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OAK RIDGE, TENNESSEE

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TO: W. A. Jenkins
FROM: F. L. Culler

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POST OFFICE BOX P
OAK RIDGE, TENN.

May 23, 1955

~~SECRET~~

Mr. W. A. Jenkins
E. I. duPont de Nemours Company
Explosives Department
Wilmington 98, Delaware

Dear Bill:

25. The solvent radiation damage study has been extended to five exposures in the 4 watt/liter Co^{60} source - roughly 50 times the anticipated process level of exposure for a single pass through the 1A column - with no indication of solvent damage. Retention of uranium in the solvent under stripping conditions was used as the basis for detecting solvent damage.

A 2 hour feed digestion period at 2.0 M HNO_3 was just as effective in eliminating emulsification tendencies as the 3 hour digestion period previously tested. In another test using 2.5 month aged feed, 15 minute digestion at 2 M HNO_3 was sufficient to eliminate emulsion formation.

The turbine-mixer solvent reconditioner is now undergoing preliminary tests and modifications to improve its efficiency above 50% observed initially.

The slab dissolver is now in operation and will be included in detail with the next letter.

Metallex. A photo of a Th rod extruded from a 10 lb. billet of Th metal prepared by Metallurgy is attached. This rod (which looks typical of extruded rods) was 3/4 in.-D by 51 in. long and was produced from a collection of 150 g compacts produced by pressing Th amalgam from the PDA-type reduction step. The extrusion followed a 1.5 hr preheat at 800°C and was made thru a 3/4 in.-D shear die.

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. It is to be controlled and its disclosure is to be authorized.

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Thorium tetrachloride preparation continues to be a major problem. Mixing the denitrated material with starch and water and then drying at 200°C produced firmly pelletized material.

In recent work chlorination of starch-pelletized material at 625°C for 2-1/2 hours produced a 90% yield of anhydrous ThCl_4 . Feed was prepared by thermal denitration of hydrated thorium nitrate at 250°C for 2 hours, which removed approximately 78% of the nitrogen and 62% of the water.

Chlorination of Thorium Oxalate. Chlorination of pelletized thorium oxalate for 2.5 hours at 600°C, a free Cl_2/Th molar ratio of 6 to 7, and C/Th ratios of 2.2 to 2.6, gave almost exactly reproducible results with ThCl_4 yields of 95%. A decrease in time to 2 hours decreased the yield to 89%, while an increase in time to 4 hours caused no increase in yield. A decrease in C/Th ratio from 2.2 to 1.4 decreased the yield to 78%, while an increase to 2.8 showed no increase in yield. The use of CCl_4 only as a chlorinating agent gave yields of 90%, but left a carbon residue, which was volatilized out of the bed by a chlorine purge at 600°C to 500°C.

It was shown that the oxalate was <20% decomposed by pre-heating the bed to 400°C before admitting chlorine, and that at 300°C, the oxalate is <10% decomposed. Chlorination at 250 to 350°C using chlorine only, decomposed 75% of the oxalate and yielded a product 27% chlorinated.

