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TABLE OF CONTENTS

	Page
<u>Summary</u>	3
<u>Radioelements Research</u>	
Uranium-234	6
<u>Isotope Separation</u>	
Helium-3 Separation and Purification	8
Helium-3 Thermometer	8
Carbon-13	9
Neon	13
Xenon	14
Thermal Diffusion Theory	16
<u>Alpha and Neutron Source Development</u>	
Neutron Sources	18
Alpha Sources	18
<u>Analytical</u>	
Coating Resistance to Thorium Residue	21
Calorimetry	21
<u>Adhesives and Plastic Research</u>	
Plastics	26
Adhesives	29

SUMMARY

Radioelements Research

Uranium-234 Milligram quantities of uranium-234 are being separated from aged plutonium solutions. In support of this work, methods are being developed for analyzing uranium in the presence of expected cation impurities. A previously reported determination with 1-(2-pyridylazo)-2-naphthol (PAN) indicator was modified to remove thorium, aluminum, and iron impurities prior to the absorbance reading. The PAN-uranium complex was precipitated and filtered; then excess PAN, which contained the cation impurities, was removed with a 1:1 water-acetone mixture.

A second analytical method of uranium analysis was investigated to overcome the problem of cation impurities. Uranium was extracted into 0.1 *M* TOPO (tri-*n*-octyl phosphine oxide) from 2.0 *N* nitric acid containing 300 mg sodium fluoride per sample. Uranium in the organic phase was measured with PAN as the indicator. The fluoride complexed Al^{+3} and Fe^{+3} so that neither was extracted. The accuracy of this method for 20-100 micrograms of uranium was 5-10 per cent.

The absorption of uranium on an anion exchange column from a high nitrate salt, low nitric acid medium was investigated. Analysis indicated that 85 per cent of the uranium was in the first elutriate, and less than one per cent was in the second.

Isotope Separation

Helium-3 Separation and Purification A thermal loading pump designed for filling cylinders with purified helium-3 gas was tested. After seven cycles through alternately heated cylinders the product increased in pressure to more than twice the feed pressure (20 psig). The results of the test indicated, however, that a cooling system must be added to reduce the cold pressure of the gas. It is expected that the gas pressure in the modified system will be increased to about 100 psig after the seventh cycle.

Helium-3 Thermometer Preliminary tests were made with helium-4 in the system to be used for determining thermomolecular pressure corrections for helium-3 vapor pressure. A quartz bourdon tube was used to measure the vapor pressure alternately through 1/4-inch and 1/32-inch sensing tubes. At a temperature of $1.2592 \pm 0.0069^\circ\text{K}$ the pressure measurements obtained in the 1/32-inch tube were not reproducible. A monitor of pressure drift showed none in the larger tube; however, the pressure in the small tube increased steadily to a suspected asymptote. A comparison of these results with values calculated by the Weber and Schmidt Equation indicates that the equation will probably be applicable to helium-4 vapor up to the boiling point. The equation was determined for a measured amount of helium vapor compressed to simulate lower temperatures.

Carbon-13 Total production from the 11-column, thermal diffusion cascade using natural methane, as of January 8, 1964, was 0.22 g carbon-13. The product withdrawal rate is now 250 cc methane per week, which is equivalent to a production of 0.5 g carbon-13 per month. A comparison profile of the 11-column system revealed that the holdup of C^{13}H_4 in the system was approximately 5.2 liters. Thermal conductivity sensing devices have been added to the bottom of the last two stages of the cascade system to control the withdrawal of impurities.

A 43-foot, 48-mm ID column is to be used for separation of C^{13}O from C^{12}O . Theoretically, nine months would be required for the column to come to steady-state at the nominal accumulation rate of 1.0 g of C^{13}O per day. During start-up, however, when the column product concentration is less than the design value, the column can be operated at conditions which reduce the number of theoretical stages. A start-up schedule was determined which indicated that the column can be at design conditions within 80 days.

Neon The one-one overlap system of neon thermal diffusion columns was run at two pressure conditions to determine the effect on system performance. Theoretically, the system would operate better at the higher of two pressures since the near optimum conditions, $K_c = 10K_d$ and 90 per cent of maximum separation work, are approached. However, in these two experiments sufficient column length was not available to reach desired stream concentration; thus, the product concentration was lowered. Graphs of $K_c = K_d$ and $K_c = 10K_d$ were plotted for the neon-21/neon-22 separation. The maximum time calculated for the removal of 99 per cent neon-22 from the system was 150 days.

Xenon Gas chromatography is being used for the experimental separation of krypton from xenon. Seven runs were made to determine the effect of a column half as long (9.5 cm) as one used in previous experiments. The peaks were much sharper; however, the cleanup (the ratio of xenon in the feed to xenon in the trap) was not as good.

Clathration is being considered as a method for purifying and storing xenon. In a clathrate compound one component (the guest) is enclosed within the crystalline lattice of another (the host). A lattice too large will permit the guest to escape, and a lattice too small will not accept another molecule. By choosing the proper host compound molecules can be selectively enclathrated; thus a gas, such as xenon, could be purified. Xenon can be made to form a clathrate compound with hydroquinone in the following manner. Pressurized xenon is added to an enclosed nonaqueous solution of hydroquinone supersaturated by heating. The solution, cooled slowly, yields a product which is stable at ordinary temperatures and which should contain about 27 weight per cent xenon. The gas may be released by heating the compound to near its melting point or by dissolving it.

Thermal Diffusion Theory An approximate formula for the viscosity of a binary, isotopic gas mixture has been derived from the rigorous kinetic theory formula. According to this equation the viscosity of an isotopic mixture is a nearly linear function of the concentration. For a mixture of $\text{He}^3\text{-He}^4$ the maximum deviation from linearity is approximately the same as the difference between experimental and theoretical results. For heavier isotopic mixtures the deviation from linearity is smaller.

Alpha and Neutron Source Development

Neutron Sources The rate of increase of neutron emission from Pu^{239}Be neutron sources is being studied. Growth rates measured by calorimetry did not agree with rates determined by neutron counting for an experimental Am^{241}Be source. An alpha spectrum was obtained to determine if other alpha emitters are present. Preliminary results indicate that other alpha emitters are present.

Two Pu^{239}Be sources were shipped. One contained 4 g of plutonium and emitted 1×10^6 n/sec. The other contained 0.4 g plutonium and emitted 5.97×10^6 n/sec. The lower value was attributed to an incomplete reaction of plutonium with beryllium to form PuBe_{11} .

Alpha Sources Four polonium alpha sources were fabricated to determine the validity of two design criteria. First, it had been assumed that recoil nuclei would damage the window. After 78 days, however, there was no leakage from two sources prepared with their windows contacting the polonium. Second, it was assumed that the minimum window was 0.00013-inch stainless steel; windows of three layers of gold foil also retained the polonium with no leakage.

Large area, high intensity alpha sources are being developed. These sources, though not wipe-free, must retain 95 per cent of their activity over one half-life. After 50-60 days only two of nine sources had retained 95 per cent of the polonium. The two sources had gold-plated nickel backings with a tie-down layer of gold. However, the tie-down layer had diffused into the backing and loss of the polonium was imminent.

