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Date April 6, 1956

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Recovery of Zirconium Tetrachloride Powder

Short Title of Document

L.A. Lee (Leader) and M.A. Welt
Author

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UNION CARBIDE NUCLEAR COMPANY

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MEMORANDUM

EPS-X-257

MASTER

KT-226

April 6, 1956

TO: J. Savolainen

FROM: L.A. Lee (Leader) and M.A. Welt

SUBJECT: Recovery of Zirconium Tetrachloride Powder

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INTRODUCTION

The excellent nuclear properties of hafnium-free zirconium have encouraged its use as a possible structural material in reactors. Along with its excellent nuclear properties, zirconium displays a high corrosion resistance to water at high temperatures and is now being used as a cladding on reactor fuel elements. Since the preparation of hafnium-free zirconium is expensive, it is desirable to recover it as completely as possible from the irradiated fuel elements. No actual process is in operation to carry out this recovery, but the process that has received the most attention is briefly described below.

Fuel elements containing uranium, zirconium, and fission products are dissolved in hydrofluoric acid. Aluminum nitrate is added to complex the fluorides and thus prepare this solution for solvent extraction of the uranium by increasing the distribution coefficient for uranium in the organic solvent. The uranium is removed by liquid-liquid extraction and zirconium and fission products remain in the aqueous phase. The solution of fluorides is then stored until the radioactive decay has proceeded far enough (about 5 years) to enable reprocessing into zirconium

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metal. This process has the disadvantage that a large bulk of corrosive and radioactive solution must be handled and stored.

Another process, the Zircex process, has been proposed for uranium and zirconium recovery from zirconium clad fuel elements. In this process the fuel elements are treated with anhydrous hydrogen chloride at about 330°C where the following reactions take place:

At 330°C the ZrCl_4 product sublimes whereas the uranium and the majority of the fission products are left behind as a mixture of chlorides. These chlorides are dissolved in nitric acid and the chloride removed in order to decrease the corrosiveness of the solution. The uranium is then separated from the fission products by the usual organic solvent extraction. The ZrCl_4 desublimates as a fine powder and is collected and stored as a solid until reprocessing.

The advantages of the Zircex process over the fluoride process are fewer processing steps, less bulk for processing and storage, and a less corrosive system. However, many questions must be answered before its feasibility can be definitely ascertained. One of the most important of these questions is how the ZrCl_4 should be desublimed and collected. The object of this study was to investigate various types of apparatus for desublimation and collection of the solid zirconium tetrachloride. Of primary importance is the determination of particle size and distribution of the ZrCl_4 condensed; for, in general, the larger and more uniform the particle size, the easier the collection.

PROCEDURE

In order to avoid radioactivity problems, irradiated fuel elements were replaced by shavings of an unirradiated alloy of 92% zirconium and 8% uranium. These shavings were placed in an electrically heated, insulated glass hydrochlorinator. Two types of hydrochlorinators were used in this study. The initial run (E1) was carried out with an updraft type hydrochlorinator but plugging occurred in the exit gas lead and this apparatus was discarded in favor of a downdraft hydrochlorinator for the ensuing runs.

A stream of approximately 10 mole per cent anhydrous hydrogen chloride and 90 mole per cent hydrogen was passed into the reactor after heating it above 300°C and purging the air with hydrogen. For runs E4 and E5, the only runs in which steady flow rates were maintained throughout the run, the flow rates (at 25°C and 740 mm) were 0.3 liters/min. and 3.6 liters/min. for HCl and H_2 respectively. Flow rates in other runs were comparable. The hydrogen gas was added for temperature control and as a carrier gas for the ZrCl_4 formed in the reaction.

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The mixture of hydrogen, unreacted hydrogen chloride and zirconium tetrachloride gases was then passed into a condenser and then into a collecting apparatus. A water trap scrubbed the gaseous HCl out of the gas stream before it left the system. (In the actual Zircex process the H_2 -HCl gas mixture would then be recycled). The details of procedure for each run are given in Appendix A.

