contain a statement of the over-all objectives of the program, a statement of intermediate objectives, a summary of the work accomplished toward these objectives, including a brief review of experimental procedure, a discussion of the results obtained and the over-all conclusions drawn from the program.

3. The editorial style of these abstract-summaries should be similar to those in the A. E. I. - L. I. A. Expanded Research Program quarterly reports to

(INSTRUCTIONS TO CONTRACTORS)

OPERATING PROCEDURESEXPANDED RESEARCH PROGRAMAMERICAN ZINC INSTITUTE, LEAD INDUSTRIES ASSOCIATIONI. INTRODUCTION

The Expanded Research Program of the American Zinc Institute and the Lead Industries Association is sponsored by many of the major producers of pig lead and slab zinc located throughout the free world. Recognizing the need for additional research in our industries, particularly with respect to product research, these companies joined together through the existing American Zinc Institute and Lead Industries Association, where procedures had been established for collecting the funds necessary for such a research activity and where an effective means for bringing the industry's members together had been established. The Program, founded in 1958, is supported by assessments on the total production of pig lead and slab zinc of the participating companies regardless of where the resulting metals are sold. Because of the urgent need to develop new uses for lead and zinc as well as to remain competitive in existing markets, the Expanded Research Program concentrates on new product development and has excluded from its scope of activities any research on exploration, mining, beneficiation, smelting, and refining.

The participating companies are located throughout the world and for this reason the Expanded Research Program is truly an international undertaking and requires the full cooperation of all who participate. By this means the technical capabilities, market knowledge, as well as funds of our member companies are brought together through the Expanded Research Program to undertake the necessary research.

In order to get the program under way at the earliest possible moment, it was decided that we would use existing research facilities rather than attempt to build and staff a laboratory facility. For this reason we use every possible research source including such organizations as independent research institutes and foundations, government laboratories, the laboratories of our own participating companies, and colleges and universities. Our basis for selection of a specific source is that laboratory which we believe can most effectively conduct the research we desire, and the awards are based on merit rather than other considerations. As a result, with our research scattered widely across the world, the problems in communications can complicate our program; however, by effectively managing the operation, we believe the problems of distance can be greatly minimized. We have had many notable successes from the participating laboratories, and we recognize them as essential to our continued success.

II. SCOPE OF THE RESEARCH

As mentioned in the preceding paragraphs, our investigations are directed principally toward developing new knowledge about lead and zinc and their compounds as well as developing new uses for these materials. An essential part of the Program is to improve existing products so that they can remain competitive or achieve competitive superiority. A significant portion of our Program is in fundamental research to develop new information and with no commercial objectives assigned to these investigations.

In establishing our Program initially, our industries reviewed their present position and the competition they faced. The initial phase of the research was therefore concentrated on improving existing products to maintain their competitive position. The

enable Sponsor to include them in such quarterly reports.

IX. HANDLING OF INVENTIONS

Contractor shall promptly call Sponsor's attention to any research results flowing from the subject research performed by either Contractor or any subcontractor, which research results appear to contain patentable material. Contractor shall not include such patentable material in the reports required by Article VIII, but shall furnish Sponsor with 75 copies of a special report containing a full disclosure of such patentable material, which special report shall be marked "confidential".

X. EQUIPMENT

Nonexpendable equipment necessary to carry out the subject research, purchased or fabricated by Contractor, for which Sponsor's funds are expressly provided, shall remain the property of Sponsor. After termination of the agreement and any renewal thereof, Contractor shall deliver such equipment to such place as Sponsor may direct, at Sponsor's request and expense.

XI. INTERPRETATION

In the event of any inconsistency between Contractor's proposal, Exhibit A, or any proposal for renewal on the one hand and the Articles set forth at length in this agreement on the other hand the latter shall govern.

IN WITNESS WHEREOF, the parties have executed this Agreement of the day and year first above written.