Analytical

Coating Resistance to Thorium Residue A coating material which is compatible with concrete is being sought for the storage of thorium residues containing about 50 per cent moisture. Samples of Tygon Series ATD, Gaco A, Lowe Brothers orange enamel, and a two-component epoxy were placed in a thorium sludge; and comparates were placed in distilled water. The two-component epoxy was the only coating to remain unaffected after a two-week exposure. A polonium alpha radiation test on this coating showed no apparent effect after a three-week exposure.

Calorimetry A revision of the constant current controller used to automate calorimeters was installed and tested. Under the least favorable conditions, a current of up to 100 milliamperes could be selected to within 0.06 per cent and maintained to two parts per million for several hours.

Design and construction of a simplified prototype water bath calorimeter for accountability checks on inter-site transshipments of solid plutonium-238 compounds has reached the final assembly and testing stage.

A panel board is associated with each calorimeter and is used (1) to adjust the bridge current, (2) to set in a heater current to either of the heaters, both heaters in series, or the heater leads, and (3) to select the heater potential measuring voltages. In April 1963 a calibration procedure was established which gives two correction factors for each panel board, one for the voltage divider and the other for a current measuring resistor. The factors are obtained without removing the standard resistors from the panel boards. The correction factors are based on the resistances of two standard resistors which are measured once a year by the Albuquerque Operations Primary Standards Laboratory.

Adhesives and Plastics Research

Plastics Twenty thermosetting plastic molding powders, provided by the D-20 Subcommittee of the American Society for Testing Materials, were evaluated by extrusion through the Monsanto Capillary Extrusion Rheometer. The instrument gave results with good reproducibility; differences between hard and soft flowing samples of the same formulation were easily determined.

Adhesives A Polyol-MOCA cured Adiprene conductive adhesive formulation had good tensile bond strength, but it did not retain good electrical conductivity after heating at 160°F.

A phenolic resin, Bakelite BR-0014, when added to a lead oxide cured polysulfide formulation increased the peel strength of the formulation from 6.5 to 8 pounds per inch when used in a concentration of 0.2 per cent by weight. When used at a concentration of 0.7 weight per cent, the resin caused a reduction in the tensile strength of the formulation.

RADIOELEMENTS RESEARCH

Basic and applied research on a number of radioelements is being conducted to determine physical properties, develop analytical techniques, and study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologs.

Uranium-234

Milligram quantities of uranium-234 are being separated from aged plutonium-238 solutions. The uranium is separated from the bulk of the plutonium in nitrate solution by an anion exchange process. Then, extraction of the uranium into hexone further reduces the concentration of plutonium and most other impurities. Finally, thenoyltrifluoroacetone (TTA) extraction removes the last traces of plutonium from the uranium. Two aged plutonium samples were processed according to this scheme, and 84 mg of uranium-234 were recovered. A third sample containing 2 g of uranium-234 is being prepared for processing. Concurrently, uranium analytical procedures and the behavior of uranium on an anion exchange column are being investigated.

Plutonium seriously interfered in the determination of microgram quantities of uranium with the indicator, 1-(2-pyridylazo)-2-naphthol (PAN); the control of pH is also critical. Therefore, a modification of this method is being evaluated. In this method the PAN-uranium complex is precipitated and filtered; then the excess PAN is removed with a 1:1 water-acetone mixture. Thorium, aluminum, and iron complexes are soluble in the water-acetone mixture and are also removed. The uranium complex can be dissolved in hydrochloric acid and its absorbance measured at 440 millimicrons. The detailed procedure for the indirect PAN method is as follows.

1. Evaporate a sample containing 20-440 micrograms of uranium to dryness.
2. Dissolve the residue in 3 ml of 0.32 *N* hydrochloric acid; add 2 ml ethylenediamine tetracetic acid-tartrate to complex the solution, 10 ml 0.1 per cent PAN indicator, and 5 ml pH 9.5 buffer solution, and stir. Let the solution stand 20-25 minutes, swirling periodically.
3. Filter the solution and wash the beaker and precipitate with portions of 1:1 water-acetone mixture; discard the filtrate.
4. Dissolve the precipitate in 10 ml concentrated hydrochloric acid, and wash the filter with distilled water.
5. Dilute the solution to 50 ml with distilled water, and measure the absorbance at 440 millimicrons.

This method gave good results over the range of 40-440 micrograms of uranium. The indirect method has a better reproducibility than the direct method, and the time element does not seem to be as critical. One-milligram quantities of aluminum and thorium were tested and did not interfere. A disadvantage in this method, however, is that the uranium precipitate tends to creep up the sides of the containers; care must be exercised in washing and transferring.

A second method of uranium analysis is being considered to overcome a problem of cation interference in the PAN method. The major cation impurities which are expected in the uranium are plutonium, iron and aluminum. Uranium is extracted into 0.1 *M* TPO (tri-*n*-octyl phosphine oxide) in cyclohexane from 2.0 *N* nitric acid containing 300 mg of sodium fluoride per sample. Uranium in the organic phase is then measured using PAN indicator. The red complex has an absorption maximum at 555 millimicrons and is developed in the organic phase by the addition of pyridine. Fluoride complexes Al^{+3} and Fe^{+3} to such an extent that neither is extracted. Although plutonium is strongly complexed, a small amount is extracted. This plutonium interference is fairly

constant and allows a determination of 20-100 micrograms of uranium with an accuracy of 5-10 per cent. Further work will be performed to reduce this interference to about 1-2 per cent.

The interferences of some cations have been studied and are shown in Table 1. Thorium caused a slight negative interference; probably the ThF_4 precipitate carried down traces of uranium. Slight amounts of Pu^{+4} and Cu^{+2} were also extracted, but back washing of the organic TOPO phase with nitrate-fluoride media will be used to remove these interferences.

Table 1

CATION INTERFERENCE IN URANIUM SAMPLES

Cation	Weight (mg)	Expected Absorbance For $67 \mu\text{g } \text{U}^{234}$	Measured Absorbance
Fe^{+3}	3.3	0.645	0.650
	1.7	0.645	0.640
Al^{+3}	15	0.645	0.649
	7		0.642
Th^{+4}	25	0.645	0.600
Ce^{+4}	50	0.645	0.645
Pu^{+4}	25	0.645	0.720
Cu^{+2}	8.3	0.645	0.715
Pb^{+2}	10	0.645	0.635

The absorption of uranium on an anion exchange column from a high nitrate salt, low nitric acid medium was briefly investigated. A 10-mm diameter column containing about 3 ml of Dowex 1X4 resin was preconditioned with 20 ml 1.6 M $\text{Al}(\text{NO}_3)_3/0.3 \text{ N } \text{HNO}_3$ solution. A solution of the same composition containing 17 mg uranium was slowly passed through the column followed by 10 ml $\text{Al}(\text{NO}_3)_3/\text{HNO}_3$ solution as a wash. Twenty milliliters of 8 N hydrochloric acid was passed through the column to hold the uranium on the resin while displacing the aluminum. Finally the uranium was eluted with two 25-ml portions of 0.1 N hydrochloric acid. Analysis of the elutriates by the indirect PAN method indicated that 85 per cent of the uranium was in the first elutriate, and less than one per cent was in the second. Further work to increase the uranium recovery and to determine impurities in the uranium fraction is planned.