ZrCl₄ Condenser

Three types of ZrCl₄ condensers were used. They were (1) a natural convection air condenser, (2) a cold water condenser, and (3) atmospheric pressure steam condenser.

Collection of ZrCl₄

Apparatus used for collection of the condenser ZrCl₄ were a single Erlenmeyer flask, a specially designed collecting flask called a fines trap, and a bank of two cyclones in series followed by the fines trap (See Figure 1).

Condenser Inlet

For the air condenser, a straight ground glass fitting took the gas from the hydrochlorinator to the condenser. For the water condenser a ground glass joint followed by a narrow tube was used to cause a jet effect in the gas stream to move it quickly into the condenser. With the steam condenser a venturi-educator was used to bring the gas into the condenser. At the throat of the venturi was an inlet through which more hydrogen could be brought into the system to aid in cooling and collecting the zirconium tetrachloride.

Particle Size of ZrCl₄

To determine particle size, the collected ZrCl₄ solids were dispersed in light mineral oil with the aid of an electric field⁺ supplied by a Tesla coil. Photomicrographs taken of these dispersions were enlarged and printed. The particles were measured and counted. About 800 particles were counted per photo. In addition, sedimentation studies were made on samples collected from the air condenser (See Appendix B).

RESULTS

Equipment Studies

The better of the two hydrochlorinators used was the downdraft type. Operation was continuous without the plugging encountered with the updraft type which had a narrow outlet.

On the basis of the fraction of ZrCl₄ deposited outside the collection system, the most efficient system was that used in Run E4 and E5. In run E4, at gas flow rates comparable to those used in the first three runs, no ZrCl₄ particles were

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APPARATUS
RUNS E4 & E5

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FIG.
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found in the system beyond the fines trap. This system consisted of two cyclones in series followed by a fines trap as shown in Figure 1.

Particle Size

Figures 2 through 6 and Tables I through III present the results of the particle size-weight distribution for all runs.

The average particle size increased with increasing condensing temperature. In Run E1 the number of particles in the 0.5 - 1.0 micron size range was 244 of 857 (28.5%) particles. This system employed was the natural convection air condenser. In Run E2, where a cold water condenser was used, 409 of 838 (48.8%) particles fall into that group, while in Run E4, using a steam condenser, only 3.5% were less than one micron in size. All of these samples are taken from the first sample point in each collection system (See Details of Procedure, Appendix A). In Run 3-5 (steam condenser with hydrogen through eductor) no photomicrographs were obtained from sample points 1 and 2 because the highly agglomerated particles would not disperse. However, from a comparison of points 3 and 4 from E4 and E5, it can be seen that the particles in Run E5 were much smaller although agglomeration was higher.

Particle sizes ranged from about 0.2 microns obtained with the water condenser in Run E2 up to 7 microns obtained in almost all runs.

Particle size range decreased with increasing temperature. This can be seen by comparing the slopes of the lines in Figures 4 and 5 and noting that the flatter slope is that which corresponds to Run E4 while the steeper is that of E3.

DISCUSSION OF RESULTS

Effect of Temperature on Particle Size

It was found that by increasing the desublimation temperature, i.e., decreasing the ΔT between the hydrochlorinator and the condenser, it was possible to obtain as much as a 400% increase in the smallest size particle measured. This can be seen by referring to Table I. By using higher desublimation temperatures and thereby obtaining larger particles, the overall collection efficiency was increased. In the first steam condenser run (E4), no particles were noticed outside the collection system, i.e., in the lines leading to the HCl scrubber. In the second steam condenser run (E5) particles were noticed beyond the collection system and this result will be discussed below.

