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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.

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TABLE OF CONTENTS

DISCLAIMER

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 PROJECT Exploratory work, aimed at determining the physical properties of mica-filled diallyl phthalate, has begun. The purpose of this work is to develop background information and establish a basis for comparison between plain and epoxy-modified mica-filled DAP. Work is planned with epoxy modified DAP in an attempt to develop a homogeneous formulation with superior physical and chemical properties.

Four formulations were made with mica. The only variations involved were in the fillers. B184 contained a combination of C-3000 English Mica[*] (60 phr) and Kaomica[+] (40 phr). B185 used only C-3000 mica as a filler. B186 was made using Mycalex[++] Synthetic Mica (-325 mesh) as the sole filler. B187 used a combination Kaomica (60 phr) and Mycalex (-325 mesh) (40 phr).

EXPERIMENTAL DAP FORMULATIONS[a]

Batch	Filler Parts per 100 parts of DAP -35	Type
B184	60 40	Kaomica English Mica C-3000
B185	100	English Mica C-3000
B186	100	Mycalex (-325 Mesh) Synthetic Mica
B187	60	Kaomica Mycalex (-325 Mesh)

[a] All formulations contained 300 parts acetone, two parts calcium stearate, two parts catalyst (t-butyl perbenzoate), 0.03 parts inhibitor (hydroquinone) and 2.5 parts pigment (Harshaw scarlet). All parts based on 100 parts of DAP-35 (prepolymer).

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[*] Trademark of the English Mica Co.

[+] Trademark of Edgar Plastic and Kaolin Co.

[++] Trademark of Mycalex Corp., a subsidiary of Synthetic Mica Corp.

Processing was identical for all batches:

1. The filler was prewet with 10 per cent varnish then 50 per cent varnish was added to give the 100 parts resin.
2. The rest of the ingredients were added and high speed stirred for at least eight hours, then the mixture was transferred to the small sigma blade mixer and the solvent evaporated under vacuum.
3. Batches were removed from the mixer and milled on the differential roll mills, then ground through the Cumberland grinder.
4. The ground material was dried in a circulating air oven.
5. Tensile, Izod Impact and heat distortion specimens were molded.

MILLING DATA

Sample No.	Mill Time Minutes	Mill Temperature °C	Mill Power kw	Relative[a] Mobility Seconds	Cup Weight g
B184	16¾	66	1.45	11.11	38.99
B185	17½	68	1.65	10.91	40.51
B186-1	12¾	78	1.05	8.90	40.00
B186-2	12½	78	1.05	8.48	40.00
B187-1	17¼	80	1.25	8.62	39.47
B187-2	20	79	1.25	8.82	39.38

[a] at 5 tons force

Physical test results are given below:

IZOD IMPACT STRENGTH

Run No.	Ft. Lbs/inch Notch
B184	0.280
B185	0.295
B186	0.288
B187	0.280

TENSILE STRENGTH

Run No.	Psi
B184	7300
B185	7185
B186	7324
B187	7414

Both the impact and tensile strength values compare favorably with asbestos-filled DAP formulations. The tensile values compare with the upper limit tensile strength values for asbestos-filled formulations.

In general the mica alone gave a higher density than a combination of mica and Kaomica. Average values were 1.71 g/cc and 1.68 g/cc respectively.

The heat distortion temperatures were also higher on the mica-filled material -- 172°C and 168°C as compared with 160°C and 159°C of the combination material.

ADHESIVES Formulations were prepared during this report period containing MOCA*, (4,4' methylene-bis-(2-chloroaniline)), T-12 (dibutyl stannic laurate) and an epoxy system of vinyl cyclohexene dioxide-HET anhydride (1;epoxyethyl-3,,4-epoxy-cyclohexane)-(1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]-5 heptene-2,3-dicarboxylic anhydride) in addition to polyol solutions of ferric acetyl acetonate (FAA) as catalysts. Of the 63 formulations, for which data will be presented in this report, 15 may have use either as presented or modified slightly to provide low viscosity characteristics. The 15 are Ad 50,51,52,53,57,58,59,60,66,77,95, 102,104,105, and 107. These represent all types of formulations given. A useful formulation will have a pot life ranging from two to four hours and it will cure to a non-tacky film overnight (18 hours) and will have reached its ultimate strength in seven days.

Adiprene* - ferric acetyl acetonate-polyol systems are polyurethane systems cured by a solution of FAA in a polyol. Some formulations contained polyol in excess of that amount which was present in the FAA-polyol catalyst solution. Formulations which contained more polyol than eight parts per 100 parts of resin (phr) usually did not cure regardless of the time interval. This was true regardless of the type Adiprene resin used or of the amount of FAA or other catalysts used.

Table 1

ADIPRENE - FERRIC ACETYL ACETONATE - POLYOL SYSTEMS

Formulation	AD 50	AD 51	AD 52	AD 53	AD 54	AD 57	AD 58	AD 59	AD 60
Adiprene 100	25	--	25	--	25	--	--	25	--
Adiprene 167	--	--	--	--	--	25	25	--	--
Adiprene 213	--	25	--	25	--	--	--	--	25
FAA	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
1,5 P[1]	1.072	1.072	--	--	--	--	--	--	--
1,2,6 H[2]	--	--	1.072	1.072	1.072	1.072	--	--	--
1,1,1-TMP[3]	--	--	--	--	--	--	1.072	1.072	1.072
Pot life (hrs.)	½	½	½	1	1	¾	2	1½	¾
Time to cure to nontacky film (days)	<2½	<2½	<2½	3	3	⅔	¾	¾	1

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*Trademark of E. I. du Pont de Nemours

The formulations in Table 1 formed tough rubbers upon cure. Their viscosity was probably too great for application by brushing technique. Because of their high viscosity, the next set of formulations were modified by the addition of excess polyol or polyols. Since no literature was available concerning the amounts of polyols to be used to obtain the desired viscosities, the polyol content was varied and various polyols were contrasted for degree of viscosity modification.

