MOUND LABORATORY PROGRESS REPORT FOR NOVEMBER 1960

Date: November 30, 1960

Issued: APR 23 1961

The Mound Laboratory Progress Report, issued monthly, is intended to be a means of reporting items of current technical interest in research and development programs. To issue this report as soon as possible after the end of the month, editorial work is limited; and since this is an informal progress report, the results and data presented are preliminary and subject to change.

These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports.

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO CHEMICAL COMPANY

M O U N D L A B O R A T O R Y

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. GOVERNMENT CONTRACT NO. AT-33-1-GEN-53

This document is
PUBLICLY RELEASABLE

Hughy Kinner
Authorizing Official

Date: *5/26/09*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	Page
<u>PLASTICS RESEARCH</u>	3
Plastics	3
Adhesives	3
<u>RADIOELEMENTS</u>	7
Half-Life of Radium-223	7
Ionium Project	11
<u>REACTOR DEVELOPMENT PROGRAM</u>	12
Plutonium Alloy Research	12
Plutonium-Bearing Glass Fibers	13

PLASTICS RESEARCH

Work is being directed at the development of methods of producing plastics and adhesives having characteristics superior to those currently being used at Mound Laboratory and elsewhere. Variations in plastic formulations and molding procedures are being studied in an effort to produce plastic which consistently meet specifications.

PLASTICS Physical testing and evaluations of Dacron*-filled diallyl phthalate produced in the Plastics Production Facility were performed during this report period. Tensile strengths, run on every third batch from W-48 through W-75, gave an average figure of 4,280 pounds per square inch. Impact resistance tests resulted in an average impact strength of 3.88 foot pounds per inch of notch.

The Watson-Stillman press is again available and the new four-guide-pin cup flow die has been installed. The "break-in" has been accomplished and after minor adjustments, it will be possible to obtain final evaluation data on the Dacron-filled material.

ADHESIVES The Plastics Research Group gave technical assistance in the development of a quality control program for the two adhesives.

The description of these two adhesives follows:

1. Two parts Epon⁺828, an epoxy resin, to one part Versamid^{**}140, an amine curing agent. This is a room-temperature curing adhesive with a pot life of several hours.
2. Five parts Goodrich A-916-B, ⁺⁺ a commercial adhesive; 5 parts MEK, a solvent; 3 parts Epon 828, an epoxy resin; and 7 parts Versamid 140, an amine curing agent. This adhesive must be oven-cured at approximately 150° F for 4 hours. The material is used as a binder for Kel-F.

A tensile test of a dogbone casting made from the 828: 140 glue and a peel test for the Kel-F glue was performed. The following is an abbreviated description for these tests.

Tensile Testing of Epon 828: Versamid 140 At least three test specimens per batch were made by pouring the adhesive into Teflon molds. The mold cavity is an ASTM-D412-51T, Die-D shape. After a 24-hour room-temperature cure, the specimens should be tested at 0.5 inches per minute travel rate of the Instron cross-arm.

The criterion for acceptable material will be the shape of the stress-per cent elongation curve. The shape of the reference curves will be determined when a testing machine is installed in the production area and dogbones are cast in Die-D molds. Figure 1 is a graph of experimental curves which illustrate the effect variation of formulation has on the shape of the stress elongation plot. Figure 2 illustrates the effect of cure time on the stress-per cent elongation curve. These curves were obtained with a Die-C dogbone at 1.0 inch-per-minute test speed, and are the type which will be determined for the quality control testing.

Peel Testing for Kel-F Adhesive This test follows Federal Test Method Standard 175, 1041.1 fairly closely. The test rate is 5 inches per minute rather than the standard 6 inches per minute and the bonded area is 3½ inches long rather than the standard 6 inches.

* Trademark of Food Machinery and Chemical Corp.
† Trademark of Shell Chemical Corp.
•• Trademark of General Mills, Inc.
++ Trademark of Goodrich Chemical Corp.