Effect of Venturi-Eductor on Particle Size and Collection

The particles of $ZrCl_4$ collected when using the venturi-eductor with the hydrogen lead clamped off were larger than the particles obtained while using the hydrogen stream. In sample E4-3 only 9% of the collected particles were one micron in diameter or less, while sample E5-3 revealed 33% of the particles as

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY ENGINEERING PRACTICE SCHOOL UNION CARBIDE NUCLEAR COMPANY A Division of Union Carbide and Carbon Corporation			
WEIGHT-SIZE DISTRIBUTION SAMPLE E1			
DATE 4-19-56	DRAWN BY L.A.L.	FILE NO. EPS-X-257	FIG. 2

LEGEND
E2-2-O E2-1-X

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WEIGHT-SIZE DISTRIBUTION
RUN E2

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FIG.
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LEGEND
E3-1-○ E3-2-X

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WEIGHT-SIZE DISTRIBUTION RUN E3			
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PARTICLE SIZE (MICRONS)

LEGEND

E4-1 — +   E4-2 — Δ
E4-3 — x   E4-4 — o

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WEIGHT-SIZE DISTRIBUTION

RUN E4

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TABLE I

RESULTS OF PARTICLE COUNTS

Sample No.	-----Number of Particles of Each Size (microns)-----								
	0 - 0.25	0.25 - 0.5	0.5 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7
E1	0	177	244	308	84	32	8	2	1
E2-1	0	224	409	171	29	3	2	0	0
E2-2	24	325	160	65	2	0	0	0	0
E3-1	0	18	420	239	71	25	6	2	1
E3-2	0	5	196	173	74	20	4	1	0
E4-1	0	0	17	170	218	71	8	2	1
E4-2	0	0	25	492	242	19	2	0	0
E4-3	0	0	58	321	160	11	1	0	0
E4-4	0	0	174	404	113	16	2	1	0
E5-3	0	0	69	96	30	6	2	0	0
E5-4	0	107	240	95	9	1	0	0	0

TABLE II

PER CENT OF PARTICLES IN EACH SIZE RANGE

	0 - 0.5	0.5 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7
E1	20.7	28.5	35.9	9.8	3.7	0.9	0.4	0.1
E2-1	26.7	48.8	20.4	3.4	0.4	0.3	-	-
E2-2	60.6	27.7	11.3	0.4	-	-	-	-
E3-1	2.3	53.3	30.3	9.0	3.2	0.8	0.8	0.3
E3-2	1.0	41.6	36.7	15.7	4.2	0.7	0.1	-
E4-1	-	3.5	34.9	44.8	14.6	1.6	0.4	0.2
E4-2	-	3.2	63.1	31.0	2.4	0.3	-	-
E4-3	-	10.5	58.3	29.1	2.0	0.1	-	-
E4-4	-	24.5	57.0	15.9	2.3	0.2	0.1	-
E5-3	-	34.0	47.3	14.8	3.0	0.9	-	-
E5-4	23.7	53.2	21.0	2.0	0.1	-	-	-

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TABLE III

WEIGHT PER CENT OF PARTICLES IN EACH SIZE RANGE

Sample No.	0 - 0.5	0.5 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7
E1	0.2	2.7	27.7	25.4	23.1	11.3	5.8	3.8
E2-1	0.8	13.5	45.2	25.9	6.3	8.3	-	-
E2-2	7.7	30.0	29.6	27.0	5.7	-	-	-
E3-1	0.03	6.2	28.0	28.1	23.5	10.9	3.3	-
E3-2	0.02	3.5	24.9	35.8	23.0	9.0	3.8	-
E4-1	-	0.1	10.2	42.2	33.7	7.4	3.8	2.6
E4-2	-	0.2	32.9	54.6	10.2	2.1	-	-
E4-3	-	0.8	33.0	55.6	9.0	1.6	-	-
E4-4	-	2.2	40.7	38.4	2.9	3.1	2.7	-
E5-3	-	3.1	33.6	35.5	16.8	11.0	-	-
E5-4	1.0	18.2	57.6	18.4	4.8	-	-	-

