This document was prepared in conjunction with work accomplished under Contract No.
DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

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

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: orders@ntis.fedworld.gov online ordering: http://www.ntis.gov/ordering.htm

Available electronically at http://www.doe.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728, email: reports@adonis.osti.gov

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-83-366
ACC. NO. 97393

CC: S. D. Harris, Jr., 773-A, A-214
J. W. Stewart, II, 773-A
J. P. Howell, 773-A, C-121
M. R. Buckner, 773-A, A-230
C. B. Jones, 773-A, D-118
M. K. Jones, 773-A, D-111
A. M. Ofalt, 773-A, D-109
H. B. Peacock, Jr., 773-A, D-113
J. D. Stewart, 773-A, D-155
D. R. Leader, 773-A, D-117
J. J. Fisher, 773-A, F-112
SRL Records File (2)

April 5, 1983

MEMORANDUM

TO: R. L. FOLGER

FROM: W. C. MOSLEY WC Mosley

TIS FILE
RECORD COPY

PRODUCTION OF U_3O_8 USING MACROPOROUS SULFONATE CATION EXCHANGE RESINS IN THE BEAD FORM

INTRODUCTION

The use of cation exchange resin to produce U_3O_8 suitable for powder metallurgy fabrication of reactor fuel tubes with Al-U_3O_8 cores is being investigated. An ion exchange resin process could also facilitate onsite recycle of enriched uranium from separations activities. Previous studies showed that conversion of uranyl-loaded macroporous sulfonate resin in granular form (AG MP-50 from Bio-Rad Laboratories) produced U_3O_8 powders with narrow particle size distributions and high tap densities suitable for the powder metallurgy process.[1] Subsequently, G. A. Burney of the Actinide Technology Division identified a less expensive macroporous sulfonate resin, Duolite® (Diamond Shamrock) C26 available in bead form for possible use in the resin process. Also, John Fisher, formerly of the Nuclear Engineering Division, purchased several samples of AG MP-50 resin in bead form from Bio-Rad Laboratories. Conversion of these uranyl-loaded, bead-form resins to U_3O_8 has been studied. Influences of conversion parameters on U_3O_8 powder properties have been determined. About 600 grams of U_3O_8 have been prepared from uranyl-loaded Duolite® C26 resin for powder metallurgy fabricability tests. This memorandum presents the results of these studies.

SUMMARY

U_3O_8 powder with particle size distributions suitable for powder metallurgy fabrication of Al-U_3O_8 reactor fuel tubes can be prepared using macroporous sulfonate resin in bead form. Particle size distributions of Grade 108 aluminum powder and U_3O_8 powder made from Duolite® C26 resin purchased from Diamond Shamrock match almost exactly which indicates that these two powders should blend well. Also Duolite® C26 resin at ~$80 per cubic foot offers a significant cost savings over AG MP-50 resin available at ~$250 per cubic foot. It may be possible to control Duolite C26 conversion parameters to produce U_3O_8 powders with particles in the form of integral spheres. Rapid decomposition at 500-1000°C appears to favor production of sperical U_3O_8 particles. Such spherical U_3O_8 particles may improve material handling and powder blending.

DISCUSSION

PRODUCTION OF U_3O_8 FROM DUOLITE® C26 RESIN

Description of Duolite® C26 Resins

Duolite® C26 resin is a macroporous sulfonate (strong acid) resin. It can be purchased in the form of 40-80 mesh beads for about $80 per cubic foot. (Note: AG MP-50 resin costs $200-250 per cubic foot). Duolite® C26 resin is supplied in the sodium-form whereas AG MP-50 resin is purchased in the hydrogen-form. [Care must be taken to remove all the sodium during conversion of Duolite® C26 resin to the hydrogen form since sodium has been shown to cause violent reaction between aluminum and U_3O_8 (the "thermite" reaction) during billet outgassing.]

Two batches of Duolite® C26 resin were used in these studies. Batch 25 consisted of a few pounds sent free-of-charge for evaluation. Batch 26 consisted of a cubic foot of purchased resin. Small scale conversion studies were performed with Batch 25 resin. Batch 26 resin was used to produce ~600 grams of U_3O_8 powder for powder metallurgy fabrication tests.

Loading of Duolite® C26 Resins

Duolite® C26 resin was converted from the sodium-form to the hydrogen-form by rinsing with ~14 bed volumes of 1.0M nitric acid.

Both batches of resin were loaded from acidic uranyl nitrate solution contining ~30 grams of uranium per liter and 0.05M nitric acid. Loaded resins contained about 200 grams of uranium per liter of resin. One liter of Batch 25 resin and seven liters of Batch 26 resin were loaded.

Loaded Batch 25 resin was dried in air at room temperature and had a uniform beige color. It was tacky and difficult to pour. Heating a small amount to 300°C in air produced ignition of small patches on the surface of the resin bed. Resin dried at 300°C could be poured easily. However, dried resin beads tended to adhere to glass and plastic surfaces because of static electric charges. While most of the resin dried at 300°C retained its beige color, some beads varied in color from white to dark brown. Batch 25 resin as-loaded consisted of beads generally 200-250 μm in diameter (Figure 1). [The presence of a few very large beads with diameters of ~750 μm suggested that this batch may have been mixed with a small amount of resin from another source.] Bead surfaces were covered with a 1-μm-thick skin that had cracked and buckled.

Loaded Batch 26 resin was dried in air at room temperature to produce a freely flowing powder. Most of the resin beads were beige, but some varied in color from white to dark brown. Static electricity caused the dried beads to stick to non-conducting surfaces. Resin bead diameters ranged from ~150 μm to 500 μm (Figure 2). No cracked skin was detected on bead surfaces.

Conversion of Uranyl-Loaded Duolite® C26 Resins to U_3O_8

Conversion of Batch 25 Resin to U_3O_8

Thermogravimetric Analysis. Thermogravimetric analysis (Figure 3) showed that complete conversion of uranyl-loaded Duolite® C26 resin to U_3O_8 occurs on heating above 700°C in air. Four distinct stages of thermal decomposition are evident. Heating to 300°C produces mostly dehydration. Resin decomposes in two stages at 300-380°C and 380-410°C to produce an intermediate product that is probably UO_3. Final decomposition to U_3O_8 occurs at about 650°C. The thermogram for Batch 25 Duolite® resin is nearly identical to that recorded for uranyl-loaded AG MP-50 resin[1] (Figure 7).

Conversion In A Muffle Furnace. Small quantities (13-53 grams) of Batch 25 resin were converted to U_3O_8 by heating to ~1000°C in air using three alumina dishes stacked in a muffle furnace. Conversion was controlled both by temperature and availability of oxygen. Resin in the dish near the top of the furnace began to decompose at a furnace temperature of ~300°C.

When the furnace was opened to observe the reaction at 400-600°C, resin in the top dish would begin to glow red hot as the resin began to burn spontaneously. Some resin beads would ignite and eject from the dish. Reaction in the top dish usually subsided before significant reaction occurred in the center and bottom dishes. Some reaction indicating incomplete conversion to U_3O_8 was noted in the bottom dish even after heating at 1000°C for about two hours.