FIGURE 1. STRESS VS. % ELONGATION CURVES OF EPON 828 - VERSAMID 140 MIXTURE CURED 24 HOURS AT ROOM TEMPERATURE (TESTED AT 1.0 INCH/MINUTE GRIP SEPARATION)

FIGURE 2. STRESS VS. % ELONGATION OF EPON 828 - VERSAMID 140 MIXTURES OF 20:1
FOR DIFFERENT ROOM TEMPERATURE CURE TIMES

The test specimens are made from two 0.015-inch thick Kel-F sheets. The glued sheets are air-dried for 30 minutes, then sandwiched, clamped and baked for 24 hours at 150°F. The sheets are cut into 1.0-inch wide specimens. At the same end of the 3½ inch glued length, one strip has a 2½ inch tab which fits into the lower test jaw. The other strip has a 6½ inch tab which is bent back at 180° to the first tab and placed in the upper jaw. A thin rigid member is placed in the lower jaw to hold the 180° angle during the test. A minimum of 20 lbs. force per inch width should be obtained for an acceptable test.

The technique of casting dogbones of Furane* resin adhesives, currently used in production processes, was tried with some success.

Tensile strength for one, three and seven-day cures on production material were 344, 955, and 1480 psi, respectively. Assuming that the material is fully cured after seven days, after one day the tensile strength had reached 23 per cent of its final strength. After the seven-day cure there was only 0.0215 inches elongation at break while after one day there was 0.608 inches. Further tests will be made to explore the usefulness of this technique in Furane testing.

Film Tensile Testing Some work has been done on testing films of Adiprene 100L Epoxy, MOCA mixtures and further testing of the Adiprene 100L: MOCA, formulation of 12:1 using new techniques of data evaluation.

* Trademark of Furane Plastics, Inc.

RADIOELEMENTS

Processes are being developed for separating and purifying radioelements and potential sources of supply are being evaluated.

HALF-LIFE OF RADIUM-223 Methods are being investigated for the preparation of carrier-free radiochemically pure radium-223. A carrier-free sample is desirable to permit its evaporation to the small volume required by the microcalorimeter.

Emphasis during the past month has been on developing an analytical procedure for determining traces of long-lived impurities in the purified radium-223. Because radium fluoride is soluble in acid solution, while actinium and thorium fluorides are quite insoluble, a relatively simple method would consist of co-precipitating traces of actinium and thorium with cerous fluoride. The radium-223 would be expected to remain in solution.

A series of tests was run to determine the efficiency of the cerous fluoride separation:

A solution of actinium-227 in equilibrium with its decay products (AEM) was used as source material. One milliliter of AEM was transferred to a 15-milliliter centrifuge tube with one milligram of cerium (III) carrier and varying amounts of barium holdback carrier. The solution was diluted to nine milliliters with 0.1 normal nitric acid and mixed. One milliliter of approximately one normal hydrofluoric acid was added, and the mixture was stirred for fifteen minutes. The cerous fluoride precipitate was centrifuged down and the supernate decanted to a second centrifuge tube. One milligram of cerium (III) carrier was added to the fluoride supernate, and the mixture was stirred for fifteen minutes. The precipitate was centrifuged down and the supernate decanted to a third centrifuge tube. Sufficient barium carrier was added to the fluoride supernate to make a total of 10 milligrams of barium. The solution was mixed, and two drops of 50 per cent sulfuric acid was added. The mixture was stirred fifteen minutes and centrifuged. The supernate was discarded, and the barium sulfate precipitate was washed with 0.1 normal nitric acid. The mixture was centrifuged, and the supernate was discarded.

The two cerous fluoride precipitates and the barium sulfate precipitate were mounted on stainless steel disks, evaporated to dryness, ignited at red heat, cooled, and alpha-counted daily to determine the distribution of actinium-227, and thorium-227, and radium-223.

A one-milliliter sample of AEM was mounted directly on a stainless steel disk and used as a standard for determination of the yields of the three principal radioelements in the various fractions. No self-absorption correction was made for the cerous fluoride. The barium sulfate alpha-counting yield was taken as 85-per cent. The results are shown in Table 1.