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less than one micron in diameter. This may be due to the effect of the cold (room temperature) hydrogen stream on the hot $ZrCl_4$ vapor leaving the hydrochlorinator, which would tend to increase the ΔT between the hydrochlorinator and the condenser and result in small particle formation. The photomicrographs revealed, however, that there was increased agglomeration in the collected particles when using the hydrogen in the venturi-educator. This increase in agglomeration is probably due to the effect of increasing the mechanical agitation of the molecules by the introduction of the hydrogen stream into the low pressure area at right angles to the $ZrCl_4$ vapor stream. The effect of the hydrogen introduction into the venturi-educator resulted in increased gas velocity throughout the collection system (the same hydrogen flow rate was maintained into the hydrochlorinator in Run E4 and E5); this coupled with smaller particle size resulted in fines being carried out of the system.

The venturi improved the flow characteristics of the hydrochlorinator exit gas stream by causing the confinement of the desublimation to an axial stream in the steam condenser. Little turbulence was noted in the condenser and no desublimation was noted on the heated walls of the condenser.

CONCLUSIONS

- (1) Average $ZrCl_4$ particle size increases with desublimation (condenser) temperature.
- (2) With the system shown in Fig. 1 it was possible to recover essentially all the $ZrCl_4$ particles formed.
- (3) Increased agglomeration can be obtained by use of the venturi-educator.
- (4) Improved flow characteristics can be obtained in the condenser by using a venturi in the line connecting the downdraft hydrochlorinator with the condenser.

RECOMMENDATIONS

- (1) Brown (1) suggests modifying the conventional cyclones with a "shave-off," e.g., a slit in the cylinder placed near the top, one full turn from the inlet, which removes the fine particles immediately without letting them spiral down below the level of the gas exhaust to the core where they might be re-entrained and carried out in the discharging gas.
- (2) Piping should be kept as short as possible in order to prevent desublimation of the $ZrCl_4$ in the connecting lines. Where the concentration of $ZrCl_4$ is highest in the system, it would be advisable to include external heating to avoid plugging in the system.

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(3) Other Types of Collection Apparatus

- (a) Impingement Collectors - It is suggested that an "impingement separator" be investigated. When the $ZrCl_4$ laden gas impinges on a body, the gas will be deflected around the body, whereas the $ZrCl_4$ particles, by virtue of their greater inertia, will tend to be collected on the surface. A possible set-up is shown schematically below.

- (b) High Pressure Steam - The data obtained during this investigation indicated that by lowering the ΔT between the hydrochlorinator and the condenser, a larger mean particle size was obtained. A high pressure steam condenser would lower the ΔT much more and would possibly result in much larger and more easily collectable particles.
- (c) It was noted that the venturi-eductor apparatus improved the flow characteristics of the collection system, but the introduction of the "cold" hydrogen stream caused smaller $ZrCl_4$ particle formation. The overall venturi-eductor contribution would probably be increased by heating the hydrogen before admitting it to the eductor.
- (c) An alternative to using hydrogen in the eductor would be to use CCl_4 vapor. This change should provide a major improvement in the particle collection since the CCl_4 vapor would tend to condense around the $ZrCl_4$ particles (seeding effect) thereby increasing the effective particle weight considerably and therefore allowing them to be collected more easily and completely. Bralove (2) describes a venturi-scrubber system which could be modified (by using CCl_4 vapor) for use in the Zircex process. The CCl_4 could easily be removed from the collected $ZrCl_4$ particle by vaporization and recycle within the system.