ISOTOPE SEPARATION

Processes are being developed for separating and purifying the isotopes of a number of elements including hydrogen, the noble gases, carbon, and uranium. Potential sources of supply of these materials are being evaluated.

Helium-3 Separation and Purification

A thermal loading pump was designed for filling cylinders with helium purified by thermal diffusion. The system consists of four cylinders which are alternately heated to increase the gas pressure. The pump was tested using commercial helium. Feed pressure was maintained at 20 ± 2 psig while the gas was loaded into a 500-ml lecture bottle. In seven cycles (94 minutes) the pressure in the product vessel increased to more than twice the feed pressure. Table 2 shows the data taken during this run. All values are for the hot cycle, i.e., the highest pressure reached by the heated gas.

Table 2
THERMAL PUMP PRESSURE READINGS

Cycle	Heater 1 (psig)	Heater 2 (psig)	Heater 3 (psig)	Heater 4 (psig)	Product Vessel (psig)
1	25	25	29	31	--
2	25	26	32	33	--
3	28	--	--	--	40
4	28	30	37	45	42
5	28	30	43	47	44
6	--	--	--	--	--
7	30	33	40	49	47

The following are the data for the cold cycle, taken when the gas was at its lowest temperature:

Cycle	Heater 1 (psig)	Heater 2 (psig)	Heater 3 (psig)	Heater 4 (psig)
1	19	18	26	27
2	20	--	--	--

These results show that a cooling system is necessary. On the second cycle very little additional gas was fed into the system because the cold pressure was nearly equal to the feed pressure. When a cooling system is added to the pump, the final pressure at the end of seventh cycle is expected to be about 100 psig.

Helium-3 Thermometer

Preliminary runs are being made with the apparatus to be used for determining thermomolecular pressure corrections for helium-3. For testing the system helium-4 was used as a coolant in place of helium-3. The vapor pressure bulb was loaded with 728 torr of helium-4 gas at 4.2°K; then the bulb was closed off from the supply to avoid flooding with excess liquid during condensation of the inner bath. The pressure over the helium-4 bath was reduced with a specially sealed vacuum pump to a pressure near 1.0 torr. (1.00087 torr is equivalent to 1.270°K on the 1958 helium-4 vapor pressure scale). Next, helium-4 was condensed in the inner bath space by helium-4 transfer gas (at about 0.2 torr) in the vacuum jacket. The pressure over the inner bath was then reduced with the specially sealed pump.

A quartz bourdon tube was used to measure the vapor pressure of the liquid in the bulb alternately through 1/4-inch and 1/32-inch stainless steel sensing tubes. The minimum pressure attained in the bulb was 0.848 ± 0.042 torr. On the 1958 helium-4 vapor pressure scale this pressure corresponds to $1.2446 \pm 0.0077^\circ\text{K}$. As helium-4 in the outer bath boiled off, the temperature rose to $1.2592 \pm 0.0069^\circ\text{K}$ where it was held constant for the remainder of the test.

The pressure measurements obtained with the bourdon tube instrument were not reproducible; however, fluctuations were not as great in the 1/4-inch tube as in the 1/32-inch tube. The comparative fluctuations indicated a nonequilibrium condition in the smaller tube, a condition which was verified subsequently.

The pressure change in the sensing tubes was monitored to determine any pattern. None was indicated for the 1/4-inch tube; therefore, the pressure in that tube was used as a null value. In comparison, the pressure rose steadily in the 1/32-inch tube. After an hour, the pressure continued to rise but at a decreasing rate, indicating that it was approaching an asymptote. At the end of the test the pressure in the 1/4-inch tube was remeasured; there was only a slight difference from the null pressure measured 80 minutes before. These results are shown in Figure 1.

The Weber and Schmidt Equation indicates a 0.164 torr pressure difference at an operating temperature about 1.26°K . In this experiment the greatest observed difference was about 0.157 torr for an unequilibrated system. The agreement is satisfactory, and it shows that the required precise measurements can be made at Mound Laboratory. Second, the equation of Weber and Schmidt, which was determined by experiments with helium-4 vapor pressurized to simulate lower temperatures, will probably be found applicable to equilibrium (saturated) helium-4 vapor.

Carbon-13

Thermal Diffusion Total production from the 11-column, natural abundance, thermal diffusion cascade as of January 8, 1964, was 0.22 g of carbon-13 enriched to approximately 93 per cent in 91 per cent methane. The product withdrawal rate is now 250 cc of methane per week, equivalent to a production of 0.5 g of carbon-13 per month. On December 27, 1963, a composition profile was measured for the 11-column system. Results are given in Table 3. Integration of the composition profile over the volume of the system revealed that the holdup of C^{13}H_4 in the system was approximately 5.2 liters. This amount represents 3.0 g carbon-13. Of this quantity 2.2 g were transported into the thermal diffusion cascade system since startup in April 1963. A batch addition of 0.7 g of carbon-13 from earlier thermal diffusion experiments was made in October 1963, and the remaining 0.1 g of the holdup was the natural abundance of carbon-13 in the volume of methane required to fill the system.

Control of withdrawal of impurities from the bottom of the cascade has been substantially improved by the addition of thermal conductivity sensing devices to the last two stages. A voltage proportional to the difference in thermal conductivity between the impure methane at the middle of the last stage and the substantially pure methane at the middle of the next to last stage is recorded on a potentiometric recorder. A continuous record of the methane purity in the last stage is thus obtained. The withdrawal rate of impurities can be adjusted on the basis of this information to maintain the methane content of the last stage at a constant desired level.

Carbon Monoxide Distillation Two factors are involved in bringing a distillation column to its steady-state operating condition: (1) accumulation of column inventory of the various components, and (2) establishment of equilibrium between the phases at all points within the column. Since distillation separation of C^{13}O from C^{12}O involves a low relative volatility (1.01), a large number of theoretical separating stages are required. Therefore, the column inventory of carbon-13 will be relatively large and will be the factor which determines the time required to reach steady-state. The 43-foot, 48-mm ID column planned for this separation will contain about 270 g carbon-13 at design conditions. Therefore, about nine months would be required to reach steady-state at the normal accumulation rate of 1.0 g per day.

Figure 1. Helium-4 Thermomolecular Pressure Difference.