Very truly yours,

F. L. Culler per ACJabous

F. L. Culler, Director
Chemical Technology Division

FLC:ACJ/pms

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1.0 25 PROCESS ASSISTANCE

1.1 Solvent Radiation Damage

An aliquot of 6% TBP in treated Amsco diluent has been carried through 5 mixed phase irradiation cycles in the ~4 watts/liter Co⁶⁰ source. The AF:AS:AX ratio was 100:20:40, the AF being tubular element dissolver solution (1.8 M Al, ~3.8 g/l U, 0.005 M Hg²⁺ and 1 M HNO₃), and the AS being 0.75 M Al(NO₃)₃ - 0.02 M Fe(NH₂SO₃)₂ - 3 M HNO₃. Each cycle consisted of ~10 min irradiation while mixing the phases with an electric stirrer, separation of the phases and subsequent exhaustive stripping of the organic with 5 double volumes of water. The organic was analyzed for retained U after each strip as an indication of irradiation decomposition products present--DBP in particular. The solvent was given the standard wash procedure, i.e., two 1/5 volumes of 0.1 M Na₂CO₃, 0.1 M HNO₃ and H₂O, just prior to each irradiation. The total cumulative dosage was 3.1 to 3.5 β-watt-hr/liter of solvent or approximately 50 times the anticipated process level for a single pass through the 1A column, i.e., 0.067 β-watt-hr/liter of solvent. A nonirradiated control sample was simultaneously given exactly the same treatment. No significant difference in uranium retention was noted between the irradiated sample and nonirradiated control even after the 5th irradiation cycle, indicating that no cumulative build-up of radiation decomposition products had occurred and that the flow-sheet solvent recovery procedure is adequate for decomposition product removal. In all cases, 3 strips were sufficient to reduce the uranium concentration in the organic to 0.001 g/l, or less, which corresponds to the tolerable process loss of 0.01%.

1.2 Organic Emulsion Study

A 2S aluminum bar-stock solution (1.8 M Al, 0.008 M Hg²⁺, 1 M HNO₃), which produced stable organic emulsions when batch-equilibrated with 6% TBP-Amsco in the presence of neutral 0.75 M Al(NO₃)₃ - 0.02 M Fe(NH₂SO₃)₂ scrub in AF:AS:AX ratio of 100:20:40, was used as feed in this experiment. Concentrated HNO₃ was added to an aliquot of the bar-stock solution such that the final H⁺ concentration was 2.0 M at Al concentration of ~1.7 M. The solution was then digested at the boiling point (111°C) for 2 hours, after which time it was evaporated to b.p. = 130°C (Al ~3.6 M, H⁺ ~1.2 M), and subsequently diluted back to the original feed volume with water (Al = 1.8 M, H⁺ = 0.59 M). The treated solution was batch equilibrated as specified above and no stable organic emulsion was obtained, showing that 2 hr. digestion at 2 M H⁺ is sufficient to dehydrate the emulsion-producing impurities.

Another experiment was performed using bar-stock solution which had aged approximately 2-1/2 months, so a control

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rerun was made using the untreated solution as feed. The emulsion obtained was not the very stable, fine, milky-white type originally observed that did not break on several days standing, but rather consisted of large, clear bubbles that broke after 1-1/2 to 2 hours, leaving the interface essentially clean. Apparently, aging the 1 M H^+ solution at room temperature over a long period of time will gradually bring about dehydration or coagulation of the emulsion-forming impurities present.

However, when the solution was brought to 2 M H^+ by the addition of concentrated HNO_3 and digested at the boiling point for only 15 minutes, evaporated to b.p. = $130^\circ C$ and diluted back to the original volume with H_2O prior to batch-equilibration, the aqueous and organic phases cleared in ~ 30 seconds and 2-1/2 minutes, respectively, with a clean interface being obtained in about 4 minutes. This is a significant improvement over the results reported above for the untreated feed.

1.3 Turbine-Mixer Solvent Reconditioner

Shakedown tests of a three-stage, turbine-mixer continuous solvent reconditioning apparatus were carried out using 6% TBP in Amsco Special Naphtha No. 1 as a contaminated feed. The "hot" solvent (1.24×10^7 Gr γ c/m/ml) was pumped through a 0.1 M Na_2CO_3 wash, 0.1 M HNO_3 wash, and a demineralized water wash at a flow rate corresponding to the solvent flowrate of the 0.75 in.-D column (40 ml per minute).

The first run indicated that the product had a gamma DF of only 6; a control sample batch equilibrated with the same solutions and at the same volume ratios ($O/A = 1/3$) gave a gamma DF of 88. Additional runs have been made with the apparatus after modifications to (a) increase the recirculation of organic phase and (b) provide deentrainment of contaminated aqueous from the solvent effluent streams. Incomplete results indicate that the efficiency of the machine was increased in the third test run to 50%. The apparatus is being modified to increase its efficiency still further.