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A. Details of Procedure

Run E1

The updraft hydrochlorinator was used and charged with 30 grams of the Zr-U alloy shavings. After lubricating all high temperature joints with graphite and low temperature joints with stopcock grease, the system was purged with hydrogen gas for at least fifteen minutes (This purging was also done in all succeeding runs). The gas flow rates were measured by orifice flowmeters; a manometer was connected across the reactor-condenser system to indicate any plugging of the system. After raising the hydrochlorinator temperature to 300°C (Sim-ply-trol temperature control system), hydrogen chloride gas was introduced into the hydrogen inlet gas stream. After the few minutes necessary to initiate the reaction, dense clouds of gas were visible in the condenser. The particles ~~settled~~ out of the condenser and were collected in an Erlenmeyer flask. The temperature in the reaction flask was controlled both by adjustment of the hydrogen flow rate and by manual control of the hydrochlorinator heater.

Run E2

A downdraft type hydrochlorinator was charged with 30 grams of Zr-U alloy. A standard laboratory water condenser was connected to the hydrochlorinator outlet. Cold water was circulated through this condenser. The system was brought to reaction temperature as in Run E1 and the sample E2-1 was collected in an Erlenmeyer flask connected to the condenser. A small cyclone was connected to the outlet of the Erlenmeyer flask to collect some of the finer particles that were carried out with the gas stream. Sample E2-2 was taken from this cyclone.

A glass wool plug was inserted in the bottom of the hydrochlorinator to prevent any solids from being carried out in the gas stream. Another plug of glass wool was inserted in the top of the hydrochlorinator to prevent any gaseous zirconium tetrachloride from being carried back into the feed line by convection currents.

Run E3

The same apparatus was used as in Run E2 with two changes. A fines (See Fig. 1) trap was connected directly to the condenser and the Erlenmeyer flask connected to it. Sample E3-1 was taken from the Erlenmeyer flask and sample E3-2 was taken from the film of particles coating the walls of the fines trap. No cyclone was used in the collection system.

Run E4

Two major apparatus changes were made in the apparatus used for Runs E2 and E3. A venturi-eductor was inserted between the hydrochlorinator and condenser and the collection system after the condenser was replaced by two cyclones in series followed by the fines trap. The venturi was heated to prevent plugging.

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A photograph of this apparatus is seen in Fig. 1. Instead of circulating cold water through the condenser, atmospheric pressure steam (740 mm) was allowed to condense in the cooling jacket. Sample E4-1 was taken from the tubing directly below the condenser, sample E4-2 from the first cyclone, sample E4-3 from the second cyclone, and E4-4 from the fines trap.

Run E5

This run used the same apparatus and condensing temperature as Run E5. Hydrogen gas (at 25°C) was, however, passed into the throat of the venturi. Sample E5-1, 2, 3, and 4 were taken from the same points as in Run E4.

Run E6

This run using the same apparatus as Runs E4 and E5 was attempted under vacuum. The outlet of the system was connected to the laboratory high vacuum supply. No samples were taken of this run since no product was obtained.

Run E7

An inverted cyclone (inlet near bottom rather than at top) was used to collect particles in this run, to check the collection efficiency of such a collector against a standard cyclone.

Particle Size Determination

The sample particles of $ZrCl_4$ were dispersed by shaking a small quantity with 10 ml. of light mineral oil. A drop of this dispersion was placed on a glass slide and subjected to the field of a Tesla coil for approximately thirty seconds. The drop was covered with a cover glass and placed under the objective of the microscope. Photomicrographs were taken at magnifications of 500 and 1000X. These photographs were enlarged to twice original size and printed.

The diameter of the particles in each photo was measured with a transparent millimeter scale and the number of each size was counted. The number of each diameter class was multiplied by the cube of the diameter to obtain a weight distribution according to size. The weight distribution by size was plotted on logarithmic probability paper as suggested in Perry's Handbook (3). This measuring and counting procedure is recommended by the American Society for Testing Materials* for particles in this size range.

B. Sedimentation Study

The collectors in the Zircex process will probably involve the use of gas-solid settling chambers. In order to obtain some indication of the settling rate as a function of solids content, sedimentation data were obtained by using $ZrCl_4$.