Table 3

**COMPOSITION PROFILE IN THE NINE-STAGE, 11-COLUMN,
METHANE THERMAL DIFFUSION CASCADE, DECEMBER 27, 1963**

Location of Sample	Purity of Methane	Mass 17 Enrichment from Methane Analysis (%)	Carbon-13 Enrichment from Carbon Dioxide Analysis (%)
Waste Stream	99.60	0.96	----
Feed	99.62	1.09	----
First Stage Bottom	99.32	1.31	----
Second Stage Bottom	99.21	2.45	----
Third Stage Bottom	99.32	3.82	----
Fourth Stage Bottom	99.18	6.93	----
Sixth Stage Bottom	97.50	48.90	----
Seventh Stage Bottom	97.46	83.31	----
Eighth Stage Bottom (Product Withdrawal Point)	91.10	97.24	93.18
Ninth Stage Middle	55.92	97.95	----

During start-up, when the column product concentration is less than the design value, the column can be operated at conditions which reduce the number of theoretical stages. The procedure for a column of specific design is as follows:

1. The highest usable boilup within pressure drop limitations is selected as a starting point.
2. At the selected boilup the number of theoretical stages in the column is determined from column characteristics.
3. A bottoms concentration and $C^{13}O$ recovery is assumed, and minimum theoretical stage requirements are determined. The calculated rates of carbon-13 accumulation were inversely related to recovery, but 20 per cent was selected as the lowest practical recovery and was used for the final calculations.
4. The reflux ratio is determined from the actual and minimum theoretical stages and the minimum reflux ratio by using the Gilliland correlation.
5. With reflux ratio, boilup and recovery known, the feed and rate of carbon-13 accumulation is calculated.
6. This procedure is repeated at various bottoms concentrations up to the design value.
7. When the actual trays and minimum traps approach the same number, it is necessary to calculate carbon-13 accumulation rates at several boilups and to plot these for selection at the optimum boilup.
8. The column inventory of carbon-13 at any bottoms concentration can be calculated from the average concentration and column holdup. The curve of inventory as a function of bottoms concentration during start-up is used to calculate the time required to reach each concentration. A stepwise calculation is required for a schedule of conditions to be used until the required inventory of carbon-13 is accumulated.

This procedure gave the start-up schedule shown in Figure 2, which indicates that the column can be at design conditions less than 80 days after operations start.

Figure 2. Start-up Period of Carbon Monoxide Distillation; Calculated Conditions for a 43-foot Column: Relative Volatility = 1.01; ID = 48 mm; Podbelniak Heli-pak No. 3013.

Neon

The four-column, two-stage, neon, hot-wire thermal diffusion unit was realigned to run a two-column, two-stage overlap system for the enrichment of neon-20 and neon-22. Two additional columns are being arranged in a two-stage cascade system with a reservoir at one end to process the intermediate neon stream for the enrichment of neon-21.

The one-one overlap system was run at two pressure conditions to determine the effect on system performance. The operating conditions and results are given in Tables 4 and 5. Theoretically, the system should operate better at the higher pressure since the condition $K_c = 10K_d$ was approached and since separative work was 90 per cent of maximum. At increased separative work, however, sufficient column length must be available to reach the desired stream concentration. In Experiment 2 lack of column length caused lower stream concentrations. These data agree with previously calculated results for a 3-1 overlap, in which the product concentration decreased for the higher operating pressure approaching $K_c = 10K_d$ although the flow was constant.

Table 4
OPERATING CONDITIONS FOR SEPARATION OF NEON
ISOTOPES IN 1-1 OVERLAP SYSTEM^a

	Experiment 1		Experiment 2	
Feed Rate (ml/hr)	90.0		80.0	
Time to Steady Condition (hrs)	48		72	
	1st Stage	2nd Stage	1st Stage	2nd Stage
K_c/K_d	2.4	1.6	5.5	3.4
Pressure				
(mm Hg)	1000	900	1210	1080
Drawoff				
(ml/hr)	top-71.0	top-5.00 bottom-7.60	top-58.6	top-12.3 bottom-2.60

^aExperiment 1 was run near maximum separation, Experiment 2 near maximum separative work.

Table 5
NEON ISOTOPE CONCENTRATIONS FOR OPERATING
CONDITIONS SHOWN IN TABLE 4

	Experiment 1			Experiment 2		
	Ne ²⁰ (%)	Ne ²¹ (%)	Ne ²² (%)	Ne ²⁰ (%)	Ne ²¹ (%)	Ne ²² (%)
Feed	90.47	0.30	9.23	90.47	0.30	9.23
1st Stage, Top	99.72	0.08	0.20	99.51	0.11	0.38
2nd Stage, Top	73.56	2.26	24.18	99.44	1.44	8.12
2nd Stage, Bottom	0.07	0.07	99.86	0.68	0.49	98.83

For the neon-21 separation the maximum time required to remove most of the first component in the neon mixture was estimated by calculating reservoir, or initial, concentrations as a function of final concentration at the top of the cascade; in this case neon-22 was separated from neon-21 in an equivalent volume mixture. The graphs for $K_c = K_d$ and $K_c = 10K_d$ are shown in Figures 3 and 4. The maximum time calculated for the removal of 99 per cent neon-22 from the system was 150 days. The actual time for removal of the first component is expected to be between 1.5 and 5 months. Draw-off time of the second component (neon-21) will be estimated.

Xenon

Experimental Chromatograph Chromatography is being used for the experimental separation of krypton from xenon. Seven runs were made to determine the effect of a shortened column half as long as the previously used one. For this purpose a tubular column, 9.5 cm long and 2.54 cm in diameter, was filled with 50/60 mesh activated coconut charcoal adsorbent. The carrier gas was precooled helium. The peaks were sharper than those for a longer column; however, the cleanup (the ratio of xenon in the feed to xenon in the trap) was not as good. Activated sites in the heterogeneous surface cause tailing, precluding the use of a shorter column which would give acceptable performance in the shortest time. If another adsorbent is found to exhibit less tailing, a short column may be satisfactory.

Clathration for Purification and Storage of Xenon Although the rare gases seldom enter into chemical combination with other substances, there is one type of compound that can be formed by reaction to give stable, solid crystals at room temperature. These compounds are clathrate compounds, an inclusion type compound in which a molecule of one component (the guest) is completely enclosed within the crystalline lattice of another component (the host). Since a crystalline lattice is rigid, the cage surrounding the cavity will retain guest components that come within a definite range of size and shape. If the guest is too small it will pass through the openings in the cage walls. If the guest is too large for the cavity, the host will not enclathrate it during the crystallization process. Therefore, when considering the clathration of a given guest molecule, it is necessary to choose a host which will yield an open crystalline structure just large enough to trap the guest.

The two components of a clathrate do not combine chemically with each other. The guest component of the clathrate is physically trapped within the lattice network of the host. In order to release the guest from the cage, it is necessary to break down the crystalline lattice either by melting the crystal or dissolving it in some suitable solvent.

Of the rare gases, argon, krypton, and xenon have been enclathrated successfully. Up to now, all attempts to form clathrates of helium and neon have failed. Evidently helium and neon atoms are too small to be retained by the host molecules that have been employed. Because of the selectivity exhibited by the host molecules in the clathration process, it is possible to separate mixtures of substances such as the rare gases. A system is suggested here for the purification of xenon using the techniques of clathration.