The nature of the U_3O_8 product was influenced primarily by the location of the dishes in the muffle furnace. U_3O_8 powder particles from the bottom dish generally retained the spherical shape of the resin beads (Figure 4). Powder from the top dish consisted of segments of spheres. Slower heating rates also seemed to increase the percentage of U_3O_8 particles in the bottom dish that were fractured. These observations suggest that production of integral spherical particles of U_3O_8 might be accomplished by heating uranyl-loaded Duolite® C26 resin rapidly to 500-1000°C before beginning decomposition.

U_3O_8 powder with spherical particles (R25E) had a very narrow particle-size distribution about an average diameter of 132 µm (Figure 5 and Table 2). Powder consisting of segments of spheres (R25B) had a particle-size distribution skewed towards diameters smaller than 100 µm. As shown in Figure 6, the grain size of U_3O_8 powders made from Batch 25 Duolite® C26 resin at 1000°C was ~1 µm.

Glass beads several millimeters in diameter were found in the U_3O_8 product in some of the dishes. It is suspected that Batch 25 resin was contaminated with glass.

Conversion in a Rotary Calciner. Two conversion experiments with Batch 25 resin were performed using a one-inch-diameter rotary calciner described previously.[1] In the first experiment, the calciner was operated at 1000°C with a tilt of 16°. Residence time in the hot zone was 2 to 3 minutes and conversion was only 88% complete. About 25 grams of resin were calcined in 45 minutes of operation. In the second experiment, the calciner was operated at 1040°C with a tilt of 6°. Residence time was 7 to 13 minutes and conversion was over 99% complete. About 50 grams of resin were calcined in 45 minutes. A tar-like condensate formed on the cool exhaust end of the calciner tube causing some U_3O_8 product to stick to the tube. Much less condensate formed in the second experiment than in the first. Also, in the first experiment, flames and white fumes formed in the calciner tube when resin was fed into the hot zone too fast. No flames formed during the second experiment but some sparking and white fumes were detected at fast resin feed rates.

U_3O_8 powder produced in the second rotary calciner experiment is shown in Figure 7. The U_3O_8 particles retained the spherical shape of the resin beads although some appear on the verge of segmenting. Some of the particles appear hollow. The hollow particles caused the powder to have a low tap density of 2.5 g cm^{-3}.

Conversion of Batch 26 Resin to U_3O_8.

Three liters of uranyl-loaded Batch 26 resin were converted to about 600 grams of U_3O_8 powder for use in powder metallurgy fabrication of one "mini"-fuel tube. Conversion was performed in two muffle furnaces. Resin, contained in three alumina dishes stacked in each furnace, was heated in air at ~9°C per minute to 900-1000°C and held at temperature for four hours. Conversion completeness was monitored by comparing the masses of the resin and product. Incomplete conversion occurred during the first run in dishes filled with ~70 grams of resin to produce a bed depth of ~20 mm. In subsequent runs, dishes were loaded with only 30-55 grams of resin and conversion was complete. Ratios of resin mass to product mass varied from 3.16 to 3.95 because of differences in uranium loading.

Figure 8 shows that U_3O_8 powders from the top dishes in the two muffle furnaces were significantly different even though conversion parameters were nearly identical. Particles of one powder generally retained the spherical shape of the resin bead while the other powder consisted mostly of sphere segments. Spheres with diameters larger than 100 μm tended to fracture. Fractured spheres often exhibited hollow interiors. Powders prepared in both muffle furnaces were mixed to provide enough U_3O_8 for powder metallurgy fabricability tests. Figure 8C shows a representative sample of the mixture which consisted predominantly of integral spheres. This observation is consistent with the results of studies on Batch 25 resin which showed that conversion in the lower dishes produced more integral spheres. U_3O_8 powder made from Batch 26 Duolite® C26 resin at 900-1000°C had a grain size of ~0.5 μm. U_3O_8 powder from Batch 26 resin had a tap density of ~3.3 g cm^{-3}.

Figure 5 shows that U_3O_8 powder from Batch 26 resins has a smaller average particle size [d(50)=98 μm] and a wider size distribution than powders produced from Batch 25 resin. Such differences are expected based on the wider range of bead sizes in Batch 26 resin compared to Batch 25 resin (excluding the small number of ~750 μm beads). The particle size distribution of U_3O_8 powder from Batch 26 resin matches almost exactly that of Grade 108 atomized aluminum powder.[3] Therefore, these two powders should blend well during powder metallurgy fabrication of Al-U_3O_8 cores.

Production of U_3O_8 from Bead-Form Ag MP-50 Resin

Description of AG MP-50 Resins

AG MP-50 resin is normally available as 20-50 mesh beads and 50-10, 100-200 and 200-400 mesh granules prepared by grinding the beads. However, three one-liter batches of AG MP-50 resin in the form of 50-150 mesh beads made specially by the DOW Chemical company were purchased from Bio-Rad Laboratories. These resin batches were identified as BRX45028, BRX45029 and BRX45030.

Loading of AG MP-50 Resins

Small 0.1-liter volumes of the three batches of AG MP-50 resin were loaded from acidic uranyl-nitrate solution containing ~30 grams of uranium per liter and 0.15 M nitric acid. Loaded resins were dried in air at room temperature to form freely flowing powders.

Conversion of AG MP-50 Resin to U_3O_8

AG MP-50 resins were converted to U_3O_8 by heating ~30 gram quantities in air to ~950°C at ~10°C per minute and holding at temperature for about 3 hours. Conversion was carried out with the resins contained in three alumina dishes stacked in a muffle furnace. Ratios of resin mass to product mass were 3.54, 3.29 and 3.15 for batches BRX45028 (bottom dish), BRX45029 (center dish) and BRX45030 (top dish), respectively. It is thought that conversion was complete for all three batches and that ratio differences are caused by differences in uranium contents of the loaded resins.

Scanning electron microscopy revealed differences in the U_3O_8 powders made from the AG MP-50 resins (Figure 9). Particles of U_3O_8 made from all three resins had shapes related to the spherical shapes of the parent resin beads but there were distinct differences in particle cracking and fracturing. In U_3O_8 powder made from Batch BRX45028 resin, spheres with diameters smaller than 50 µm were not cracked and spheres larger than 50 µm, although cracked, remained integral. U_3O_8 made from Batch BRX45030 resin consisted of spheres with diameters larger than 75 µm. Nearly all the spheres were cracked and some had fractured into segments of spheres. U_3O_8 from Batch BRX45029 resin consisted of spheres larger than 100 µm in diameter. Many spheres had cracked and fractured into shells and segments producing many fine particles.