Lead Industries Inc.
(sponsor)

By _____

(Title) _____

(Contractor)

By _____

(Title) _____

second major step was to investigate those areas which offered promise of new markets and to review our materials to determine where the fundamental knowledge of our materials was deficient. These suggestions came to us from within our industry and from outside sources. The major portion of our Research Program came from ideas generated within the frame-work of our industry. We are more than pleased to review unsolicited proposals for research, but it should be pointed out that the principal planning has come from within our own industries.

Where outside laboratories propose research to us for investigation we recommend strongly a preliminary review of these proposals with us so that unnecessary expense and time required for proposal preparation are avoided if the proposed research has already been done but the information is not generally available. We cannot exist nor conduct our Program without the research sources mentioned above. For this reason we are always pleased to meet with their people and discuss potential new areas for investigation.

III. WHERE IS OUR RESEARCH CONDUCTED?

We have used and are using every conceivable source of investigation from private organizations to government laboratories, from our industry laboratories to universities and colleges. As we have mentioned before, the awarding of a contract for research is based principally on merit and the capabilities of the individual laboratory. Research has been undertaken with organizations such as Battelle, Armour, and Arthur D. Little. We have used industry laboratories of our member companies as well as the industrial laboratories of associated companies. We have utilized the outstanding capabilities of government laboratories here and abroad and our fellowships have been awarded to colleges and universities throughout the world. At the present time we have research under way in Holland, England, Canada, Australia, and the United States. We have tried to establish a single procedure for all the participating organizations in order to minimize problems in communication, patents, and other contractual matters.

IV. PROJECT INITIATION

When we have determined that an area is deserving of investigation, the staff of the Expanded Research Program together with its industry committees, which will be discussed in following paragraphs, develop a work statement which defines the problem and establishes the scope and objectives of the research investigation. In the area of fundamental research, the definition of the problem is made as broad as possible to give flexibility to the investigator undertaking this research. The more applied the problem becomes, the easier it is to define the problem and delineate the scope of the research. This work statement is submitted to the potential contractor(s) for review and preparation of his research proposal.

As covered in following paragraphs, this proposal is, in many cases, the only contact between the contractor and those who will review and recommend acceptance of the proposal. Therefore, it is contingent upon the contractor to prepare his proposal as carefully as possible and to clearly and concisely state the program which he proposes to undertake. The proposal will be read and reviewed by the entire industry supporting this program; therefore, it is imperative that clarity and completeness be emphasized.

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If a problem is to be undertaken where a single contractor is clearly outstanding in the field, then the work statement is submitted only to that single source and his single proposal is reviewed by our industry. On the other hand, where a problem is rather broad in nature and there is no single laboratory so outstanding that a single source can be recommended, then the work statement and invitation to bid is submitted to more than one potential contractor. The proposals are required to be prepared and to be in our hands by a given date for industry review. Once the proposals are in our hands, it may take from one to three months before award of the contract. If no suitable proposals are received, it is obvious that new invitations to bid will be requested. As has been mentioned before, our basis for selection is the capability of the people who will undertake the research, and this is expressed by the program outline and proposal for the investigation to be undertaken.

In preparing the proposal the contractor should provide a detailed outline of the program and method of attack. Where possible a time schedule should be included where a new product or products are to be evaluated to meet specific markets. As defined in the statement of the problem, the procedures for evaluation should be spelled out (i.e. corrosion testing, analytical data, physical property determination, etc).

A. Personnel and Capabilities

Following this a paragraph or paragraphs should be included which list personnel to be assigned to the experimental phase of the project, the supervision which will be provided, the experience and qualifications of professional engineers and/or scientists to be assigned to the work, the man-year effort to be devoted to the project as proposed - broken down as to professional and subprofessional man-years, the experience of your organization as a whole in the field, together with a listing of pertinent publications or research which has been done by your organization in the particular field in question.

B. Facilities and Special Equipment

Where unique facilities or highly specialized equipment are required for the study, an itemization of this equipment together with a statement of the capabilities of your people in operating this equipment is necessary. When purchase of equipment is necessary, the arrangements under which it will be provided must be specified.

C. Subcontractors

A statement is to be included as to whether or not any of the program is to be sub-contracted, itemizing the subcontractor(s) to be selected, work he will carry out, and the need for such work outside the prime contractors facilities.