Before deciding on a particular method of preparation for the clathrate, it is necessary to select the proper clathrating agent, the host. It is desirable to choose one which will give a solid at ordinary temperatures, a high yield of the xenon clathrate, and a product which is stable at room temperature. Of the xenon clathrates prepared thus far, only the xenon clathrate of hydroquinone fulfills the above conditions. Therefore, hydroquinone was chosen as the clathrating agent.

Hydroquinone clathrates may be prepared in four different ways. These include crystallization from an aqueous hydroquinone solution, from a nonaqueous solution, from a melt, and by sublimation.

The nonaqueous crystallizations are generally preferred over other methods because they produce higher yields and require shorter crystallization times. For high yields in clathrating gases, it is necessary to use

Figure 3. Product Concentration as a Function of Initial Concentration for a Neon-21/Neon-22 Separation; 48-Foot Column, Infinite Reservoir, $K_C = K_d$.

Figure 4. Product Concentration at a Function of Initial Concentration for a Neon-21/Neon-22 Separation; 48-Foot Column, Infinite Reservoir, $K_C = 10K_d$.

high pressure to insure the presence of as many gas particles as possible at the sites where crystallization occurs.

A saturated solution of hydroquinone is prepared in a suitable solvent at room temperature. Then additional hydroquinone is added in the amount equivalent to the amount of the clathrate desired. The mixture is placed in a pressure reaction vessel. Atmospheric gases are then purged from the system, and xenon is added to the vessel to a pressure of about 175 psig. The pressure reaction vessel is heated to 60°C or to a temperature which will insure complete dissolution of the excess hydroquinone. The reaction vessel is cooled slowly to room temperature after which the excess xenon is pumped off. The resulting xenon-hydroquinone clathrate is stable at ordinary temperatures but decomposes readily at temperatures above 165°F. Under the conditions described here, the clathrate should contain about 27 weight per cent xenon. The theoretical maximum for the xenon-hydroquinone clathrate is 28.4 weight per cent. To release the enclathrated gas, it is sufficient to heat the compound to near its melting point or to dissolve it in a solvent.

Thermal Diffusion Theory

An approximate formula for the viscosity of a binary, isotopic gas mixture has been derived from the rigorous kinetic theory formula. According to this equation the viscosity of an isotopic mixture is a nearly linear function of the concentration. For a mixture of He³-He⁴ the maximum deviation from linearity is approximately the same as the difference between experimental and theoretical results. For heavier isotopic mixtures, the deviation from linearity is smaller.

In the thermal diffusion column theory being developed, it had been planned to use the rigorous kinetic theory formulas for the viscosity and the thermal conductivity. However, since these equations are cumbersome to use, it was decided to investigate the possibility of using approximate formulas. Several authors have obtained approximate formulas for these quantities which are applicable to mixtures of monoatomic gases.¹ These approximate formulas, although much simpler than the rigorous formulas, are still complicated. For the viscosity of a mixture of heavy isotopes, Hirschfelder gives the approximate formula,²

$$\frac{1}{\sqrt{\eta}} = \frac{x_1}{\sqrt{\eta_1}} + \frac{x_2}{\sqrt{\eta_2}}$$

where x_1 and x_2 are the concentrations of Components 1 and 2; and the value

$$\eta_1 = 266.8 \times 10^{-7} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)}}$$

The equation for η_2 is similar to the above expression.

Recently, the rigorous formulas were used to calculate the viscosity and thermal conductivity of some isotopic systems at several concentrations.³ Those results are represented by the linear equations.

$$\eta = \eta_2 + (\eta_1 - \eta_2) x_1$$

$$\lambda = \lambda_2 + (\lambda_1 - \lambda_2) x_1$$

¹E. A. Mason and S. C. Saxena, *Phys. Fluids*, 1, 361 (1958); R. L. Brokaw, *J. Chem. Phys.*, 29, 391 (1958).

²J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, New York, John Wiley and Sons, 1954.

³MLM-1152, pp. 5-6.

Since these equations are simpler than any of the other approximate expressions, an attempt was made to derive them in a rigorous manner.

By expanding the kinetic theory equation for viscosity in a power series about $\sqrt{M_1} = \sqrt{M_2}$, the following expression was obtained.

$$\eta = \eta_2 + (\eta_1 - \eta_2) x_1 + \frac{1}{2} \frac{(\eta_1 - \eta_2)^2}{\eta_2} \frac{(39A^* - 25)}{10(1 + 0.6A^*)} x_1 x_2$$

where A^* is a weak function of temperature which is approximately equal to one. By retaining only the first two terms in this series, the linear expression given above is obtained. The fractional error introduced by ignoring the third term is approximately,

$$\frac{(\eta_1 - \eta_2)^2}{\eta_2^2} \frac{(39A^* - 25)}{20(1 + 0.6A^*)} x_1 x_2$$

For a mixture of helium-3 and helium-4 this quantity is less than 0.3 per cent, and it is smaller than this for heavier isotopic mixtures.

ALPHA AND NEUTRON SOURCE DEVELOPMENT

Mound Laboratory is responsible for producing alpha and neutron sources, manufactured from polonium-210 and plutonium-239, which cannot be produced by American industry at the present time. The techniques of fabricating these unusual sources are being developed and publicized.

Neutron Sources

The rate of increase of neutron emission for Pu^{239}Be neutron sources is being studied. It has been found that the growth rates from calorimeter measurements of heat output do not agree with growth rates determined by neutron counting using an experimental Am^{241}Be source (HAM-1) as the standard. An alpha spectrum was obtained on the same batch of americium-241 as used in HAM-1 to determine if other alpha emitters are present. Preliminary results indicate that other alpha emitters are present.

One PuBe source, on loan to ORSORT for use in a dime irradiator for the New York World's Fair, was shipped. Eight PuBe sources were recanned and shipped, closing out the program. All but one of the sources loaned to users during the program have been returned. A final report on the recanning program is being prepared.

A one-curie PuBe source (M-88) was shipped to Armour Research Foundation to be exchanged for M-75, which has been exposed to 5×10^{11} thermal neutrons per cm^2 per second since 1957. Prior to 1961 it operated bare in an uncooled position in a graphite stringer in the reactor with a temperature rise of $300\text{--}400^\circ\text{C}$ above ambient. In 1961 an extra cadmium can was installed on the source which reduced the temperature rise to $30\text{--}50^\circ\text{C}$. After the gamma activity of the source has decreased sufficiently, M-75 will be returned to Mound Laboratory for evaluation.

The only previous case of significant neutron irradiation of a PuBe source was M-71. The outer container of this source, which appeared to be in good condition, was removed in August 1963. The inner tantalum container showed severe overheating; it had nearly disintegrated, being completely permeated with many small cracks. This was probably due to thermal stresses from the sudden heating. Source M-75 will be examined to determine if changes occurred due to its thermal and irradiation cycle treatment.