The solutions of FAA in polyols were made by dissolving 0.26 gram of FAA in 10.0 grams polyol and adding 1.1 grams of this solution to the formulation. Beginning with formulation AD 79 it became desirable to have a more concentrated FAA-catalyst-polyol solution. One gram FAA was dissolved in 20.0 grams of the respective polyol. Whereas, 1.1 gram of the original FAA polyol solution contained 0.028 grams FAA and 1.072 grams polyol, 0.59 grams of the new concentration FAA-polyol solution contained 0.028 grams FAA and 0.562 grams polyol. As was noted previously, there seems to be a limit of approximately eight parts per 100 parts of resin (phr) of excess polyol above which amount a formulation will not cure properly. This observation is born out by formulations AD 78 through AD 90, inclusively, which did not cure even though two to five times the normal amount of FAA catalyst was employed with a polyol excess greater than eight phr. Most of the formulations in this group which did cure in seven days or less were too viscous after degassing for good brushing technique. Also, they degassed slowly with excessive foaming. The effect of modifying Adiprene-167 by the addition of more reactive Adiprene-213 did not reduce the viscosity, because the present stock of Adiprene-213 has thickened by partial crosslinking through exposure to the atmosphere during previous formulation preparation.

1,1,1-Trimethylol propane is a solid at room temperature and its use tends to thicken the formulation; also, the present stock of Adiprene-213, because of its exposure to atmosphere, tends to increase the viscosity. On the other hand 1,3 butanediol, 1,5 pentanediol and 1,2,6 hexanetriol are viscosity reduction modifiers. Formulations AD 82 and AD 83 contrast the effect of addition of Adiprene-213 to Adiprene-167 with polyol in excess of eight phr. (This seems to be the one observed exception to the eight phr excess polyol noted earlier).

Adiprene-167 does not cure with twice the normal amount of FAA catalyst present in AD 82. But if Adiprene-167 content is reduced 20 per cent and an addition of 32 per cent by weight of Adiprene-213 (on basis of original Adiprene-167 content) is made, the resulting mixture will cure to a nontacky film in four days despite the presence of an abnormal excess of polyol content. It should be noted however, that 1,1,1-trimethylol propane is present and the mixture resulting from the use of 1,5 pentanediol does not cure, but remains a liquid after 15 days time. The greater reactivity of Adiprene-213 is shown by formulations AD 85,86 and 87 which contain Adiprene-213 and large excess contents of less reactive polyols. These formulations, while not desirable for adhesive work with the limited specifications, will cure in 11 or more days to a nontacky film. Formulation Ad-89 has slowly thickened after 35 days to a point where it is just about to jell.

Formulations AD 91-94 and AD 96 show that Adiprene-167 is less reactive than Adiprene-213; also, they show the sensitivity of the system to addition of polyol in excess of eight parts per hundred resin (phr). Even polyols with primary hydroxyls such as 1,4 butanediol and 1,5 pentanediol are not reactive enough to cure the system at polyol excess above eight phr. AD 95 has 2.248 phr of 1,4 butanediol excess while AD 96 has 9.248 phr excess 1,4 butanediol. AD 95 cured to a nontacky film in two days while AD 96 has not progressed farther than a viscous liquid in 28 days.

Table 2

ADIPRENE - FERRIC ACETYL ACETONATE - POLYOL SYSTEMS (WITH EXCESS POLYOLS)

Formulation	AD 55	AD 56	AD 61	AD 62	AD 63	AD 64	AD 65	AD 66
Adiprene 167	--	26	25	25	25	25	25	25
Adiprene 213	25	--	--	--	--	--	--	--
FAA	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
1,3 Butanediol	--	--	--	--	--	--	--	--
1,5 Pentanediol	--	1.072	--	13.05	10.0	7.5	5.0	--
1,2,6 Hexanetriol	9.772	8.70	--	--	--	--	--	--
1,1,1 TMP[1]	--	--	14.122	1.028	1.028	1.028	1.028	2.028
Pot life (hrs.)	½	1	1	120	2½	1	very viscous	1
Time to cure a nontacky film (days)	>11	>11	No cure obtained only slight thickening					

[1] Trimethylol propane

Formulation	AD 67	AD 68	AD 69	AD 70	AD 71	AD 72	AD 73	AD 74
Adiprene 167	25	25	25	25	25	25	25	25
FAA	0.028	0.028	0.028	0.028	0.028	0.028	0.039	0.028
1,3 Butanediol	--	5.0	7.5	10.0	1.0	2.0	3.0	3.0
1,1,1 TMP	6.028	6.028	6.028	6.028	1.562	2.562	3.771	3.562
Pot life (hrs.)	very viscous	very viscous	>4	18	1	1	1	1
Time to cure to nontacky film (days)	no cure viscous liquid	no cure obtained viscous liquid			No cure obtained after 11 days - only viscous liquid			

Table 2 (Con't)