D. Project Expenses

1) Proposal - The proposed bid should also include an itemization of costs broken down as to personnel, special equipment, overhead and materials. It should also advise payment requirements (i.e., monthly, quarterly, or annually). If advance payment is necessary, note should be made of this fact.

2) Payment - All bills should be submitted to the Director of Research of the Expanded Research Program, American Zinc Institute and the Lead Industries Association for approval for payment.

V. PROJECT AND PROPOSAL REVIEW AND SCREENING

Regardless of whether the proposal is from a single source or a set of proposals received as a result of an invitation to bid submitted to more than one contractor, these proposals are submitted first to our technical working committees, either for lead or zinc as the case may be. There are three committees which operate in each of these industries.

A Metallurgical Subcommittee has been established which reviews research on mechanical behavior of our materials, physical metallurgy, techniques for producing consumer or industrial products, architectural applications, and the like.

A Chemical Subcommittee reviews all that research which pertains to paints, porcelain, ceramics, organic and inorganic chemicals, and related products.

The Electrochemical Subcommittee monitors those projects which deal with corrosion, power packages (batteries), electroplating and related processes, and cathodic protection.

Based on approval of and a selection of the best proposal submitted by the contractor(s), the project selected by the appropriate technical subcommittee is submitted to the Technical Steering Committee which reviews the selected proposal on the basis of scope, and its place in our over-all Research Program, and provides a second broad technical review of the potential of the project. After approval at the Technical Steering Committee level the selected project is submitted to the Industry Development Committee of the appropriate industry, where it is reviewed for its market potential or the general need for information (fundamental research). After approval at the marketing level it is submitted to the Board of Directors for final approval of the expenditure of funds and for assessment of the participating industry members, so that from a financial standpoint, the research can be undertaken. After receipt of approval at the technical working level, the technical policy level, the sales level, and the management level, the Director of Research will award the contract, as approved, to the selected contractor and at that point the research is initiated.

As the contractor submits reports (to be discussed in subsequent paragraphs) these reports are submitted to the Technical Subcommittees and to the Technical Steering Committee for review and critique of the research results. Our participating members frequently submit suggestions, comments, and recommendations to the Director of Research who in turn passes these comments, plus his own, to the contractor for review. In the event that it is believed that the contractor is not conducting the research with appropriate emphasis and technique, the Director of Research will contact him and arrange for a necessary meeting with the steering committee and the Director of Research to clarify the problems in question. In a manner similar to that described above, the committees at all levels review the research at the completion of the contract to consider renewing the contract and continuing the investigation in subsequent years. The mechanism for review and screening is exactly as covered before.

VI. BUDGET PLANNING

In the fall of each year the various technical subcommittees meet to review the research under way and to either recommend cancellations or continuation of the research. At these meetings the committee will also consider new areas of research based on ideas developed by the industry or submitted to the industry from outside sources. While the great majority of the program is developed at this time (starting on or about September 1) new contracts can be initiated any time during the year.

At the budget meetings, those contractors who can readily visit with our committees (the meetings are usually held in New York City) are invited to attend to discuss the research which they have undertaken in the past, their proposals for continuation, or their submission of proposals for new investigations. This personal contact with the working committees permits a full exchange of information and can clarify any matters which are not effectively handled in the normal written reports.

It should also be pointed out that meetings may be held during the year at which time the contractors will be invited to meet with the committees at a central point or it may be arranged to have the technical committees meet with the contractor at his facilities to review the research, meet the personnel undertaking the investigation, and examine samples, processes, etc.

Referring again to the budget meetings, the working technical subcommittees review the entire proposed program and recommend the problems to be investigated and suggest the sums which they feel should be spent to conduct the research in question. Then the proposed budgets of each of the Technical Subcommittees are consolidated and submitted in toto to the Technical Steering Committee of the appropriate industry group (lead or zinc). After a second technical review, they are submitted to the Industry Development Committee where market potentials are considered, and finally to the Board of Directors for final approval and assessment of the participating companies to obtain the funds necessary to support the research in question.