Two Pu^{239}Be neutron sources were made, one containing 4 g of plutonium with an emission of 1×10^8 n/sec and the other containing 0.4 g plutonium with an emission of 5.97×10^6 n/sec. The relatively low neutron production of the second is attributed to an incomplete reaction of the plutonium with the beryllium to form PuBe_{13} . In the smaller sources a limited amount of reaction heat is available in relation to the total heat capacity of the source assembly. In all source fabrication equipment used to date the heating capacities available have been large enough to reach the initiation temperature for the PuBe_{13} reaction; but, the heat supplied has not been sufficient to reach the $1750\text{--}1800^\circ\text{C}$ melting point of PuBe_{13} without the aid of additional heat from the reaction.

Alpha Sources

Two types of experimental polonium alpha sources are being evaluated to determine the validity of two design criteria for polonium alpha sources. First is the assumption that windows cannot be placed in direct contact with high intensity polonium deposit due to damage from recoil nuclei; the other is that the 0.00013-inch thick rolled stainless steel is the thinnest material which could be used safely as a covering for high intensity alpha sources. This thickness of stainless steel attenuates approximately 30 per cent of the energy of polonium alpha particles transmitted at right angles from the source.

Four sources were fabricated September 23, 1963, as follows:

	Source			
	T-1	T-2	T-3	T-4
Window	0.00013 in. stainless steel	0.00013 in. stainless steel	Gold ^a Leaf	Gold ^a Leaf
Window to Po Distance (in.)	0.016	0	0.016	0
Source Diameter (in.)	0.75	0.75	0.75	0.75
Po (curies)	9.13	12.30	9.21	15.09
Po Concentration (curies/cm ²)	4.56	6.15	4.60	7.54
Alpha Range (%)	72.5	74.5	83	83

^aThree layers of beaten gold leaf.

There was no change in construction from standard sources except for window substitution in two cases and slight modification to permit zero window clearance in two. The sources were stored on holders attached to stoppers in test tubes containing Drierite. Wipe checks for leakage, alpha range checks, and calorimeter checks were made. As of December 10, 1963, 78 days after fabrication, there has been no leakage from any of the sources. The 0.00013-inch stainless steel foil has numerous "pin holes" which transmit strong light. The gold foil is also permeated with similar "holes". It appears that these may not be holes but merely thin areas. From tests on welded neutron and heat sources it had been found that polonium will migrate through holes which are detectable only at the 10^{-9} cc/sec range of a helium leak detector.

These sources will be measured periodically, and additional sources will be fabricated and studied to gain statistically significant data. Gold foil windows of one and two layers will also be tested. A single layer of gold foil is only six percent of a polonium alpha particle range.

Large area, high intensity alpha sources are being developed which, though not wipe free, will not lose more than five per cent of their activity within a half-life. A hold-down material deposited on the polonium may not be more than 5-10 per cent of an alpha particle range. These sources consist of approximately one curie polonium-210 per cm² of backing.

Five to six curies of polonium were vacuum deposited on a one-inch diameter backing; then gold was electroplated on the polonium. The following variations were used for evaluating sources prepared by this general method:

1. Four sources had copper backings. The polonium on these sources separated from the copper while the gold layer was being electroplated.
2. Seven sources had nickel backings. The polonium layer separated from the backing on four sources, and three were suitable for further tests.
3. Four sources were prepared with gold-plated copper backings. All were successfully electroplated and were retained for further tests.

4. Three sources with gold-plated nickel backing were successfully prepared.

5. Two sources with platinum backing were acceptable for additional tests.

Nine of the acceptable sources were stored for life tests. After 50-60 days they were wiped to remove loose activity and calorimetered. Of the nine sources only two retained more than 95 per cent of the initial polonium. Both sources had gold-plated nickel backings. The outer layer of gold had diffused through the polonium into the nickel; therefore, these two sources were discarded since loss of the polonium was imminent. The other seven sources had retained from 0.5 to 88 per cent of the polonium. None of the sources were satisfactory in the application.

ANALYTICAL

Methods of analyzing elements and compounds are being developed to support other programs at Mound Laboratory. These methods include instrumental techniques and classical wet methods.

Coating Resistance to Thorium Residue

A coating material is being sought for use in storing thorium residues. The coating must be compatible with concrete and resistant to thorium residue containing about 50 per cent moisture. Metal strips (5/8 x 2 inches) were dipped in the coatings and air dried. Then the strips were placed either in a thorium slurry or in distilled water (for comparison). The results at the end of two weeks were:

Coating	Thorium slurry	Distilled water
Tygon series "ATD"	blistering and discoloration	blistering and discoloration
Gaco "A"	blistering	blistering
Lowe Brothers Orange enamel	discoloration	discoloration
Two-component epoxy	no effect	no effect

A polonium alpha radiation exposure on the two-component epoxy showed no apparent effect after three weeks.

Calorimetry

Constant Current Controller Two constant current controllers have been used since October 1961⁴ to maintain the heater currents for high precision calorimetric assays. Several modifications of the original circuit are incorporated in Figure 5. The reference resistance (R_1) was moved in series with the calorimeter heater instead of the batteries. In the previous arrangement the sum of the current to the heater and the voltage divider were controlled. Consequently, as the leads from the panel board to the heater changed resistance with temperature, the current through the heater changed slightly. Moving R_1 to the present position has increased the heater potential in lead No. 2 (HPL_2) by the voltage drop in R_1 which is always equal to the voltage of the standard cell. The heater potential (HP) has been increased by the voltage drop in R_1 divided by the voltage dividing factor (F). The potential in heater lead No. 1 (HPL_1) has not changed and is still the first voltage to equal the maximum range of the potentiometer as the current is increased with a heater current (HI) measuring resistance of 10 ohms. Since the heater resistance is given by Equation 1,

$$R_s = \frac{F(HP) - HPL_1 - HPL_2}{HI} \quad (1)$$

it is apparent that R_s , for small currents is determined by subtracting two large numbers with a resulting loss in precision and accuracy. The loss is not serious, however. At a heater current of 20 milliamperes in a heater of 100 ohms, the loss is not over 0.002 per cent as indicated in the next section on calibration of panel boards. Calorimeter 90 used in conjunction with the constant current divider has a heater resistance of 105 ohms and produces 42,000 microwatts at 20 milliamperes. The probable error of the calorimeter at this power (or less) is three microwatts, or 0.007 per cent. As the current is decreased to 10 milliamperes, the loss in precision in measuring R_s would be doubled, or 0.004 per cent, and the probable error in the calorimeter would be quadrupled, or 0.028 per cent. Thus, the effective loss in precision in moving R_1 to the present position decreases as the heater current decreases and causes no significant loss of precision at any current.

⁴ MLM-1125.

Figure 5. Constant Current Controller for a Calorimeter Heater.

The water bath that was the environment for the thermal circuit for R_2 and R_3 has been replaced by a block of aluminum, five inches OD by six inches long with a 1.438-inch axial hole for positioning the thermal assembly.

Originally, R_1 consisted of a five-decade box with resistances from 0.01 to 999.9 ohms. A narrower selectivity of heater current was desired, so a 0.1 to 999.9 Leeds and Northrup decade box was shunted with a 1 to 9999 ohm Leeds and Northrup box. By means of the two boxes, the least favorable situation up to 170 milliamperes is a current selectivity within 0.06 per cent.