U_3O_8 from Batch BRX45029 resin had needle-like grains ~1 μm wide and tens of microns long oriented along spherical radii whereas U_3O_8 from the other two resins had spherical grains ~0.5 μm in diameter (Figure 10). [U_3O_8 made from granular AG MP-50 resin consisted of similar submicron spherical grains.[1]] Cracking of the U_3O_8 particles occurred along grain boundaries to produce cells varying in size from several microns to several tens of microns. These cells exhibited columnar and equiaxed structures depending on the shapes of the U_3O_8 grains. Some of these cells broke off to form the fine particles in the U_3O_8 powders. Fracturing of particles to form small cells also occurred in U_3O_8 powders made from granular AG MP-50 resins.[1]

Particle size distributions of U_3O_8 powders made from AG MP-50 resins are shown in Figure 11. The small average particle size, d(50)=52 μm, of U_3O_8 from Batch BRX45028 resin probably reflects the presence of small beads in the parent resin. The broad size distribution and larger portion of particles smaller than 40 μm for U_3O_8 from Batch BRX45029 resin is probably caused by the severe fracturing of spheres into small cells. Particle sizes of U_3O_8 powders prepared from these three batches of AG MP-50 resin fall between that of fine Grade 101 aluminum powder and those of the coarser Grades 102, 108 and 1204. The closest match of particle size distributions occurs between Grade 102 aluminum powder and U_3O_8 prepared from Batch BRX45030 resin.

Tap densities were not measured on the small quantities of powders made from bead-form AG MP-50 resins.

REFERENCES

1. Mosley, W. C., **Use of Cation Exchange resins for Production of U_3O_8 Suitable for the Al-U_3O_8 Powder Metallurgy Process,** DPST-82-388, March 1982.

2. Gray, L. W., **Unexpected Meltdown of Scrap Uranium-Aluminum Cermet Cores During Outgassing, Nuclear Safety 15(4),** July-August 1963, p. 455.

3. Mosley, W. C., **Characterization of Aluminum Powders,** DPST-83-345, March 1983.

TABLE 1

Conversion of Batch 25 Uranyl-Loaded Duolite® C26 Resin to U_3O_8.

				U_3O_8 Product			
Designation	Resin Mass g	Dish Location	Heating Rate °C/min	Mass g	Mass (Resin) / Mass (Product)	Form	Tap Density g/cc
A	43.3	Bottom	3.3	–	–	–	4.0
B	53.0	Top	3.3	16.0	3.31	Segments	3.2
C	38.1	Top	4.2	11.3	3.37	Spheres & Segments	3.8
D	36.5	Center	4.2	11.0	3.32	–	4.2
E	34.3	Bottom	4.2	10.3	3.33	Spheres	4.3
G	15.7	Top	13.0	4.7	3.3	Segments	–
H	13.0	Center	13.0	3.8	3.4	–	–
I	13.0	Bottom	13.0	4.0	3.3	Spheres	–
J	52.2	Top	2.0	15.8	3.30	Spheres & Segments	3.2
K	32.0	Center	2.0	9.8	3.3	–	3.7
L	21.8	Bottom	2.0	6.7	3.3	Spheres & Segments	3.1

TABLE 2

Characteristics of U_3O_8 Powders Made From Bead-Form Macroporous Sulfonate Resins

Designation	d(50) µm	d(16) µm	d(84) µm	Δd* µm	d(50)/d(16)	d(84)/d(50)
Duolite C26 Resin						
25B	112	76	145	69	1.47	1.29
25E	132	118	160	42	1.12	1.21
26	98	56	138	82	1.8	1.41
AG MP-50 Resin						
BRX45028	52	37	72	35	1.4	1.4
BRX45029	58	32	90	58	1.8	1.6
BRX45030	72	48	99	51	1.5	1.4

---

* Δd = d(84) - d(16).