Table 1

A - DISTRIBUTION OF ACTINIUM-227 AS A FUNCTION OF BARIUM HOLDBACK CARRIER

Ba Added (mg.)	First CeF ₃ (%)	Second CeF ₃ (%)	BaSO ₄ (%)	Total Recovery (%)
0	93.7	-	-	93.7
0.006	89.8	2.3	-	92.1
0.5	97.1	0.7	3.4	101.2
2.2	91.7	10.6	2.9	105.2
5.0	68.4	8.9	3.4	80.7

B - DISTRIBUTION OF THORIUM-227 AS A FUNCTION OF BARIUM HOLDBACK CARRIER

0	92.6	1.1	-	93.7
0.006	92.1	-	-	92.1
0.5	82.2	1.9	0.1	84.2
2.2	77.4	6.0	0.8	84.2
5.0	66.3	6.7	1.0	74.0

C - DISTRIBUTION OF RADIUM-223 AS A FUNCTION OF BARIUM HOLDBACK CARRIER

0	92.0	1.3	0.4	93.8
0.006	90.7	1.3	0.2	92.2
0.5	18.9	19.9	55.8	94.6
2.2	7.1	7.0	92.9	107.0
5.0	2.8	3.5	99.6	105.9

The results in Table 1 show that the actinium and thorium behaved as expected; coprecipitation on cerous fluoride was essentially quantitative for all experiments. (No significance should be attached to the apparently wide variations in total recovery, because of the difficulty of obtaining reproducible counting data from slurry mounts.) In all cases, the bulk of the actinium and thorium appeared in the first cerous fluoride precipitate, with small residual amounts being taken up by the second precipitate.

The radium-223, however, was almost quantitatively carried by the first cerous fluoride precipitate when barium holdback carrier was absent. Even the presence of 0.5 milligram of barium did not prevent substantial loss of radium-223.

It is extremely unlikely that this coprecipitation is due to an inherent difference in the chemical behavior of radium and barium. It is more probable that traces of sulfate in the AEM or in the reagents caused radiocolloid formation followed by surface adsorption of the carrier-free tracer.

To test the effect of volume on the coprecipitation of radium-223, a group of three experiments was run, in which the volume was doubled, other conditions remaining the same. There was no significant difference in the distributions of the radioisotopes from those shown in Table 1.

To test the effect of acidity, one experiment was run in which the nitric acid concentration was increased from 0.1 normal to one normal. A slight improvement in the recovery of the radium-223 was noted (4.2 per cent as compared with 0.4 per cent).

To provide a source of radiochemically pure radium-223, a sample of AEM was passed through an anion exchanger prepared from Dowex^{*}-1 resin (8 per cent cross-linked, 200-400 mesh). The following procedure was used:

Insert a small glass wool plug in the tip of a medicine dropper. Transfer to the dropper enough Dowex-1X8 resin to form a column approximately one inch high. Wash the resin with distilled water, and stir it with a small glass rod. Allow the resin to settle, and remove the fine particles. Repeat the washing until the resin settles rapidly, leaving a clear supernate. Check the flow rate of the column under a full (one-milliliter) head of distilled water. (The flow rate should be about five minutes per milliliter.)

Convert the resin to the nitrate form by passing approximately five milliliters of 50 per cent ammonium nitrate solution through it. Check the effluent solution for chloride ion by adding one drop of five per cent silver nitrate solution to a milliliter of effluent. Continue passing ammonium nitrate through the column until the addition of silver nitrate produces no turbidity within one minute.

Pass through the resin a dilute ammonium hydroxide solution prepared by adding three drops of concentrated ammonium hydroxide (from a fresh stock bottle) to three milliliters of recently boiled and cooled distilled water. Allow the column to drain until there is no head of liquid above the resin. Discard the effluent solution.