While this may appear to be a complicated procedure, it is actually quite simple and is entirely analogous to the handling of research budgets in individual companies with the single exception that a more thorough and complete review and screening is given our proposed research program than ordinarily occurs in any individual company.

Once the program has been approved and all the individual projects selected, the Research Director will advise the contractor of renewal of his contract or will develop work statements and submit invitations to bid to appropriate contractors for proposal preparation for new projects as covered above.

VII. APPENDIX A - EXPANDED RESEARCH PROGRAM GENERAL CONTRACT

Attached to this document as "Appendix A" is a sample of the Expanded Program general contract. For the most part this contract is to be accepted as submitted; however, in certain cases we will negotiate such changes as may be required to arrive at a mutually satisfactory document. If at all possible, we recommend that potential contractors accept the contract as submitted as it has been developed over a number of years to suit the particular requirements of our industries.

It should be pointed out that all contracts cover only a one-year period, and that they are automatically cancelled at the end of that contract year without notice. All contracts are to contain a cancellation clause as shown in the attached document. It should be clearly understood that this cancellation at the end of the contract year is firm, and that no notice need be provided the contractor. If the contract is on a calendar year basis (i.e. from January 1 to December 31 of a given year) he must submit recommendations for renewal of the contract in accordance with our normal budget planning procedure. On the other hand, if the contract has been initiated during the calendar year, and if he recommends continuation of the research effort, then he must submit to the Director of Research of the Expanded Research Program such a recommendation for continuation together with a brief outline of the proposed work to be carried out on the subsequent phase of the investigation, and a statement of funds required in a manner similar to submission of the original

proposal. The Director of Research will immediately forward the proposed proposal for continuation of the research to the committees for review and screening. If submitted to the Director of Research no later than 90 days prior to termination of the contract, sufficient time will be provided to permit the contractor to continue his work immediately upon completion of the most recent phase of the investigation.

The contractor will note the requirements on patents and publications, contract initiation, termination, extension, cost, and payment clauses. Reference is also made to equipment and to communications with the Director of Research. The contractor's authority for initiation of the contract, for change in scope, for submission of reports, etc. is the Director of Research of the Expanded Research Program, and the contractor is to accept instructions from no other source.

With regard to personnel and capabilities, the contractor is obligated to advise the Director of Research of any change or reassignment of personnel conducting the investigation. In the original proposal, the personnel to conduct the research have been listed and therefore any changes to this personnel assignment must be brought to the attention of the Director of Research of the Expanded Research Program at once.

The Director of Research of the Expanded Research Program reserves the right to review critical research reports prepared by the contractor as well as the fiscal data covering the bills which are submitted to the Expanded Research Program for payment. This is to clarify any problems which may arise with regard to payment and/or ultimate patenting of inventions arising out of this research.

VIII. REPORTING PROCEDURE

Attention is also called to the requirements for report submission. Unless otherwise noted, all progress reports will be required on a quarterly basis. If, however, a critical phase of the program is reached requiring an immediate report such report may be made even though it does not fall within the normal quarterly period. It may also be necessary to have reports submitted on a monthly or bimonthly basis rather than on a quarterly basis. Unless other arrangements are made with the Director of Research, quarterly reports will be required. 75 copies of all reports are to be sent to the Director of Research of the Expanded Research Program. At the close of each contract year, however, or on completion of a particular research program, a detailed final or summary report is to be submitted to the Director of Research of the Expanded Research Program in the amount of 200 copies. These reports are most important in advising our supporting members of the research being undertaken and the progress of the program. This reporting system is the most effective means of communication between the contractor and those supporting the program through the Director of Research of the Expanded Research Program.