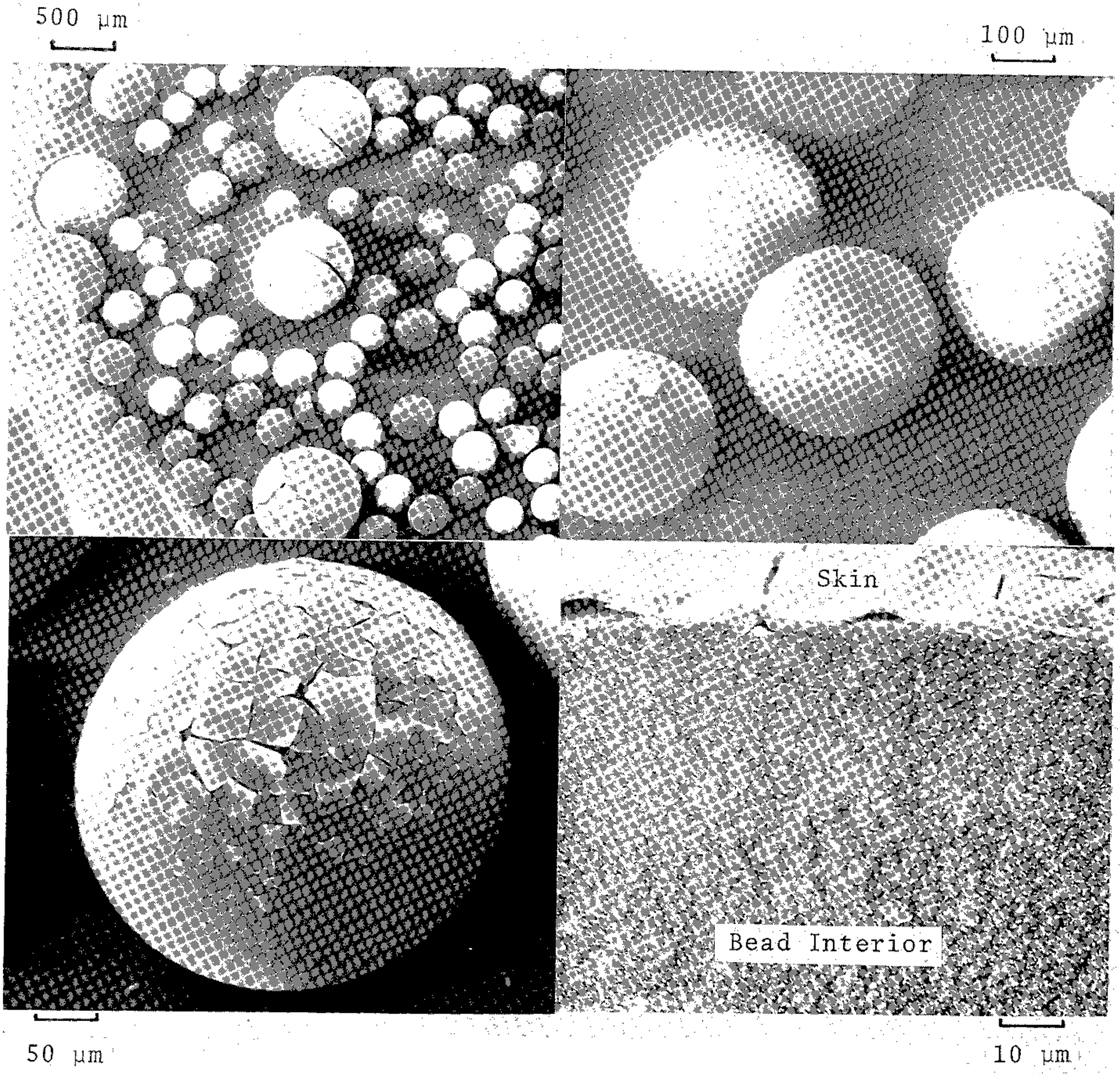


Figure 1. Batch 25 Duolite C26 Resin Loaded With Uranium and Dried

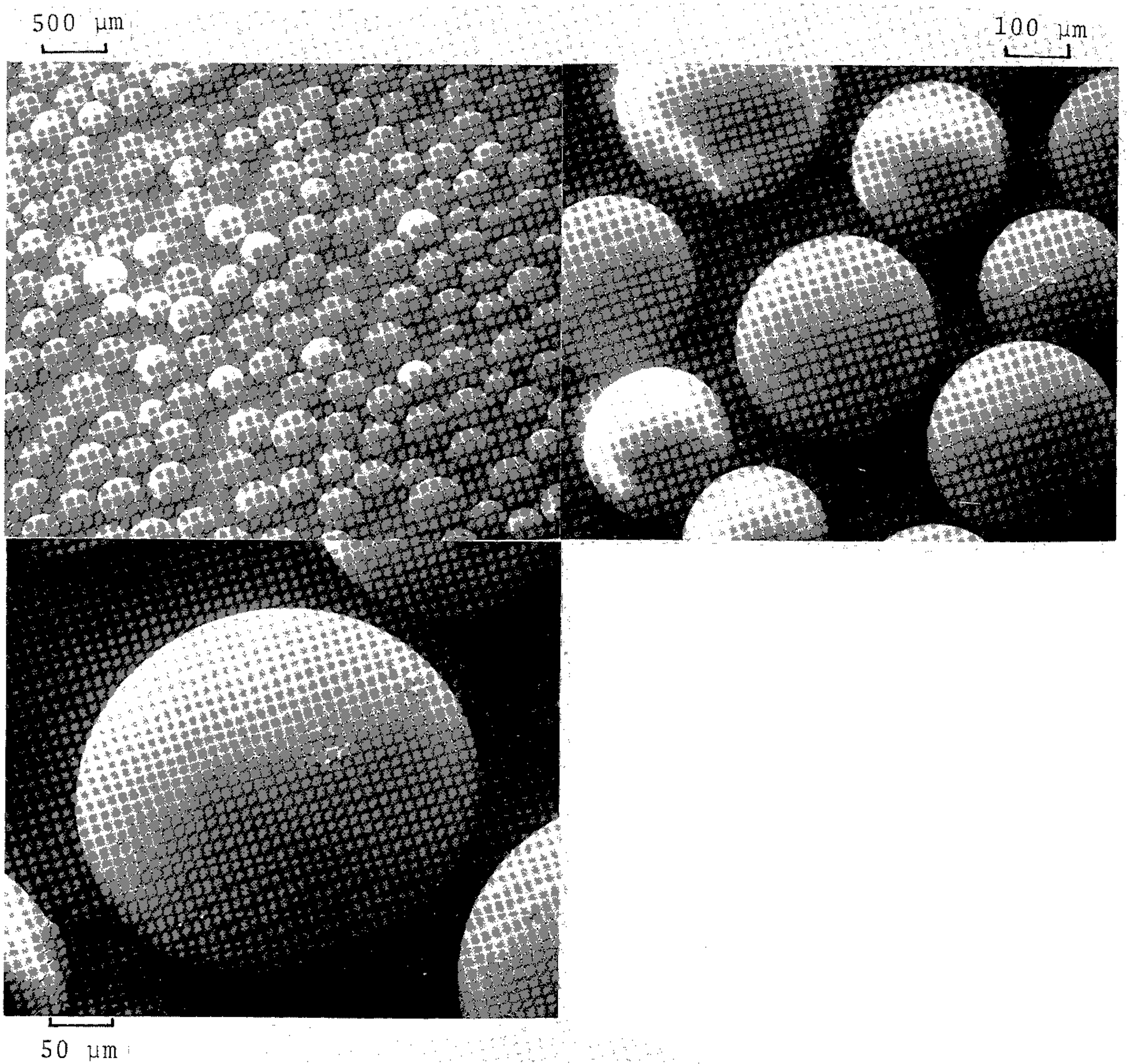


Figure 2. Batch 26 Duolite C26 Resin Loaded With Uranium and Dried

PART NO. 930252

DUPONT INSTRUMENTS

SAMPLE: Uranyl- Loaded Duolite C26 40-80 mesh beads Batch 25 SIZE ~50 mg.	X-AXIS TEMP. SCALE 100 °C/inch SHIFT 0 inch	Y-AXIS SCALE 50 %/inch (SCALE SETTING X2) U_3O_8 = 100% SUPPRESSION ____ mg.	RUN NO. ____ DATE ____ OPERATOR Mosley HEATING RATE ~10 °C/min. ATM. Air TIME CONSTANT 2 sec.