ADIPRENE - FERRIC ACETYL ACETONATE - POLYOL SYSTEMS

Formulation	AD 75	AD 76	AD 77	AD 78	AD 79	AD 80	AD 81	AD 82
Adiprene 167	25	25	25	25	25	25	25	25
FAA	0.028	0.028	0.028	0.028	0.056	0.056	0.14	0.14
1,3 Butanediol	4.0	5.0	0.5	1.0	5.0	1.0	4.0	7.0
1,1,1 TMP	3.562	3.562	1.562	2.062	4.124	2.124	2.81	2.81
Pot life (hrs.)	1½	>4	none too viscous	>2	>2	none too viscous		3
Time to cure to nontacky film (days)	No cure obtained after 11 days - only viscous liquid		7		No cure obtained after 11 days only viscous liquid			

Formulation	AD 83	AD 84	AD 85	AD 86	AD 87	AD 88	AD 89	AD 90
Adiprene 167	20.0	25	--	--	--	--	--	10
Adiprene 213	8.0	--	25	25	25	25	25	15
FAA	0.14	0.028	0.028	0.028	0.14	0.056	0.056	0.056
1,3 Butanediol	7.0	--	--	--	--	--	--	--
1,5 Pentanediol	--	--	--	4.072	--	--	6.124	6.124
1,2,6 Hexanetriol	--	3.072	5.072	--	10.96	6.254	--	--
1,1,1 TMP	2.81	--	--	--	--	--	--	--
Pot life (hrs.)	3+	4+	1	1	1	too viscous	too viscous	1
Time to cure to nontacky film (days)	4	4	11	>11	>11	3	no cure liquid	no cure liquid

Formulations AD 97 through AD 112 contrast the effect of epoxy modifications of Adiprenes-100, -167, -213. Allylglycidyl ether (AGE) is a mono-epoxide reactive diluent; butanediol diglycidyl ether (RD-2), vinylcyclohexene dioxide (Epoxide*-206), and Epon+-812 are di-epoxide prepolymers and reactive diluents. Di-epoxide reactive diluents are probably better reactive diluents than Adiprene modifiers.

In a few instances, because of pouring and measuring viscous materials, errors were made in preparing formulations by weighing. Where an error in weight was made, the quantity in the data tables has been underlined to denote that the weight given is the actual weight used, but is not the desired quantity.

Table 3

ADIPRENE 167 - FERRIC ACETYL ACETONATE - POLYOL SYSTEMS

Formulation	AD 91	AD 92	AD 93	AD 94	AD 95	AD 96
Adiprene 167	25	25	25	25	25	25
Ferric Acetyl Acetonate	0.028	0.028	0.028	0.028	0.028	0.028
1,3 Butanediol	2.0	--	2.0	--	--	--
1,4 Butanediol	--	--	--	2.0	0.562	2.562
1,5 Pentanediol	--	3.072	1.072	1.072	--	--
1,1,1 Trimethylol propane	0.562	--	--	--	--	--
Pot life (hrs.)	>4	>4	>4	>4	>4	1
Time to cure to nontacky film (days)	Gummy liquid - no cure after 28 days.				2	no cure liquid 28 days

In Table 4, three new catalysts are used: MOCA (4,4-methylene-bis-(2-chloroaniline)), T-12 catalyst (dibutyl-tin-laurate), and an epoxy system (Epoxide-206 (vinyl cyclohexene dioxide) plus HET anhydride (1,4,5,6,7,7-hexachlorobicyclo-[2.2.1] - 5 heptene - 2,3 - dicarboxylic anhydride)).

Formulations AD 101 - AD 112 which contain MOCA are based on the formulation of:

Adiprene-100	10	pbw (parts by weight)
MOCA	0.9	pbw
Epon 828	1.0	pbw

which appears in the paper from *Adhesive Age*, April, 1959, "Room Temperature Curing of Polyurethane Adhesives" by M. J. Bodnar and E. R. Kelly. Epon-812 was substituted for Epon-828 on the basis of epoxide equivalents. The proportions of Epoxide 206-HET anhydride reported are based upon data presented in: "The Advance Technical Report" Bulletin #F-40132C, July, 1959, The Union Carbide Chemical Co.

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*Trademark of Union Carbide Chemical Corp.

+Trademark of Shell Chemical Corp.

Table 4

ADIPRENE - MOCA SYSTEMS WITH EPOXY MODIFIERS

Formulation	AD 97	AD 98	AD 99	AD 100	AD 101	AD 102	AD 103	AD 104
Adiprene-100	21.6	25	21.6	21.6	21.6	21.6	--	--
Adiprene-167	--	--	--	--	--	--	21.6	22.37
MOCA	1.98	1.98	1.98	1.98	2.14	1.94	1.94	1.94
T-12 Catalyst	1.00	1.13	1.00	--	--	--	--	--
AGE	3.60	7.20	--	--	--	--	--	--
RD-2	--	--	--	3.6	--	--	--	--
Epon 812	--	--	3.74	--	3.60	1.56	1.56	1.65
HET Anhydride	--	--	--		--	--	0.80	0.268
Epoxide 206	--	--	--	--	--	--	0.76	0.252
Pot life (hrs.)	¾	2 - 3	½	2	2 - 3	2 - 3	none too viscous	2
Time to cure to nontacky film (days)	1	11	1	7	1	6	3	3

An analysis of the effect of the variables in formulations AD 97 thru AD 112 is difficult if not impossible; however, it is apparent that Epon-812 rather than slowing down the rate of cure tends to increase it. The relative effect of the presence of the epoxy mix of HET anhydride - Epoxide-206 is less noticeable, yet formulation AD 108 has neither MOCA nor Epon-812 present and cures in six days with the epoxy mixture as sole catalyst.