To a sample of AEM in dilute nitric acid add one drop of phenolphthalein indicator and enough concentrated ammonium hydroxide to make the solution ammoniacal. Mix the solution, and transfer it to the anion exchange column. Collect the effluent solution in a volumetric flask. Allow the column to drain to the top of the resin. Wash the original vessel four times with dilute ammonium hydroxide prepared by adding one drop of concentrated ammonium hydroxide to one milliliter of recently boiled and cooled water. Transfer the wash to the column and collect the effluent in the volumetric flask, allowing the column to drain to the top of the resin after each wash.

To the volumetric flask, add one drop of phenolphthalein indicator and enough dilute nitric acid to make the solution at least 0.1 normal in acid. Dilute the solution to volume with distilled water, and mix it thoroughly.

Recover the actinium-227 from the resin by washing the column with three milliliters of distilled water and three milliliters of 0.1 normal nitric acid.

Transfer an aliquot of the solution in the volumetric flask to a 50-milliliter centrifuge tube. Add one milligram of cerium (III) carrier. Add barium carrier in the amounts indicated in Table 2. Dilute the solution to ten milliliters with 0.1 normal nitric acid. Add one milliliter of one normal hydrofluoric acid. Stir the mixture fifteen minutes. Without centrifuging, add one milligram of cerium (III) carrier and stir fifteen minutes. Centrifuge the mixture and discard the supernate. Wash the precipitate by adding 10 milliliters of 0.1 normal hydrofluoric acid and stirring for five minutes. Centrifuge five minutes, and discard the supernate.

Transfer the cerous fluoride precipitate, as a slurry in distilled water, to a stainless steel disk previously prepared with a one-quarter inch retaining ring of Krylon plastic spray coating. Evaporate the slurry to dryness, and ignite the disk at red heat. Allow six hours for the decay of lead-211, and alpha count the sample daily to determine the radioisotopic composition. The results are shown in Table 2.

^{*} Trademark of Dow Chemical Company

Table 2

**RADIUM-223 CARRIED BY CEROUS FLUORIDE AS A
FUNCTION OF BARIUM HOLDBACK CARRIER**

Barium Holdback (mg)	Radium-223 Carried (%)
0	83.3
1	8.2
10	2.5
50	0.3
100	0.6

The results in Table 2 are compatible with those in Table 1-C, showing that the addition of barium holdback carrier is necessary to prevent substantial coprecipitation of radium-223 on cerous fluoride. Even the relatively massive addition of 100 milligrams of barium did not prevent some carrying of radium-223.

Differential decay analysis indicated that the ammonium hydroxide effluent from the anion exchange column contained approximately 0.25 per cent of the original actinium-227 and 88.8 per cent of the original radium-223. Only 1.2 per cent of the decay of actinium-227 is by alpha emission, while the alpha count from radium-223 in equilibrium with its short-lived decay products is four times that of the radium-223 alone. Thus, the coprecipitation of as little as 0.5 per cent of the radium-223 would have a significant masking effect in any attempt to analyze for actinium-227 directly. An improved separation method was, therefore, desirable.

To an aliquot sample of the ammonium hydroxide effluent 0.5 milligram of iron and one milligram of cerium (III) carriers were added. The solution was diluted to 10 milliliters with 0.1 normal nitric acid and made just alkaline to phenolphthalein with concentrated ammonium hydroxide. The mixture was stirred for five minutes and centrifuged. The supernate was discarded, and the precipitate was dissolved in two drops of concentrated hydrochloric acid. The solution was diluted to 10 milliliters with distilled water, and one milliliter of one normal hydrofluoric acid was added. The mixture was stirred fifteen minutes, and one milligram of cerium (III) carrier was added. The mixture was again stirred for fifteen minutes and centrifuged. The supernate was discarded and the precipitate was washed with ten milliliters of 0.1 normal hydrofluoric acid. The mixture was centrifuged, and the supernate was discarded. The precipitate was mounted and alpha-counted.

Differential decay analysis showed that the cerous fluoride carried 0.7 per cent of the radium-223. Since no barium holdback carrier was added throughout the separation, this represented a considerable improvement over the results obtained with direct cerous fluoride precipitation.