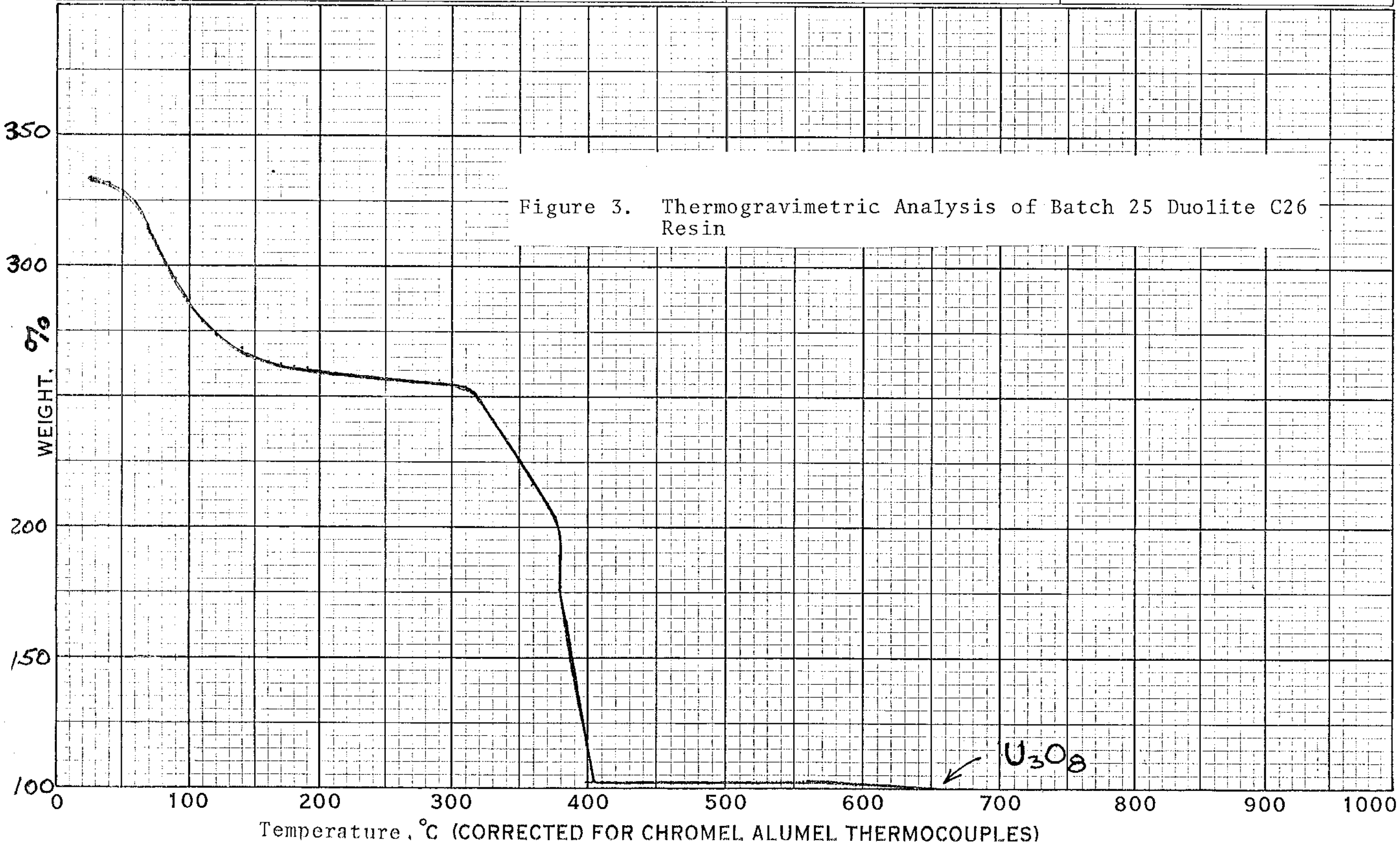


Figure 3. Thermogravimetric Analysis of Batch 25 Duolite C26 Resin

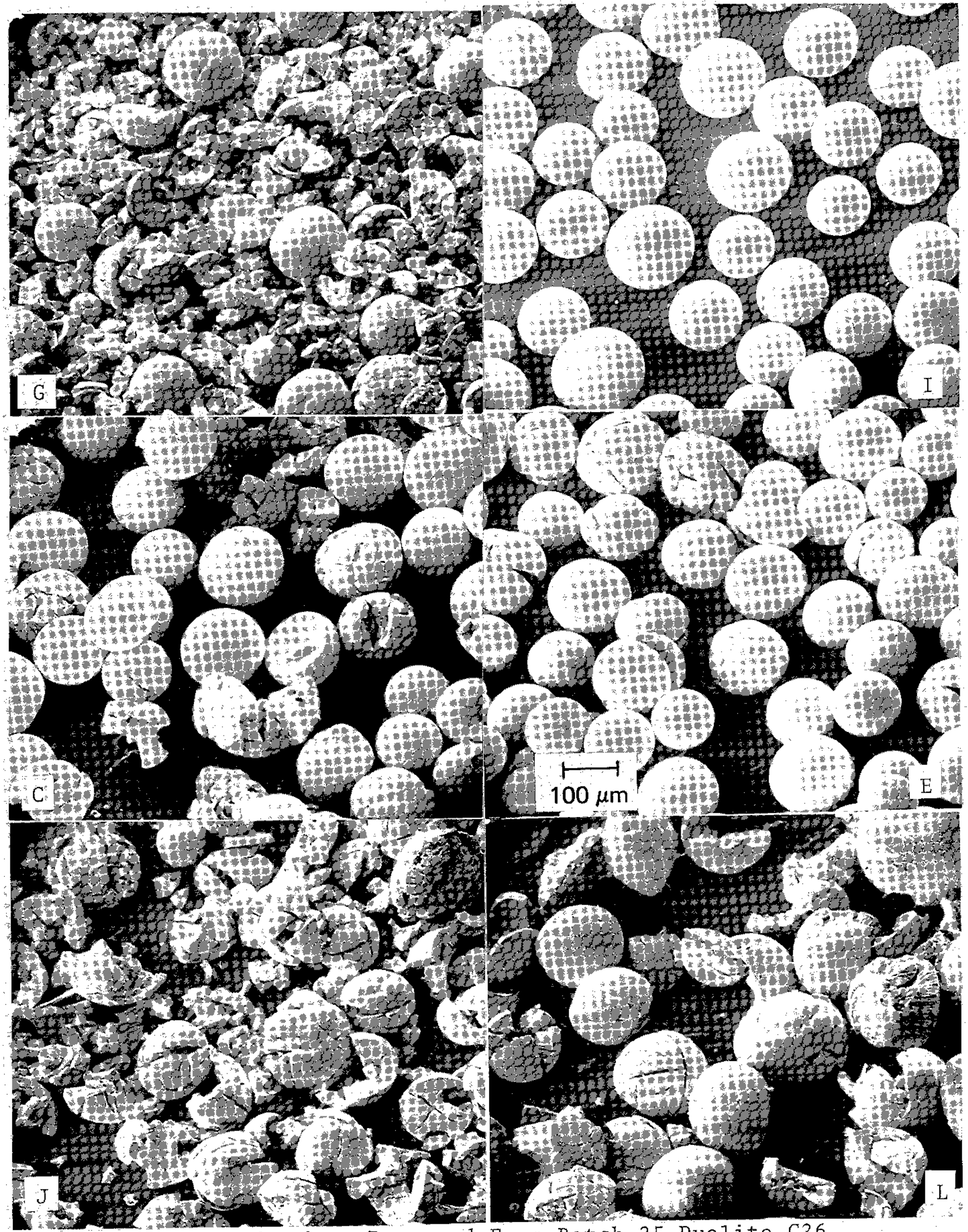


Figure 4. U_3O_8 Powders Prepared From Batch 25 Duolite C26 Resin. Designations Are as Given in Table 1. G, C, and J-Top Dishes. I, E, and L-Bottom Dishes. G and I-Fast Rate. C and E-Moderate Rate. J and L-Slow Rate.