Formulations AD 102, 104, 105 and 107 gave films which cured quickly. At first they cured rapidly to give nontacky surfaces, but the interior of the film was somewhat soft. As a result, the films had low tear resistance. Each succeeding day of additional cure-time improved the tear strength until, at the end of seven days, they had developed their maximum strength. Formulations AD 109 - AD 112 are variations of AD 102, 104, 105 and 107 using Adiprene-213 in place of Adiprene-167. As is evident from the data, the use of Adiprene-213 accelerated the cure so much that AD 110 and AD 111 jelled before they had been completely degassed. The amount of Adiprene-213 used is much less than previous formulations involving Adiprene-213. A study of data appearing in literature relating to Adiprenes-167 and -213 indicated that 5.4 grams of MOCA are necessary to cure 21.6 grams of Adiprene-213. Since the previous formulations had only 1.94 grams of MOCA, the amount of Adiprene-213 was reduced from 21.3 grams to 7.76 grams. This reduction may explain the greater rate of cure of the Adiprene-213 containing formulations, as compared to those using Adiprene-167. It seems to follow that the formulation previous to AD 109, probably, had too much Adiprene-167 and -100. Future formulation work should investigate this discrepancy. The two sources of formulation data mentioned in this report differ by a wide degree on the proper formulation data to be employed.

Table 5

ADIPRENE - MOCA SYSTEMS WITH EPOXY MODIFICATIONS AND ADIPRENE - EPOXY SYSTEMS

Formulation	AD 105	AD 106	AD 107	AD 108	AD 109	AD 110	AD 111	AD 112
Adiprene 167	21.6	21.7	21.6	21.6	--	--	--	--
Adiprene 213	--	--	--	--	7.76	7.76	7.76	7.76
MOCA	1.94	--	--	--	1.94	1.94	1.94	--
Epon-812	2.34	1.56	1.56	--	1.56	1.56	2.34	1.56
Epoxide-206	0.252	0.76	1.512	1.512	---	0.46	0.252	1.512
HET Anhydride	0.268	0.80	1.608	1.608	--	0.49	0.268	1.608
Pot life (hrs.)	1	3 - 4	3 - 4	4 - 8	none very visc.	jelled while being degassed		2
Time to cure to nontacky film (days)	3	6	¾	6	⅕	could not form film too fast		½

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

IONIUM PROJECT Ionium (thorium-230) is useful as a thorium tracer and as a source for the production of protactinium-231 and uranium-232 by neutron irradiation. In FY-1956 Mound Laboratory separated and purified approximately 0.7 kg of ionium. The source was a limed raffinate residue from the Mallinckrodt uranium refinery, known as "Airport Cake". In anticipation of a further demand, alternate sources of kilogram quantities of ionium are being investigated.

A preliminary survey has been completed on 49 samples received from 17 uranium mills and processing plants. A sample of the "Airport Cake" retained from previous processing has also been analyzed. To eliminate a time consuming development of digestion conditions for each solid sample, a standard, hot concentrated nitric acid digestion procedure was adopted. Such a procedure dissolves only the readily available ionium, but the method is satisfactory for this preliminary survey.

The samples received were of three types; solids (usually dry), clear solutions, and slurries. The slurry samples were allowed to settle and a rough estimate made of the relative volumes of solid and supernate. The supernates were then separated by filtration or centrifugation, and the solids were dried in an oven at 50°C. All dry solid samples were digested and prepared for analysis by the following procedure:

1. Weigh out 10 g of the dry solid in a 250 ml beaker. Add 20 ml of conc. HNO_3 and heat the slurry one hour on a hot plate at near boiling temperature.
2. Transfer the supernatant solution to a 50 ml centrifuge tube, centrifuge, and decant to a storage bottle. Wash the insoluble residue twice with dilute HNO_3 either in the beaker or in the centrifuge tube. Centrifuge the wash solutions and add the supernates to the storage bottle. Dilute the solution in the storage bottle to 100 ml and shake thoroughly to mix.

Several of the liquid samples contained small precipitates, possibly due to hydrolysis. In most cases, these precipitates were slurried before samples were taken and apparently caused no difficulty in the analyses. Clean liquids, or aliquots of the solutions from digestion of the solid samples were analyzed by one of the two following methods:

Method A Direct CeF_3 Precipitation Procedure

1. Transfer the liquid sample to a 50 ml centrifuge tube. Use 25 ml of the clear liquid solutions or 10 ml of the digest solutions from solid samples diluted to 25 ml with water. (If a yield determination is to be made, add a known amount of ionium at this point).
2. Add NaOH solution until the pH is 10 or greater. Stir 5 minutes. Centrifuge 5 minutes. Decant and discard the supernate.
3. Add 2-ml of conc HCl, stir until the precipitate dissolves or is homogeneously dispersed. Add 1-2 mg of cerium carrier (as cerous nitrate). While stirring, add 10 ml of approximately 1.5 N HF and continue stirring for 10 minutes. Centrifuge 10 minutes. Decant the clear supernate to a second 50-ml centrifuge tube.
4. Wash the precipitate with 5 ml of 0.1 N HF, stirring 5 minutes. Centrifuge 5 minutes, and decant the wash solution to the second tube.

5. Slurry the CeF_3 precipitate in about 0.5 ml of water and transfer the slurry to a 2-inch stainless steel disc previously prepared with a ¼ inch plastic retaining ring. Rinse the tube twice with 0.5 ml portions of water and add the rinse to the slurry. Evaporate to dryness under a heat lamp and ignite the disc to burn off the plastic ring and residual moisture.