Because of the many industries and organizations associated with the lead and zinc industries, it is necessary that the results of each program be given wide distribution. This is accomplished by distributing a quarterly report issued by the Director of Research of the Expanded Research Program in which the progress of each contract is concisely summarized. To facilitate compilation of this report each contract quarterly report and summary report must include an abstract-summary of the work accomplished during the last period for direct inclusion in the Expanded Research Program quarterly report. The abstract of the quarterly report should be between 100 and 500 words in length and may include brief tables of data obtained but no figures. It should include statements concerning over-all objectives of the program, intermediate objectives reached during the report period, work accomplished, and a brief review of the experimental procedure and high lights of the results obtained. It should also include a brief statement of future work to be conducted in the next report period. On the other hand, the abstract for the summary report should be between 750 and 1,500 words and contain a statement of the over-all objectives of the program, a statement

of the objectives achieved, together with a brief review of experimental procedures, a discussion of the results obtained, and conclusions drawn from investigation undertaken. The editorial style of these abstracts should be similar to that in the Expanded Research Program quarterly report, a copy of which is attached for your review.

In preparing quarterly reports and/or phase reports, the contractor is advised to exclude from those reports such critical data as may effect obtaining patents on inventions developed during the conduct of this research. It is imperative that where these data are developed, the Director of Research be advised and separate confidential reports made to him detailing the results obtained and the fact that these data will be critical in preparation of patent applications. Since the reports submitted to the industry are circulated widely within the industry, and the Expanded Research Program quarterly reports are internationally distributed, it is incumbent on the contractor to be cognizant of those data which will be pertinent to the patentability of the inventions arising out of our research efforts. The confidential report will be reproduced as directed by the Director of Research.

None of the research results of the contract in question are to be published or presented at technical meetings unless cleared in advance by the Director of Research of the Expanded Research Program. We feel it is our prerogative to have such information released in areas where it can be of greatest benefit to the lead and zinc industries. However, our basic policy is to disseminate the results of our research widely.

IX. INDUSTRY ASSISTANCE

The contractor working with lead and zinc is advised that a tremendous storehouse of knowledge is available within these two industries. Should he encounter problems in such critical areas as metallography, analysis, and the like, the Director of Research should be contacted immediately so that the necessary assistance can be provided the contractor.

This should also apply when sample materials are required or other critical data not available in the contractor's library or background. Because of the outstanding cooperation given by our industries to the Expanded Research Program, we can assure you of the wholehearted support of our member companies regardless of their location.

The cooperation between the member companies is outstanding. The contractor will find that his difficulties can in many cases be solved by means of a telephone call or letter detailing the assistance required, and in turn the Director of Research has behind him the technical background and capabilities of these two outstanding industries to assist in every way possible. The contractor will be aided by every means possible through the close working relations of the member companies and the technical committees which screen and review the work in question. In addition, in certain critical areas, we are indeed fortunate to have the cooperation and assistance of related industries who can provide further help and assistance to the contractor. The point of contact in seeking such help is through the Director of Research of the Expanded Research Program.

X. LIAISON WITH THE EXPANDED RESEARCH PROGRAM

As covered in the contract requirements, the contractor is to advise which person or persons in the contractor's organization will maintain contact with him to insure adequate communication as to objectives, changes in scope, acceleration or deceleration of the program. Instructions as to the performance on the contract, and any changes to be carried out by the contractor, are to be given only by the Director of Research of the Expanded Research Program and through no other source. This is to insure minimum conflict in conducting the investigation in question. This communication also applies to reassignment of personnel on the part of the contractor as covered in preceding paragraphs. As mentioned above, the Director of Research or the staff of the Expanded Research Program will make periodic visits to the contractor's facilities to discuss the program and the progress of the research. It may also be advisable to have the Technical Subcommittees and such other industry representatives as may be designated to visit with the contractor at his facilities or have the contractor's representatives meet with the Director of Research and industry representatives at mutually suitable points. The contractor is urged to maintain close liaison with the Director of Research and his staff to insure minimum conflict and most efficient progress of the research in question.