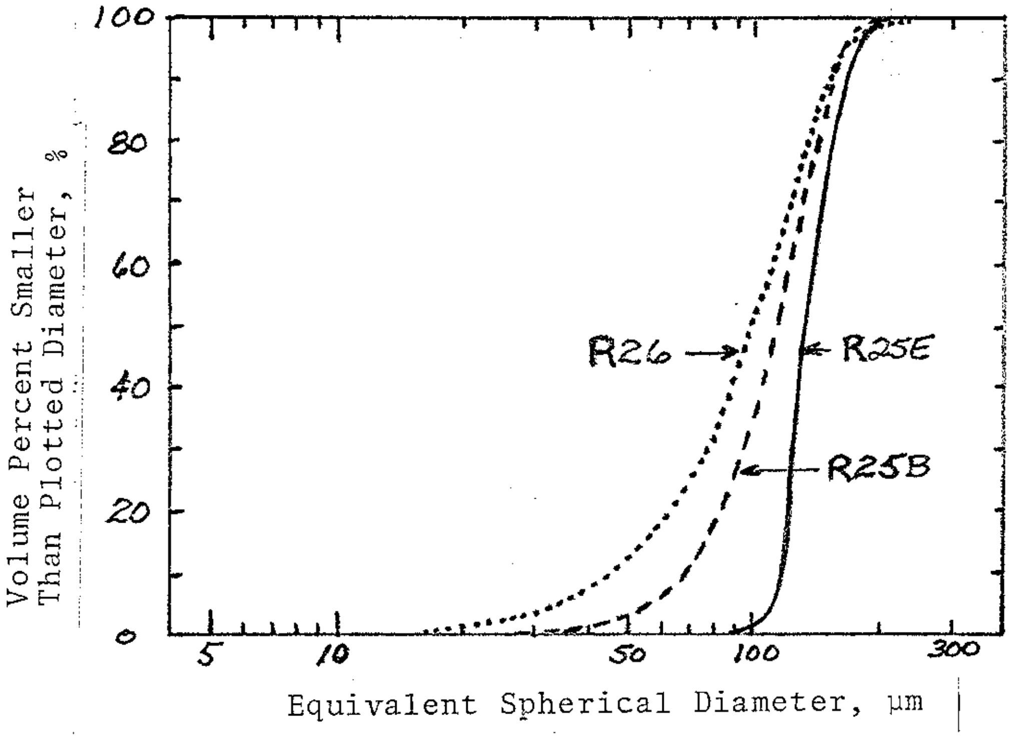


Figure 5. Particle Size Distributions of U_3O_8 Powders Made From Bead-Form Duolite C26 Resins. R25E and R25E Are From Batch 25 (Table 1). R26 is From Batch 26.

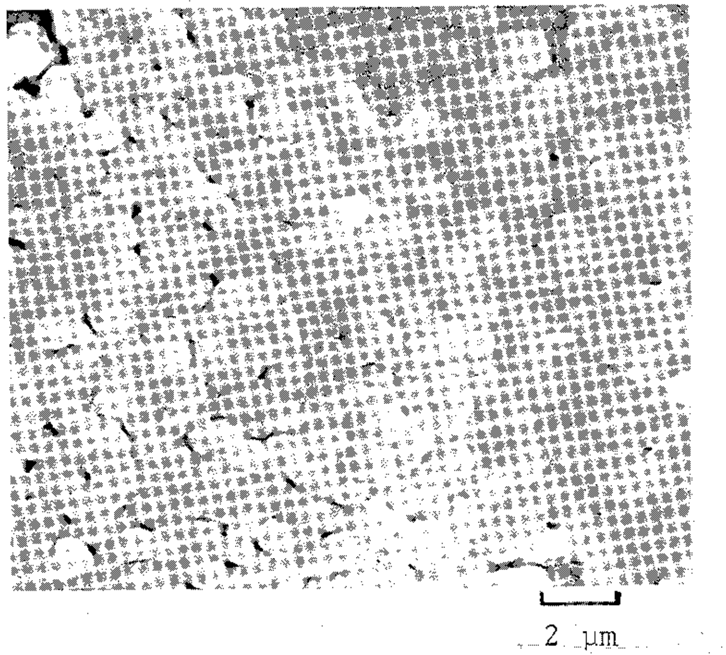


Figure 6. Grains in U_3O_8 Powder Made From Batch 25 Duolite C26 Resin at 1000°C.

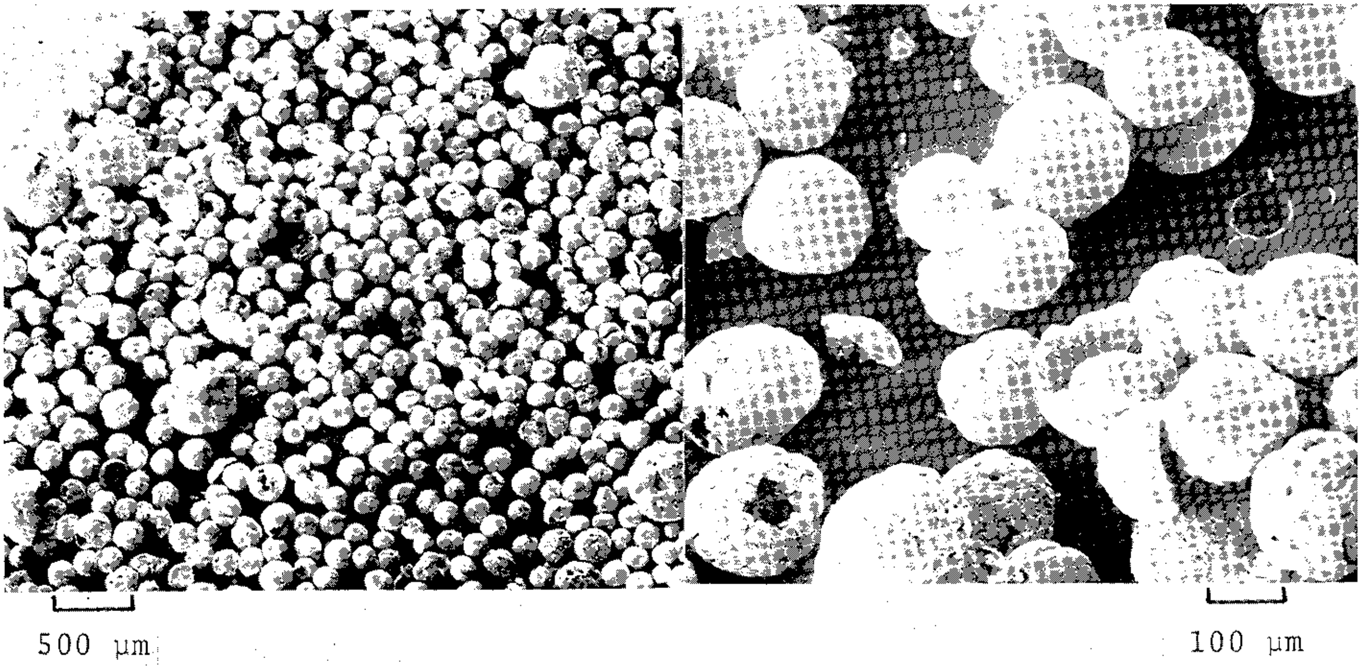


Figure 7. U_3O_8 Powder Made From Batch 25 Duolite C26 Resin in Rotary Calciner Run #2.