6. To the combined HF solutions from Steps 3 and 4, add NaOH until the pH is greater than 10. Stir 5 minutes. Centrifuge 5 minutes. Decant and discard the clear supernate.

7. Repeat the addition of HCl, cerium carrier and HF as in Steps 3 and 4. Mount the precipitate as in Step 5.

8. Alpha-count the sample discs in a ZnS scintillation counter, calibrated with a standard ionium sample. (Alpha-counting in a gas-flow proportional counter is sometimes unsatisfactory because of poor adherence of the mount.)

Note: This procedure works well with samples which give hydroxide precipitates not much larger than 5 ml after centrifugation for 5 minutes at 1500 RPM.

Method B Tributyl Phosphate - Cerium Procedure

(Steps 1 and 2 are identical with those in the direct cerium fluoride procedure.)

3. Add conc. HNO_3 in 1-ml portions, stirring until the hydroxide precipitate dissolves. Add one additional ml of conc. HNO_3. Add 18.8 g of solid $Al(NO_3)_3 \cdot 9\ H_2O$. Stir and heat until the salt is completely dissolved. The total volume should be about 25 ml.

4. Extract the solution with 5 ml of an equi-volume mixture of tributyl phosphate and benzene, previously equilibrated with HNO_3 Stir 5 minutes, centrifuge 5 minutes, and transfer the organic phase to a second 50-ml centrifuge tube. Repeat the extraction with an additional 5 ml of organic solution, and add the organic phase to the second centrifuge tube.

5. Add 1-2 mg of cerium carrier to the combined organic solution. While stirring, add 10 ml of approximately 1.5 N HF, and continue stirring for 10 minutes. Centrifuge 10 minutes. Decant the organic phase and aqueous supernate to a third 50-ml centrifuge tube.

6. Wash the CeF_3 precipitate as in Step 4 of Method A. Decant the wash solution to the third centrifuge tube.

7. Mount the CeF_3 precipitate as in Step 5 of Method A.

8. To the organic phase and HF solution in the third centrifuge tube (Step 5) add, while stirring, 1-2 mg of cerium carrier. Stir 10 minutes. Decant the organic phase and aqueous supernate to a fourth centrifuge tube.

9. Wash the precipitate as in Step 4 of Method A. Decant the wash solution to the fourth centrifuge tube.

10. Mount the CeF_3 precipitate as in Step 5 of Method A.

11. Alpha-count the samples in the ZnS scintillation counter.

Of the two procedures, Method A, the direct cerium fluoride precipitation, is the shorter and simpler; however, it can not be used for all samples. Certain samples produce a large gelatinous fluoride precipitate (probably rare earths) which can not be mounted properly. In those cases, it is necessary to use the tributyl phosphate (TBP) extraction to remove the interfering material. No sample was found which could not be analyzed by the TBP-CeF_3 method. Yield determinations (recovery of added, known amounts of ionium) consistently ran above 90 per cent with the majority above 95 per cent.

There appears to be two sources of error in these procedures. The main error arises from a probable incomplete leaching of ionium from the insoluble residue. Gamma pulse height analysis of samples of sample 24C before and after digestion, indicated that about 15 per cent of the ionium remained in the residue. No attempt was made to recover more of the ionium from the residues. The second possible source of error is coprecipitation of some of the decay products, especially radium isotopes (radium-226, radium-224, and radium-223 are expected to be present). This error should be markedly reduced, but may not be eliminated by a TBP extraction. However, mounts of several of the richer samples were recounted after a period of at least one month and no significant change was observed. Therefore, adsorption of other activities is considered to be negligible in these samples.

Duplicate analyses and a yield determination were made on each of the samples, and the results are given in the following table. In the case of slurry samples, the supernate (-S) was separated from the residue (-R) and each portion analyzed separately. For the reasons previously cited, the results are probably not accurate to more than ± 50 per cent for the low level samples. The high level samples are probably accurate to ± 10 per cent. In addition the samples analyzed were fairly small, and there is no assurance that they are representative of the total material.

IONIUM IN PROCESS SAMPLES

Identification Number	Type	Ionium Concentration		Analytical Method[a]	Ionium[b] Potential of Source
1 A-S	Liquid	28.0	μg/gal	A	51 g/day
1 A-R	Solid	0.01	ppm	A	-
2 A	Liquid	120.0	μg/gal	B	45 g/mo
6AA	Solid	0.03	ppm	A	-
7 A	Solid	0.03	ppm	B	-
8 A	Solid	0.04	ppm	B	12.5 g/day
8 B	Solid	0.017	ppm	A	-
8 C	Liquid	44.0	μg/gal	B	>100 g/day
8 D	Liquid	74.0	μg/gal	B	180 g/day
10 A	Liquid	7.5	μg/gal	A	1.1 g/day
10 B	Liquid	28.0	μg/gal	A	-
10 C	Liquid	8.9	μg/gal	A	-
10 D-S	Liquid	11.0	μg/gal	B	-
10 D-R	Solid	0.01	ppm	A	-
10 E-S	Liquid	nil		B	-
10 E-R	Solid	0.009	ppm	A	-
10 F	Liquid	nil		A	-
10 G-S	Liquid	0.07	μg/gal	A	-
10 G-R	Solid	0.017	ppm	A	-
11 A	Solid	0.02	ppm	A	-
11 B	Liquid	0.01	μg/gal	A	-
12 A	Liquid	62.0	μg/gal	B	1.2 kg
13 A	Solid	0.02	ppm	A	-
14 A	Solid	0.01	ppm	A	-
14 B	Solid	0.03	ppm	A	-