A Hewlett-Packard DC amplifier (Model 425-A) and an Epply standard cell are used in one controller. The other controller has a Leeds and Northrup (Model 935-B) and an electronic standard cell made by Sensitive Research. The two controllers are about equal in performance. The second system is more subject to static pick-up, but has slightly more long-term stability. Both controllers maintain 100 milliamperes constant to two parts per million for several hours from well-charged Willard low-discharge batteries.

Prototype Calorimeter 92 A water bath calorimeter, designated Calorimeter 92, is in final assembly stage. This calorimeter is to be used for testing the design of two identical calorimeters made for the purpose of measuring intersite solid plutonium-238 shipments. The calorimeter will be operated principally by servo systems and will record measurements so that minimal operator time will be required.

The calorimeter consists of an inner polypropylene bath containing a stirring mechanism, heaters, and a bridged resistance thermometer. The bath is designed for acceptance of any geometry sample under 16 inches in length that can pass through a seven-inch opening. The polypropylene bath is submerged in a larger, stirred, constant temperature bath which contains an integrating calorimeter. Temperature control of the bath and the output of the integrating calorimeter are maintained by use of magnetic amplifiers. A constant voltage source is used for the sensing bridge. The calculated thermal resistance is approximately $0.3^\circ\text{C}/\text{watt}$, and the water volume of the inner bath is about 8.9 gallons. The expected sensitivity of the calorimeter is 25,000 microvolts per watt.

Calibration of Panel Boards A panel board is associated with each calorimeter and is used (1) to adjust the bridge current, (2) to set in a heater current to either of the two heaters, to both heaters in series or to the heater leads, and (3) to select the heater potential measuring voltages, HI , HP , HPL_1 and HPL_2 (see Figure 5). In April 1963 a calibration procedure was established which gives two correction factors for each panel board, one for the voltage divider and the other for the current measuring resistor. The factors are obtained without removing the standard resistors from the panel boards. The correction factors are based on the resistances of two Leeds and Northrup standard resistors which are measured once a year by the Albuquerque Operations Primary Standards Laboratory. The certified values of the two resistors as of August 8, 1962, and August 2, 1963, are as follows:

Serial Number	Certified Value 8-8-62 (ohms)	Certified Value 8-2-63 (ohms)
1532218	10.0002	10.0001
1534149	100.0000	100.0000

The first correction factor (F_1) is the ratio of true to nominal resistance of the HI measuring resistor, which is obtained by comparing this resistor to the 10 ohm standard. A current of about 20 milliamperes is maintained with the current controller in the HI circuit of a panel board and also in series with the standard resistor. The voltage drops across the two resistors are compared by a potentiometer. The results for each panel board, as of April and December 1963, are given in Table 6. The precision of these measurements is about two parts per million when both resistors have the same nominal resistance, and it is about 10 parts per million when the HI measuring resistor is 100 ohms or one ohm. Complete dependence is placed on the

potentiometer in the latter case. On the average, the resistors appear to have decreased by 0.001 per cent from April to December. This is due to the 0.001 per cent decrease in the certified value of the standard and probably was caused by rounding-off. Values of 10.00015 and 10.00014 were probably obtained and rounded-off to 10.0002 and 10.0001 on the certificates. Unfortunately, a change in 0.001 per cent in this resistance changes the calculated power (I^2R) by 0.002 per cent. For half-life work, with samples of optimum power, this is quite serious since the probable error of Calorimeter 90 is as low as 0.001 per cent. It would be desirable for the Albuquerque Operations Laboratory to add another digit to the certified values. An inspection of Table 6 indicates that none of the resistors have changed more than 0.006 per cent with respect to the original certificates even though three of the resistors are 16 years old.

Table 6
CALIBRATION OF HEATER CURRENT MEASURING RESISTORS
IN CALORIMETER PANEL BOARDS

Panel Number	Original Certificate (ohms)	Resistance as of April 63 (ohms)	Resistance as of December 63 (ohms)	Change in Resistance (%)
1	10.0000(Jan 63)	10.000039	9.999953	-.0009
2	9.9999(Dec 47)	9.99950	9.999330	-.0017
3	None	0.9999756	0.9999875	+.0012
4	10.0000(June 59)	10.00020	10.000107	-.0009
5	100.000 (July 59)	100.00115	100.00115	.0000
6	10.0000(Dec 47)	9.999606	9.999496	-.0011
7	10.0000(June 59)	10.000257	10.000077	-.0018
8	10.0000(June 59)	-	10.000135	-
9	9.9999(Dec 47)	9.999486	9.999410	-.0008
13	1.00002(Dec 61)	1.0000045	0.9999832	-.0021
14	10.0000(Jan 63)	-	9.999976	-

Average Change (-.0009)

The second correction factor (F_2) is the true voltage dividing factor. It is obtained by measuring the resistance of the 100-ohm standard resistor by connecting the resistor to the panel board in place of a calorimeter heater. From the measurements of HI , HP , HPL_1 , and HPL_2 , the voltage dividing factor F_2 is obtained from Equation 2:

$$F_2 = \frac{\frac{R \times HI}{F_1} + HPL_1 + HPL_2}{HP} \quad (2)$$

where R is the certified value of the 100-ohm standard.

The calculated power for a calorimeter heater run is given by Equation 3:

$$W_h = \frac{[F_2(HP) - (HPL_1L - (HPL_2L)(HI)]}{F_1} \quad (3)$$

The voltage dividing factors for the panel boards are given in Table 7. The original certified values for the individual resistors are given in Column 2. The calculated factors are listed in Column 3. Columns 4 and 5 list the measured factors (by Equation 2) as obtained in April and December 1963. In December, the reference resistor for the current controller was located after the voltage divider as in Figure 5. On the average, F_2 has increased by about 0.001 per cent, but this again can be attributed to the average 0.0001 decrease in F_1 (see Equation 2). Since F_2 depends on four different settings of the potentiometer as well as F_1 , it has a precision of about 0.001 per cent.

Table 7
CALIBRATION OF VOLTAGE DIVIDER IN HEATER CIRCUIT
OF CALORIMETER PANEL BOARDS

Panel Number	Original Certificates (ohms)	Voltage Divider Factor (F_2) by Original Certification	Voltage Divider Factor (F_2) in April 1963	Voltage Divider Factor (F_2) in December 1963
1	1000.04 & 10000.4 (July 19, 1959)	11.00000	11.000008	11.000124
2	999.97 & 9999.6 (June 19, 1959)	10.99990	10.99963	10.99988
3	99.999 & 9999.4 (December 19, 1947)	100.9950	100.99140	100.99143
4	999.98 & 9999.5 (April 19, 1946 & November 19, 1947)	10.99970	10.999184	10.999283
5	No Divider	1.000000	—	0.999999
6	— & 10,000.1 (February 19, 1947)	—	10.999710	10.99984
7	100.002 & 10000.3 (July 19, 1959)	101.0010	100.99852	101.00112
8	1000.00 & 10000.3 (March 19, 1963 & June 19, 1959)	11.00030	—	11.000193
9	100.000 & 10,000.4 (June 19, 1959)	101.0040	101.00195	101.00155
13	100.000 & 10,000.2 (December 19, 1961 & September 19, 1961)	101.0020	100.99948	101.00189
14	1000.00 & 10,000.0 (March 19, 1963 & November 19, 1962)	11.00000	—	11.000037

In view of the excellent agreement between the April and December standardizations of the panel boards, it is no longer important which panel board is used with a calorimeter, even for half-life determinations. In fact, it seems desirable to change panel boards quite often during half-life measurements, since it will make no significant difference if the panel board factors do not change, and a change can be detected if one does occur. The calorimeter is a more sensitive comparator of panel boards than the present method.