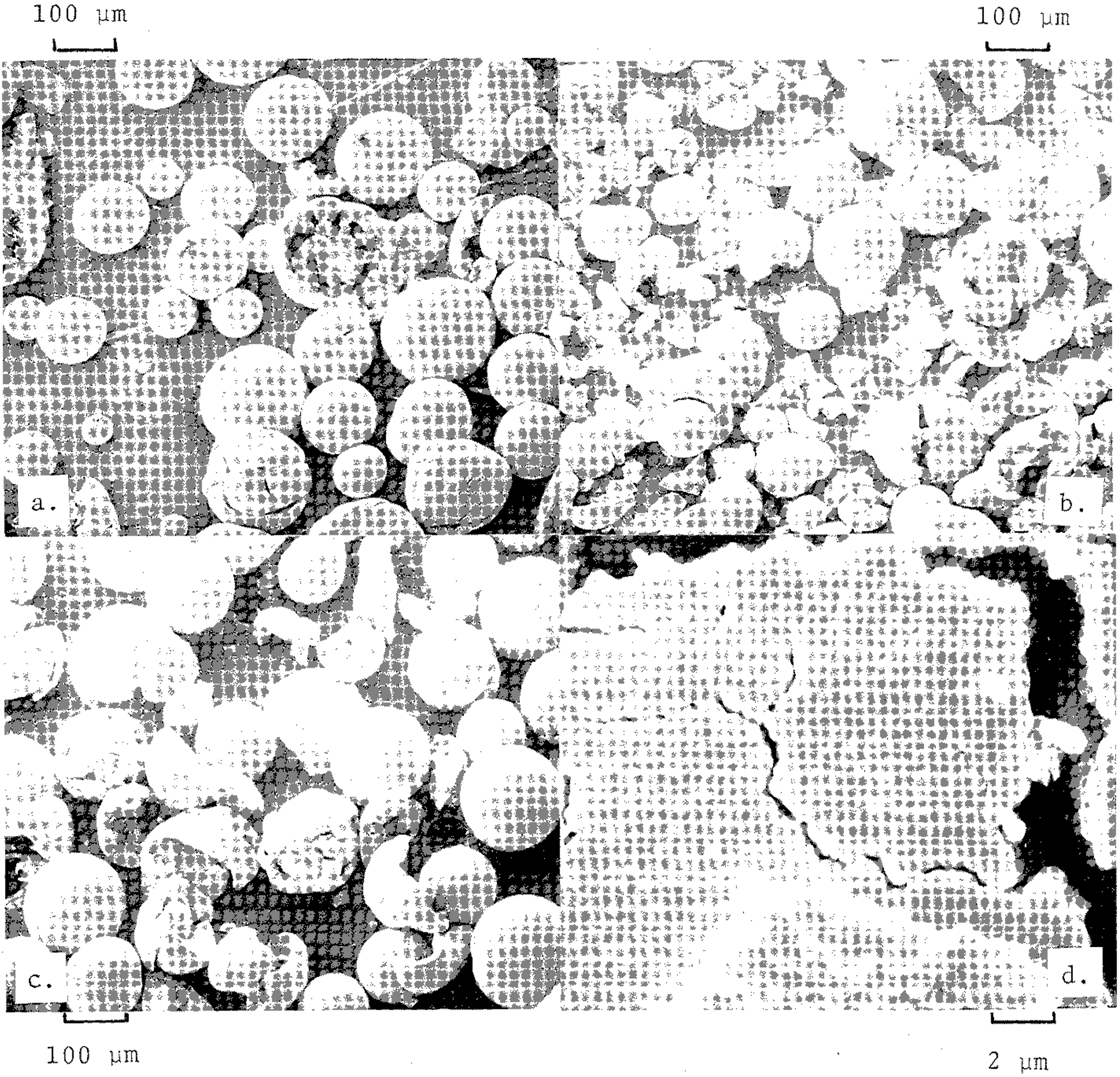


Figure 8. U_3O_8 Powder Made From Batch 26 Duolite C26 Resin. a. From Furnace A. b. From Furnace B. C. Mixture Used in Al-U_3O_8 Powder Metallurgy Fabricability Test. d. Grain Structures.