IONIUM IN PROCESS SAMPLES (Cont'd)

Identification Number	Type	Ionium Concentration		Analytical Method[a]	Ionium[b] Potential of Source
14 C	Liquid	32.0	μg/gal	B	-
14 D	Liquid	2.0	μg/gal	A	-
15 A	Liquid	28.0	μg/gal	B	>10 g/day
15 B	Liquid	9.1	μg/gal	A	-
15 C	Liquid	33.0	μg/gal	A	-
18 A	Liquid	28.0	μg/gal	B	7 g/day
18 B	Liquid	0.14	μg/gal	A	-
18 C	Liquid	0.4	μg/gal	B	0.14 g/day
18 D	Solid	0.39	ppm	A	390.0 g
18 E	Solid	2.8	ppm	B	7.0 kg
20 A	Solid	0.03	ppm	A	-
20 B	Liquid	2.0	μg/gal	B	-
20 C	Liquid	30.0	μg/gal	B	5.4 g/day
22 A-S	Liquid	7.3	μg/gal	B	-
22 A-R	Solid	0.07	μ	A	-
22 B	Solid	0.01	ppm	A	-
22 C	Liquid	26.0	μg/gal	A	-
23 A	Solid	0.003	ppm	A	-
23 D	Solid	0.013	ppm	B	-
24 A-S	Liquid	nil		B	-
24 A-R	Solid	1.1	ppm	A	10-20 g/day
24 B	Solid	0.07	ppm (wet)	A	79 g/mo
24 C	Solid	2.3	ppm	B	2.5 kg
26 A	Solid	0.12	ppm	A	-
28 A	Solid	2.1 3.7	ppm (wet) ppm (dry)	B	100-200 kg

[a] Analytical Method A = Direct CeF_3 Precipitation Method
Analytical Method B = TBP-CeF_3 Method

[b] Ionium potentials calculated from the analytical results and information from the supplier or from the literature.

An examination of the Table (Ionium In Process Samples) indicates four solid samples (18 E, 24 A-4, 24 C, 28 A) with an ionium concentration of one ppm or better. Three liquid samples had ionium concentrations above 50 micrograms per gallan and an additional eight liquid samples had concentrations above 25 micrograms per gallon. All of these samples are to be considered as possible sources of kilogram quantities of ionium. However, two of these solutions (10 B and 18 A) are intermediate process solutions and would not be available for ionium recovery. Further development work is planned for the remaining samples.

A number of the samples can be grouped into rough categories as follows:

Type	No. of Samples	Range of Ionium Concentrations
Untreated solvent extraction raffinates and ion exchange effluents	6	7.5-120 μg/gal (4 above 25 μg/gal)
Acid leached tail solutions	10	0.07-62 μg/gal (6 above 25 μg/gal)
Residues from raffinates, effluents (calcined, limed, etc.)	5	0.39-3.7 ppm (4 above 1 ppm)
Solid tailings - Acid leached	6	0.01-0.03 ppm
Solid tailings - Carbonate leached	3	0.01-0.03 ppm

The most promising liquid samples are solvent extraction raffinates and ion exchange effluents, or the tail solutions from mills using these processes. Furthermore, all of the solids with ionium concentrations over one ppm originated from raffinate or effluent solutions. Tail residues, whether leached by acid or carbonate, have far too low an ionium concentration to be considered as sources. While it is possible that more vigorous digestion of these residues would yield more ionium, it is unlikely that the apparent ionium concentration would be increased by the two orders of magnitude necessary to make these samples comparable to those derived from raffinates.

One other factor must be considered in choosing a suitable source: namely. the isotopic ratio of thorium-232 to thorium-230. Methods for determining this ratio are under development. With alpha pulse height analysis, attempts to compare the counting rates at the 4.0 Mev peak of thorium-232 and the 4.6 Mev peak of thorium-230 were unsuccessful because the lower energy peak was masked by the ionium peak. An attempt to count the 5.4 Mev peak of thorium-228 (daughter of thorium-232) was only partially successful because of incomplete purification of the sample and the low counting rates. More work is needed to develop this method. Meanwhile, a colorimetric method of determining total thorium is being developed.

The "Q-11 Metal Oxides" (24 C) has been chosen as the first sample for further development work. Several features of this material are noteworthy. It is a dry solid and about 250 tons are currently stored in steel drums. The material contains approximately the quantity of ionium desired, and it has an ionium concentration nearly as high as that of the "Airport Cake". Since the material originated from Belgium Congo ores, as did the "Airport Cake", a similar isotopic ratio is expected.

HALF-LIFE OF RADIUM-223 The purified radium-223 fraction recovered from an eight-microcurie sample of actinium-227 in equilibrium with its decay products (AEM) has been reanalyzed for impurities by the lanthanum phosphate procedure described last month; the radium-223 fraction contained 0.01 per cent of the original actinium. The thorium-227 found in the radium-223 fraction corresponded exactly to the amount of thorium-227 which would grow from actinium-227 during the time between separation and analysis, confirming that the radium-223 fraction, at the time of separation, contained no thorium-227.

A blank run on the reagents used in the lanthanum phosphate procedure yielded one alpha count per minute in the lanthanum phosphate precipitate, and there was no significant growth or decay in ten days.

The yield of the lanthanum phosphate procedure has been checked and found to be above 90 per cent. The principal loss occurs in the transfer of the lanthanum phosphate from the centrifuge tube to a counting disc. If the tube is carefully washed during the transfer, the yield of actinium and thorium is greater than 95 per cent. Less than one per cent of the actinium and thorium is lost in each precipitation. Self-absorption losses are less than one per cent.