XI. PATENT POLICY

As covered in our general contract, all inventions relating to the research conducted by the contractor or his technical personnel or subcontractors, first reduced to practice during the term of this contract or any extension thereof, become the property of the Expanded Research Program of the American Zinc Institute and the Lead Industries Association. This requirement applies whether the inventions are patentable or not and whether or not patent applications are filed on such inventions. This requirement also applies to subcontractors and their employees. The contractor, subcontractor, and their technical personnel shall sign appropriate applications for patents and assignments at the request of the Expanded Research Program and shall assist the Expanded Research Program in every reasonable way to maintain and enforce patent protection for the Expanded Research Program in the United States and in other countries of our choice.

As covered above, the contractor shall delete from appropriate reports submitted for distribution such patent information and crucial data which would seriously affect obtaining patents on the inventions or which would disclose critical know-how of inventions developed. This may be accomplished by exclusion of these data from the normal reports submitted by the contractor and included in a separate confidential report appropriately marked, or by having separate detachable sections of the report marked "confidential". This information must be handled in this manner so that there would be no effective disclosure which would hamper subsequent issuance of patents. Where the contractor takes such action (i.e. preparing a confidential report) the Director of Research should be informed so that he can in turn make appropriate arrangements for disclosing this information to the companies which provide the financial support for this entire program.

By and large patents are obtained to enhance utilization of the results achieved by this program and generally are not to be classified as restrictive unless such restriction would insure ultimate use of the results of our research effort. The declared patent policy of our Program is as follows:

The American Zinc Institute and Lead Industries Association will obtain patents in the United States and foreign countries where warranted by technical considerations or potential commercial usage. In general, the rights to both patented and unpatented inventions owned by the two organizations will be licensed on a non-exclusive, unrestricted basis in such manner as to assure maximum usage of the invention at the earliest practical date. Reasonable royalties may be charged in appropriate cases.

XII. FELLOWSHIP PROGRAMS

The major portion of the requirements detailed above apply to those contracts which are principally of an applied nature. Many of these requirements do not apply to our fellowship program as we recognize the essential difference between the normal industrial research carried on above as contrasted to assistance to students and academic institutions, particularly those students pursuing advanced degrees. Our principal objective in our fellowship effort is to support graduate research preferably at the Ph.D. level. Our major requirement is that the research be conducted in lead or zinc depending on the source of funds, that is whether the funds for the fellowship effort are to be supported by the zinc industry or the lead industry. While we may suggest research in a critical area such as in the application of lead in glasses and glazes or in porcelain enamels, we are always happy to consider the suggestions of the faculty and/or the student for a research investigation in our area of interest.

In order that the schools may select the best possible people for our Program, we will advise the institution immediately after the first of the year that a fellowship will be awarded to the institution. We would appreciate maximum advertising of the fellowship in appropriate bulletins and upon receipt of advice from the colleges or university funds will be provided the school to support the fellowship in question.

In order that we may continue to receive full support of our industry for this fellowship program, we feel that effective communications must be established between the school and ourselves so that we can advise the industry of the students who are recipients of the fellowship, and the problem to be investigated. We wish to receive once each quarter a simple letter report indicating how the investigation is proceeding. This is not to be construed as the formal quarterly report to be required for industrial-type contracts, but is simply a statement of the results achieved through the student's investigation. Ultimately we wish to obtain copies of the thesis developed through the research sponsored by our program.

We feel this fellowship program is very vital, and we are interested in its growth and continuation. To achieve this, it is obvious that effective communications are the only means whereby we can achieve such continuation and maintain the interest of our industry people.

In turn, through the quarterly report prepared and issued by the Expanded Research Program, the school, the department, the supervisor, and the student will receive publicity as each fellowship is announced and the work discussed in our reports.

We strongly urge that members having any questions regarding our Program and its continuation feel free to contact the Director of Research of the Expanded Research Program to clarify any question. In turn, we are pleased to meet with members of the faculty or the administration of the university or college where necessary. We cannot help unless we know about problems which may arise. Correspondingly, we can only obtain future support for the program if we are advised as much as possible regarding

activity on the programs being undertaken at the universities. We plan to have a member of the Expanded Research Program staff to meet with the faculty member concerned and the fellow each year to enhance our working relationship and to insure an effective fellowship program.

February 14, 1961

Shad H. Pratt