ADHESIVES AND PLASTICS RESEARCH

Plastics

Mound Laboratory is conducting research on the molding properties of diallyl phthalate in an effort to obtain superior plastic parts for the detonator program.

At the request of the D-20 Subcommittee of the American Society for Testing Materials, 20 samples of thermosetting molding powders were evaluated by extrusion through the Monsanto Capillary Extrusion Rheometer (MCER) using a die replica orifice. The Subcommittee was primarily interested in whether the instrument could distinguish between hard and soft flowing materials of the same formulation in a reproducible manner. The samples were of 10 different formulations as shown in Table 8. Each formulation was supplied as a hard and a soft flowing material and was identified by a code number.

Table 8
MATERIALS TESTED FOR D-20 SUBCOMMITTEE

Material	Filler	ASTM Type
Phenolic	CFG Cellulose	D700 - Type 2
	Flock	D700 - Type 12
	MFG Asbestos	D700 - Type 9
	MFI-20 Long Asbestos	19
	Short Glass	25
Diallyl Phthalate	SDG Short Glass	D1636 - Type I
	SDI-5 Orlon	D1636 - Type II
	GDI-30 Glass	D1636 - Type III
Silicone	MSG Mineral	MIL-M-14F-Type MSG

For the evaluation, preforms of the formulations were prepared by placing a weighed amount of material in a preform die and applying 197,000 psi pressure. In order that all preforms possess approximately equal volumes, the apparent density of a one-gram preform of each material was determined; the calculated density was used to determine the weight of material required to give a preform 0.5 inch high (preform diameter was constant). Material densities and the weight of each preform are shown in Table 9.

The samples were run by placing three weighed preforms in the purged rheometer at 150°C² and extruding at a crosshead speed of 1.0 inch per minute. Traces of pressure as a function of time of cure were recorded for each sample.

Since the chart speed was known, the time of extrusion was determined directly from the pressure-time of cure trace (Figure 6); time of extrusion was taken from the point of appearance of the extruded strand at the orifice to the point at which 950 pounds of extrusion pressure was indicated. Extrusion was calculated using:

$$\frac{W_s - W_p}{W_s} \times 100 = \% \text{ EXTRUDED}$$

² Material 10A was extruded at 130°C.

Figure 6. Typical Cure Trace of Pressure as a Function of Time During Extrusion of a Thermosetting Plastic.

where

W_s - sample weight of 3 preforms

W_p - weight of material remaining in rheometer at end of cure

The average values of three runs on each sample are shown in Table 9.

Table 9

EXTRUSION TIME OF THERMOSETTING PLASTICS

Sample	Density ($\frac{g}{in^3}$)	Preform Weight (g)	Time of Extrusion (sec)	Extruded (%)
1A	20.94	1.084	60.78	76.95
1B	20.80	1.079	56.62	72.51
2A	21.34	1.100	59.56	76.60
2B	21.28	1.098	57.54	73.88
3A	26.92	1.408	33.60	43.10
3B	26.87	1.395	31.80	41.49
4A	23.90	1.245	42.20	57.70
4B	24.03	1.243	47.50	65.97
5A	27.07	1.410	46.54	56.88
5B	27.29	1.431	41.38	53.02
6A	27.11	1.401	54.10	66.54
6B	27.40	1.420	46.42	58.22
7A	26.01	1.343	42.86	55.16
7B	26.51	1.367	47.94	60.28
8A	25.15	1.299	50.30	65.29
8B	24.33	1.260	65.98	82.84
9A	30.45	1.564	73.16	85.92
9B	30.28	1.558	62.46	74.25
10A	30.92	1.322	30.13	45.11
10B ^a	-	-	-	-

^aThis material was unextrudable due to the extremely long glass fibers used as fillers.

The MCER readily discriminated between materials of the same formulation but of different flow properties.

The reproducibility of the rheometer test was good; the average per cent error for the time of extrusion and the per cent extrusion values were 1.3 per cent and 1.1 per cent, respectively.

Adhesives

Adhesives are being developed for use with explosives and for other specialized applications. The adhesives must have satisfactory working and curing characteristics; they must retain flexibility at low temperatures and adequate tensile strength at elevated temperatures.

One polyurethane and two polysulfide formulations were prepared and evaluated to obtain flexible conductive adhesives with good heat aging properties and with adequate tensile and peel strengths. The compositions and properties are shown in Table 10.

Table 10

COMPOSITION AND PROPERTIES OF FLEXIBLE CONDUCTIVE ADHESIVES

Component	Component in Formulation (wt %)		
	CS-22	CS-23	CS-24
Adiprene L-167 ^a	16.2	-	-
LP-3 Prepolymer ^b	-	2.2	1.5
LP-32 Prepolymer ^b	-	11.7	12.9
Bakelite BR-0014 Resin ^c	-	0.7	0.2
Polyglycol 11-80 ^d	3.7	-	-
4,4 - Methylene-bis (2 chloroaniline)	1.5	-	-
Lead peroxide paste, C _s ^b	-	2.2	2.4
Toluene	-	2.9	3.0
Carbon Black Continex CF ^e	7.6	2.9	3.0
Silver powder J-2 ^f	71.0	77.3	76.9
Working Pot Life at RT (hrs)	2	1	1
Cure Schedule	24 hrs at 110°F	16 hrs at 160°F	16 hrs at 160°F
Electrical Resistivity after 2 weeks conditioning at RT (ohm-cm)	0.24	0.09	0.01
Electrical Resistivity after Heat aging at 160°F (ohm-cm)	32.	0.10	0.01
Tensile Strength (psi)	600	< 200	260
Peel strength (lb/in)	14	not determined	8

^aDupont De Nemours and Co.

^bThiokol Chemical Corp.

^cUnion Carbide Corp.

^dDow Chemical Co.

^eWitco Chemical Co.

^fEngelhard Industries

Although CS-22, a Polyol-MCCA-cured polyurethane-based composition, had good tensile and peel strengths, it did not retain good electrical conductivity after heating to 160°F. Formulations CS-23 and CS-24 were similar to CS-20 previously reported but contain a phenolic resin Bakelite BR-0014 which was added to improve peel strength. When the resin was added in a concentration of 0.2 per cent by weight, the peel strength was increased from 6.5 to 8 pounds per inch. When used at a concentration of 0.7 per cent by weight, the plug tensile strength was less than 200 pounds per square inch.