Further development of the lanthanum phosphate procedure is expected to provide a separation of actinium from thorium, eliminating or reducing the time required for differential decay analysis.

A composite AFM sample is being prepared for use as a source of several millicuries of radium-223. The composite, representing ion exchange tailings, actinium oxalate filtrates and analytical samples taken during FY-1952 processing of actinium, is chemically impure. Iron and aluminum are believed to be the principal metallic impurities. Oxalate ion is believed to be the principal anion present. The composite will be purified chemically before the radium-223 separation is made. It is not anticipated that radiochemical purification will be necessary.

The decay of a specially purified radium-223 sample has been followed for 50 days. Preliminary results for the first 16 days were reported last month. The half-life has been recalculated to include the new data, and the results are again reported as a function of the resolution time of the gas flow proportional counter (following table).

HALF-LIFE OF RADIUM-223 AS A FUNCTION OF COUNTER RESOLVING TIME (τ)

(50 Days - 26 Observations)

τ (Min. × 10^{7})	Half-Life (days)	Probable Error (days)
1.5	11.4685	0.0086
1.6	11.4019	0.0072
1.65	11.3700	0.0065
1.7	11.3364	0.0067
1.9	11.2044	0.0100

It is noteworthy that recalculation of the half-life for $\tau = 1.5 \times 10^{-7}$ minute and 1.7×10^{-7} minute resulted in lower values than those previously calculated. For $\tau = 1.9 \times 10^{-7}$ minute, a higher value was found. The earlier calculations were based on the higher counting rates of the first 16 days of decay, where the coincidence correction is of greatest significance. As additional data were accumulated, more weight was given to counting rates in which the coincidence correction was less significant.

On the basis of the data obtained thus far, the most probable value of the resolution time (τ) is 1.65×10^{-7} minute, and the most probable value of the half-life (lowest probable error) is 11.3700 ± 0.0065 days. This value is close to that reported in MLM-1093 (11.412 ± 0.014 days).

DETERMINATION OF COINCIDENCE CORRECTION Work has been resumed on the half-life method for determining the resolution time (τ) and coincidence correction in a proportional counter. The method is based on the observation that a sample of AEM is subject to losses of radon-219 unless special precaustions are taken to prevent these losses. Radon-219 decays rapidly through polonium-215 to lead-211, which has a reported half-life of 36.1 minutes. Although lead-211 is a beta-emitter, it is immediately followed by bismuth-211 and polonium-211, both of which are short-lived alpha emitters. The decay of lead-211, in transient equilibrium with its decay products, can, therefore, be followed in an alpha counter.

In previous work a sample of AEM was followed after the AEM sample was removed. No long-lived radioactivity was detected in the first two experiments; however, as the AEM aged, adherence to the sample backing became poorer, and losses of radium-223 by recoil became significant.

The technique for collecting lead-211 has been modified to eliminate contamination of the counters with long-lived radioactivity. A sample of AEM, evaporated to dryness on a stainless steel disc, but not ignited, is placed in electrical contact with ground. The sample is covered with filter paper (Reeve Angel No. 201, 4.25 cm), and a glass spacing ring is placed on the filter paper. A stainless steel disc is placed on the glass on the glass ring and fastened in place with a spring which is in electrical contact with the positive pole of a high voltage power supply.

A positive potential of 1500 volts is applied to the collection disc for at least three hours. The collection disk, containing lead-211 in transient equilibrium with its decay products, is alpha-counted periodically. The half-life of lead-211 is calculated as a function of the resolution time (τ) of the counter. It is assumed that the most probable value of τ is that which yields a half-life value with the lowest probable error.

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.*

DTA Differential thermal analyses (DTA) were made of lanthanum and praseodymium metals with samples of approximately five grams each. The results are listed below and compared to literature references.

PHASE CHANGE TEMPERATURES IN LANTHANUM AND PRASEODYMIUM

	Temperature °C						
	(alpha-beta)		(beta-gamma)		(melting point)		(freezing point)
Element	DTA	Lit.	DTA	Lit.	DTA	Lit.	DTA
La	305	310[3]	827	864[1]	932	920[2]	942
Pr	768	792[1]	-	-	924	935[2]	931

[1] Spedding, et al, J. Metals 9, Trans. AIME 209, 895 (1957).

[2] Spedding, et al, Chap. V. p 413, Pergamon Press, New York (1956), "Progress in Nuclear Energy", Vol I, Series V.

[3] Barson, Legwold, Spedding, Phys. Rev. 105, 418 (1957).

The importance of the difference between the phase change temperatures of the present material and the literature values are under evaluation.

Density Three preliminary determinations of the density of molten cerium have been made by the vacuum pycnometer method. The results are shown below.

Upon cooling, cerium had extruded from the tips of both pycnometers for the runs made at 827°C and adhered to the tips of all three pycnometers. The weights of these extrusions, inadvertently removed, were estimated.

From existing reference data, the density of solid cerium at the melting point is estimated to be 6.62 g/cm^3; therefore, the data below suggests the possibility that the density of molten cerium at the melting point may be greater than that of solid cerium at the melting point (804°C).

DENSITY OF LIQUID CERIUM

Pycnometer	Temperature °C	Density g/cm³
1	850	6.23
2	827	6.58
5	827	6.92

Viscosity A viscosity determination of molten plutonium metal from 650° to 950°C is in progress in the Mound Laboratory oscillating cup viscometer. The plutonium metal is identical in chemical purity to material evaluated in a previous determination. This redetermination is necessary since the viscosities of different batches of plutonium appear to vary because of metallic impurities or oxide inclusions.