A further improvement was made when the experiment was repeated with the addition of 10 milligrams of barium holdback carrier in the ferric hydroxide step and ten milligrams of barium in the cerous fluoride step. The cerous fluoride precipitate carried 0.03 per cent of the radium-223. Differential decay analysis indicated that the impurity in the radium-223 fraction (ammonium hydroxide effluent) was not 0.25 per cent of the actinium-227 as previously estimated, but 0.1 per cent of the thorium-227.

Further development of the analytical procedure will be needed to establish yield factors for the actinium-227 and thorium-227, but it now seems certain that an acceptable analytical procedure will be available for determining trace impurities in highly purified radium-223.

IONIUM PROJECT A survey is being made of potential sources of thorium-230 (ionium) in the United States. Thus far, 49 samples have been received from 17 uranium mills or processing sites. In addition several samples of "airport cake" from Mallinckrodt Chemical Works, retained from previous ionium processing, are available for comparison.

The procedures used to analyze the samples have been reported previously (Monthly Technical Activities Reports for 9-15-60 and 10-15-60). The only change in these procedures has been to double the amount of concentrated nitric acid used to digest the solid samples.

Nine more samples have been analyzed. Two of the samples compare favorably with the "airport cake" (28A). Sample 8D is a solvent extraction raffinate. This sample has the second highest apparent ionium content of all the liquid samples analyzed thus far. By virtue of the large capacity of the mill, the sample indicates the highest potential of any of the liquid samples. Sample 18E, a solid, has an apparent ionium concentration nearly as high as that of the "airport cake."

Because the Frisch grid analyzer is still inoperative, isotopic ratios for the analyzed samples are not yet available.

REACTOR DEVELOPMENT PROGRAM

REACTOR FUELS AND MATERIALS DEVELOPMENT

Reactor fuels and materials development includes research, development and design incident to the development of materials or techniques which lead to higher performance and/or lower costs for full scale power reactors.

Plutonium Alloy Research *Plutonium, which has a high neutron efficiency, is being considered for use in reactors of the fast breeder type. Mound Laboratory has been given the responsibility for acquiring data on some of the proposed fuel systems, and for maintaining technical cognizance of fuel cycle problems associated with the fast breeder reactors. Research has been initiated to determine the density, viscosity, thermal capacity, thermal conductivity and phase equilibria of plutonium and plutonium alloys proposed as fuels for these reactors.*

Metallographic work continued on the copper-plutonium binary system. All samples with composition above 81.8 atom per cent copper have been polished and photographed, and microhardness measurements of the different phases were made. Table 1 gives the compositions of the alloys, and the microhardness of the phases present. No significant departures were noted from the diagram obtained by differential thermal analysis.

Table 1

METALLOGRAPHIC EXAMINATION IN THE Pu-Cu BINARY SYSTEM

Composition a/o Cu	Condition of sample	Phase identified	(Vicker's Hardness Number)
81.8	slow-cooled	Pu ₄ Cu ₁₇ Pu ₂ Cu ₁₁	322-413 193-309
83.3	slow-cooled	Pu ₄ Cu ₁₇ Pu ₂ Cu ₁₁	390-464 240-320
83.3	annealed	Pu ₄ Cu ₁₇ Pu ₂ Cu ₁₁	345-429 177-322
84.6	slow-cooled	Pu ₄ Cu ₁₇ Pu ₂ Cu ₁₁	317-454 193-254
84.6	annealed	Pu ₄ Cu ₁₇ Pu ₂ Cu ₁₁	376-397 123-157
88.0	slow-cooled	Pu ₂ Cu ₁₁ Cu	105-283 112
88.0	annealed	Pu ₂ Cu ₁₁ Cu	227-327 114-117

The polishing procedure has been altered somewhat in that a proprietary diamond paste thinner called "Dymo Thinner"* is used as a lubricant for the 0.1 micron alumina wheel. This procedure gives a protective coating on the surface of the specimen and appears to be useful for alloys high in plutonium and cerium, where oxidation of the surface during polishing is a problem. Air is excluded from the sample, giving a shiny oxide-free surface.