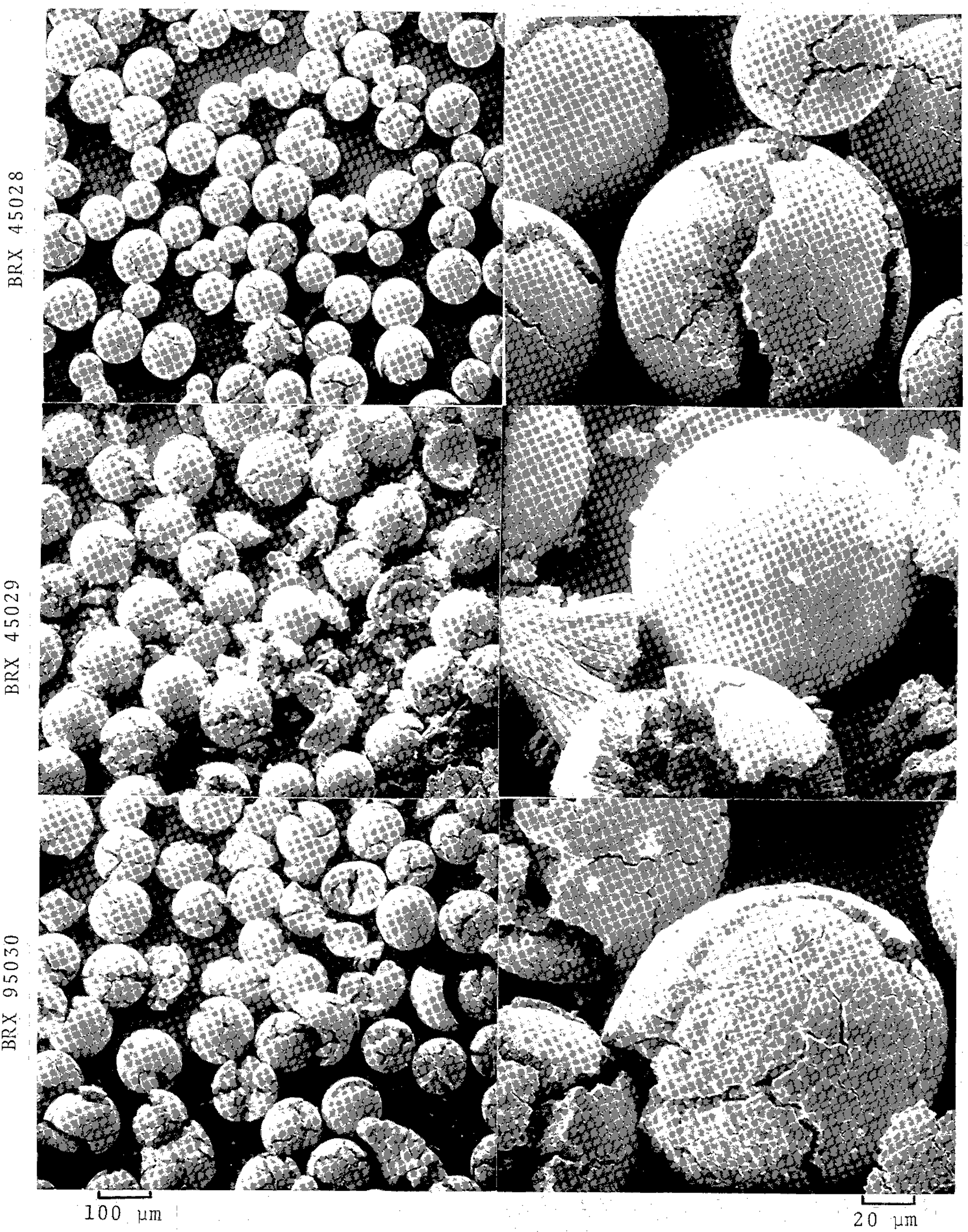
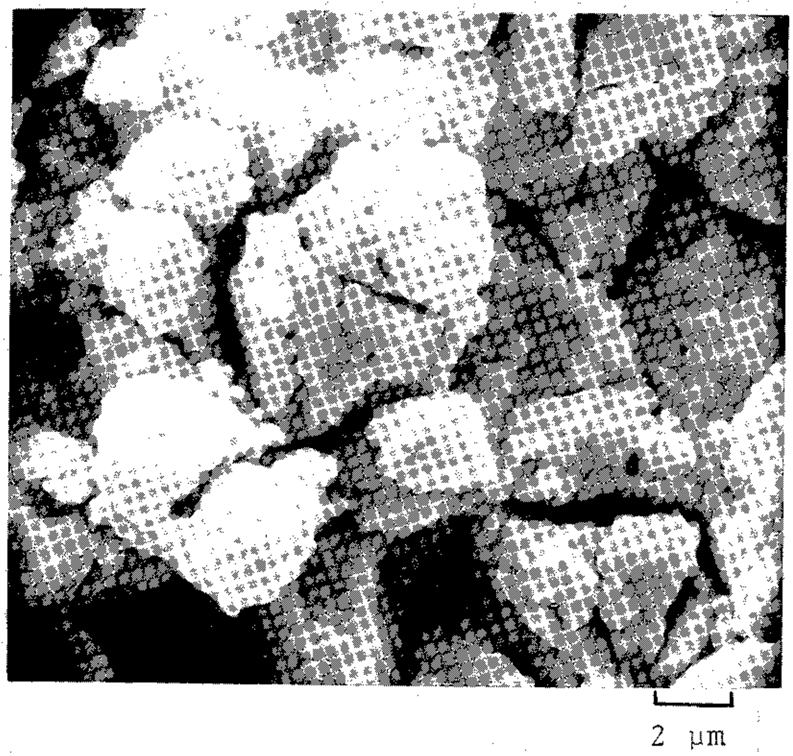
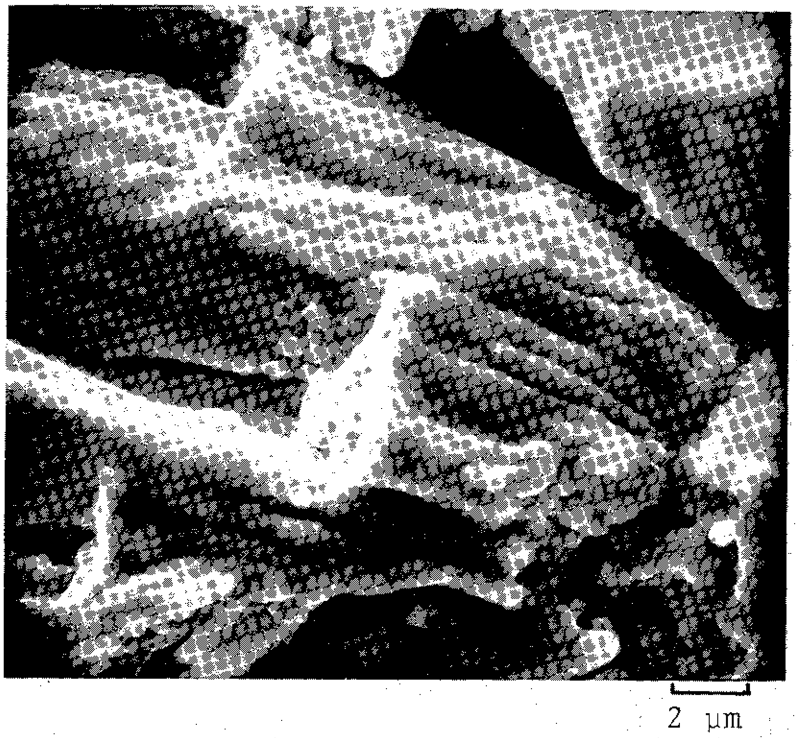


Figure 9. U_3O_8 Powders Made From Bead-Form AGMP-50 Resins at 950°C.



a. Equiaxed Cells and Spherical Grains



b. Columnar Cells and Needle-Like Grains

Figure 10. Cell and Grain Structures of U_3O_8 Powders Made From Bead-Form AGMP-50 Resins

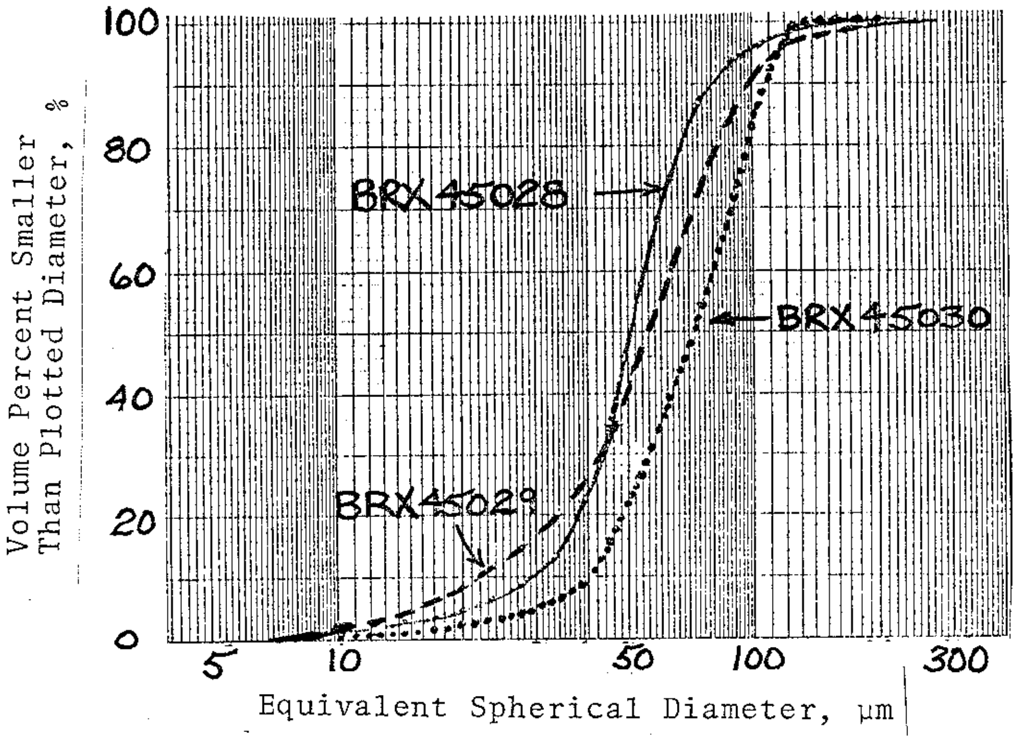


Figure 11. Particle Size Distributions of U_3O_8 Powders Made From Bead-Form AGMP-50 Resins.