When the purity of the lanthanum and praseodymium metal has been determined by differential thermal analysis and metallographic examination, their viscosities will be determined from their melting points to 1000°C.

Metallography Development work has begun with the recently constructed cathodic etcher using nonradioactive metal specimens. Some etching was obtained, although the results were inconsistent. Arc instability, particularly at lower pressures, is a problem while at higher pressures - greater than 200 microns - the arc is stable but etching is negligible. At the higher pressure the arcing occurs between the aluminum cathode holder and the anode rather than between the specimen and the anode. Shielding has been designed for the aluminum cathode holder which should aid in establishing proper ionic discharge between the sample and the anode.

High Temperature Calorimeter Construction of the high temperature calorimeter has continued. Two beryllia bridge coil forms have been wound with platinum resistance wire. These forms were alternately leached in water, acetone, and benzene to remove any oil or other impurities. These forms were baked at a high temperature to evaporate the solvents and to determine the high temperature stability of the components. The first form was fired in an electric furnace overnight at 1100°C in an air atmosphere. When this form returned to room temperature, the beryllia was undamaged, but the resistance of the platinum windings had increased by six to seven ohms from the original value of 68 ohms. The second form was fired at 900°C. The resistance of the platinum windings returned to within 0.06 ohms. The second form was fired at 900°C. The resistance bridge coils will apparently be useful to 900°C. The first coil will be rewound with new platinum wire.

The two controller heaters have been wound on their ceramic forms with the use of 0.008 inch Tophet A* wire, a nickel-chromium alloy. In the course of winding the heaters, three of these wires were welded together by placing the wires all in the same direction, twisting them together for a short length, and separating them above the twist. The twisted area and portion of the wires entering the twist were covered with a specified amount of fused borax, which formed a protective coating to exclude oxygen during the welding process. The wires were then successfully welded with a micro-size gas-oxygen torch.

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

Bonded diatomaceous earth possesses superior qualities as a thermal gradient medium for the high temperature calorimeter, but it is not commercially available in this form. A sufficient quantity of machinable forms have been prepared by the following technique: equal volumes of water and diatomaceous earth were slurried together. The excess water was necessary to reduce entrapped air bubbles. The mixture was poured into a cylinder made of kraft paper which allowed the water to seep through the bottom and the sides, leaving a moist solid cylinder. After drying 24 hours in an oven at 100°C, the cylinders were fired at 900°C for three hours. The fired cylinders had a density of 0.5 g/cm^3 and good thermal resistance. When fired at 1000°C, the density increased to 0.8 g/cm^3. Firing at higher temperatures caused the cellular structure of the form to progressively deteriorate until the thermal conductivity was high enough to render the material useless as an insulator.

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.*

Leaching tests in water and in one-tenth normal hydrochloric acid were continued on fibers of an experimental glass containing silicon dioxide, aluminum oxide, calcium oxide, sodium oxide, potassium oxide, plus ten weight per cent plutonium oxide. Analyses of the leach solutions were made periodically to determine plutonium content. Leaching in room temperature water for 857 hours resulted in a loss of 0.08 per cent of the plutonium oxide from the glass fibers, and leaching in one-tenth normal hydrochloric acid at room temperature for 834 hours resulted in loss of 0.11 per cent of the plutonium oxide from the glass fibers. Examination of the results obtained periodically during the tests indicates a continued attack on the glass by both leach solutions with no approach to equilibrium yet apparent. Additional leach tests on fibers of the same glass have been started using 85°C water and 0.5 normal nitric acid. Twenty-four hours of leaching in the hot water resulted in loss of 0.05 per cent of the plutonium oxide from the glass fibers, and 0.13 per cent of the plutonium oxide was leached out by the 0.5 normal nitric acid in the same length of time.

Plutonium oxide was easily dissolved in experimental glass compositions when the temperature was increased to 1600-1700°C. In this temperature range ten weight per cent plutonium oxide dissolved in the glass composition, previously mentioned, with relative ease. An attempt was made to dissolve ten weight per cent plutonium oxide in a glass composition containing silicon dioxide, aluminum oxide, sodium oxide, zirconium dioxide and zinc oxide; but the combined content of zirconium dioxide and zinc oxide apparently limited the solubility of the plutonium oxide. Nearly all of the plutonium oxide was dissolved, but only with difficulty and only after extensive heat treatment. Cooling the molten glass too slowly resulted in precipitation of finely divided plutonium oxide which appeared to be the primary phase for the composition. In some cases slow cooling of the glass resulted in complete devitrification. In the molten state this composition appeared more viscous than similar compositions without the zirconium dioxide and zinc oxide. When successfully cooled without devitrification, the glass was notably sound and free of cracks.

Fifteen weight per cent plutonium oxide was dissolved at approximately 1700°C in the silicon dioxide, aluminum oxide, calcium oxide, sodium oxide, potassium oxide glass in which ten weight per cent plutonium oxide was previously dissolved. Cooling too slowly or holding at too low a temperature resulted in precipitation of extremely finely divided plutonium oxide, which appears to be the primary phase for the composition. The particles were easily redissolved by raising the temperature. The precipitation might not occur, or at least not so easily, if higher temperatures could be reached for complete destruction of the plutonium oxide nuclei. After complete homogenization, the glass was drawn into fibers by the monofilament process without difficulty.