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* ASTM Design E20-33T, part 111A, p. 1219-23 (1946).

obtained from the air condenser run (E1). These particles were uniformly suspended in 100 ml. of CCl_4 . A glass-stoppered 100 ml. graduate was used in this study. The results of this study are shown in Fig. 7. These data indicate that the lower the solid-to-fluid ratio, the closer the sedimentation approaches clarification, while the 10:1 solid-fluid ratio indicates hindered settling. Perry (4) states that in all clarification problems, dilution ratio, or the weight ratio of liquids to solids, has an important bearing. All the ZrCl_4 particles to be collected in gas-solid collectors will have free movement and, except for those particles of colloidal size, settle at a constant velocity given by Stokes' formula for spheres:

$$\mu = \frac{9 D^2 (\rho_s - \rho)}{18} \quad \text{where: } \begin{array}{l} \mu = \text{terminal velocity (cm/sec)} \\ D = \text{particle diameter (cm)} \\ \rho_s = \text{solid density (gm/cm}^3\text{)} \\ \rho = \text{liquid density (gm/cm}^3\text{)} \end{array}$$

Table IV lists the settling velocity during the constant rate settling period, and Fig. 8 is a plot of constant rate settling velocity as a function of fluid-to-solid ratio. From this plot it is possible to determine the settling time for collectors if one corrects for the CCl_4 used in this study to the $\text{H}_2\text{-HCl-ZrCl}_4$ gas medium to be used in practice. CCl_4 was used as the settling medium rather than the actual gas medium since a gas settling chamber was not available.

TABLE IV

Run	$\frac{\text{gm. CCl}_4}{\text{gm. ZrCl}_4}$	Constant Rate Settling Velocity (ml/min)
2	20:1	10.2
3	40:1	20.0
4	10:1	5.0

C. Dispersant Study

In order to determine the best method of dispersing the particles collected into a slurry suitable for photomicrography, a number of dispersing agents were tried. Results obtained with each liquid used are described below.

1) Carbon tetrachloride - This dispersant had the advantage of good dispersion and good optical qualities. However, its volatility made it unsuitable for a flat microscope slide since it evaporated before the photomicrographs could be taken. Use of a well-type slide overcame the volatility disadvantage, but the depth of the liquid made high optical resolution impossible.

2) Toluene - ZrCl_4 particles dispersed in this liquid formed crystals, thus preventing determination of collected particle size.

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SETTLING RATE
 $ZrCl_4$ IN CCl_4

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FIG.
7

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SETTLING RATE VS
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FIG.
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3) Silicone Oil - The extremely high viscosity of this medium made dispersion extremely difficult, if not impossible.

4) Hexone - Crystals are again formed and it appeared that a reaction had taken place. This might be the $ZrCl_4$ reacting with the oxygen of the ketone.

5) Light Mineral Oil - When first used, this solvent showed no evidence of crystallization or reaction and did not evaporate but agglomeration of the particles seemed appreciably greater than with any of the other dispersants used. An attempt to improve the dispersion of the particles was made by subjecting the drop of mineral oil slurry on the microscope slide to the field of a Tesla coil. A marked improvement in particle disassociation was noted. It was decided that light mineral oil fulfilled the requirements for the dispersant needed and the following procedure was adopted.

Ten-ml. of oil were shaken with a small amount of $ZrCl_4$ as collected after desublimation. One drop of this suspension was placed on a glass slide and subjected to the field of the Tesla coil for 30 seconds. At the end of this time a cover glass was dropped (not slid) onto the oil drop and the air bubbles formed pressed out. The slide was then placed under the microscope and an appropriate field selected for photographing.

D. Literature Citations

- 1) Brown, G.G., "Unit Operations," John Wiley & Sons, Inc., New York, 1950, p. 119.
- 2) Bralove, A.L., Nucleonics 9, 37 (1951).
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