* Trademark of Elgin National Watch Co.

Construction work of the high temperature calorimeter which will be used to measure the thermal conductivity and the heat capacity of fuel material at elevated temperatures, has been resumed. The construction was delayed because of fabrication problems encountered in the production of beryllia coil forms, which will support the platinum resistance bridges of the calorimeter. Beryllia was chosen for this application because of its high electrical resistance at elevated temperatures and good thermal conductivity. The beryllia forms have been received, inspected, and approved for use.

The calorimeter bridge arms have been successfully wound and welded to their respective beryllia forms. The resistance of each arm was then measured, with the use of a water bath calorimeter to provide a constant temperature around the forms. The greatest difference in resistance between any two arms was found to be 0.16 ohms for this first balancing.

The sample and dummy side heaters are now being wound, although some difficulty has been encountered in welding the "Tophet A"* wire which is easily oxidized.

The four "Alsimag"* forms for the auxiliary block heaters are presently being fabricated. A small sample of diatomaceous earth, to be used as the thermal gradient medium, has been prepared so that the best method of molding the compound into the desired shape can be determined.

A series of three viscosity determinations was made on pure cerium metal with the oscillating cup viscometer over a range of temperatures. It was noted that each sample gave a very low logarithmic decrement and a large period of oscillation. Dissolution of the tantalum capsule by the molten cerium had been proposed as an explanation of these observations; so, one of the tantalum containers was sectioned following a viscosity determination. Metallographic examination of the tantalum, however, failed to indicate any attack by the molten cerium. Present information indicates that liquid cerium has a high viscosity.

Three attempts were made to measure the viscosity of zinc in graphic lined tantalum crucibles over a range of temperatures from 420 to 560°C. The graphite liners may be necessary because of a possible solubility of the tantalum in liquid zinc. Because of volatile contaminants in the graphite, the first two attempts resulted in rupture of the tantalum crucibles. The third graphite liner was outgassed at 800°C in high vacuum prior to encapsulation.

The crucible containing the outgassed liner performed satisfactorily when heated to 560°C. The results of this determination are now under evaluation.

Plutonium-Bearing Glass Fibers *At the request of the Reactor Fuels and Materials Development branch of the AEC, a cooperative experiment in the fabrication of plutonium-bearing glass fibers is being carried out by Rensselaer Polytechnic Institute, Owens-Corning Fiberglas Corporation and Mound Laboratory.*

Since plutonium oxide does not easily dissolve in glass, complete homogenization of plutonium oxide-containing glass prior to introduction into the fiber-drawing apparatus is now required. This homogenization of the glass is conducted in inductively heated platinum-rhodium alloy crucibles. Each crucible is 1.25 inches high by 0.75 inch in diameter with a circular support flange midway between the top and bottom. This support flange rests on a quartz stand which positions and supports the crucible inside the induction coil. The glass and oxide are mixed when the crucible is alternately heated, cooled, turned upside down on the quartz support, and reheated. As the glass melts and flows toward the open end of the crucible, the

* Trademark of Wilbur B. Driver, Newark, N. J.

+ Trademark of American Lava Corp., Chatanooga, Tenn.

power from the induction heater is cut off to prevent the glass from flowing out of the crucible. The crucible is unloaded by allowing the glass to flow from the open crucible through an air gap so that the droplets of glass have solidified before they fall into a receiving crucible. This technique practically eliminates the spread of radioactive material.

An experimental silicate glass containing alumina, calcia, and potassium monoxide has dissolved 10 weight per cent plutonium oxide by the above technique. No fiber fabrication nor leach tests have been performed for this composition, as yet.

Another glass composition containing zirconium oxide and zinc oxide is currently under test, but difficulty has been experienced in the dissolution of up to 10 weight per cent plutonium oxide.

Variations in compositions of the glass cullets are being examined, so that the hygroscopic character of the glass previously reported can be avoided in future mixtures.