2.0 METALLEX

2.1 Thorium Tetrachloride Preparation

Chlorination of Thermally Denitrated TNT

One hundred twenty grams of thorium oxide were prepared by thermal denitration of 220 grams of solid hydrated thorium nitrate at $250^\circ C$ for two hours. The starting material composition was, from its analysis $Th(NO_3)_4 \cdot 6.75 H_2O$. The composition of

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the final denitrated material was $\text{ThO}_{1.54}(\text{NO}_3)_{0.46}(\text{H}_2\text{O})_{1.3}$. Denitration was 77.6% complete and dehydration was 62% complete at the end of the heating period.

One hundred twelve grams of the denitrated product was mixed with 47.5 grams of arrowroot starch and enough water to make a stiff paste. The mixture was dried for 2-1/2 hours at 200°C. This amount of starch was sufficient to give 42.6% excess carbon above the requirement for conversion of all oxygen, except that bound as H_2O , to CO . Upon drying, the hard mixture was broken up into pellets in a mortar. The pellets were mechanically strong, and appeared to be quite porous.

The pellets were dried in a stream of argon gas at 300°C for one hour. Copious fumes of steam and oxides of nitrogen were given off. The temperature was then raised to 500°C. No additional gas evaluation was observed. Chlorine gas was passed over the charge, and the temperature was raised to 625°C for 2-1/2 hours. The material was cooled to room temperature in a stream of argon. The analysis showed the product to be 90% ThCl_4 , 0.33% water, 2% carbon and ~7% thorium oxychlorides and oxide.

Temperatures of 600°C and 650°C were necessary to confirm earlier runs which produced 99.5 per cent by weight of ThCl_4 when thorium oxalate was contacted with chlorine gas and carbon tetrachloride vapor.

Four chlorination runs, (Run C-52 through C-55, Table 1) were made in which chlorine gas and carbon tetrachloride vapor were metered to carbon reaction vessels for 2-1/2 and 2 hours at rates which provided molar ratios of chlorine to thorium and carbon tetrachloride to thorium of 6 and 2.3 respectively. These conditions produced 99.5 per cent ThCl_4 in earlier runs. The reactor contained thorium oxalate which was 41.3 per cent by weight thorium and 32.0 per cent by weight C_2O_4 before being heated to the initial chlorination temperature of 400°C. The composition of one batch of thorium oxalate that had been heated to 400°C over a period of one hour was 59.4 per cent by weight thorium and 38.3 per cent by weight C_2O_4 (Run C-49).

The maximum chloride content obtained in these runs was 36 per cent by weight as compared to 37.6 per cent in earlier runs performed in a similar manner.

Chloride content is used as a basis of comparison because the potentiometric titration method for chloride measurement is more accurate: $\pm 0.1\%$ vs. $\pm 2.0\%$ for Th analysis in ideal solutions.

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The only apparent difference in run conditions was in the thorium oxalate charged. In the earlier runs the feed was prepared by the manual mixing of oxalate, which had been dried for 8 hours at 165°C, with water and redrying at 165°C. In recent runs the feed oxalate was prepared by mechanically mixing thorium oxalate with water without predrying. The bulk density of the untreated pellets is 1.5 that of the heat treated. This difference in feed characteristics is somewhat nullified by the fact that both feeds, upon heating to 400°C, are reduced to fluffy beds of similar consistencies.

The unreacted carbon, which is produced when CCl_4 is decomposed, remains in the bottom one per cent of the reaction bed and may be removed by passing chlorine gas through the reactor after the flow of CCl_4 is stopped. The carbon present from the decomposition of $\text{Th}(\text{C}_2\text{O}_4)_2$ may also be removed by a chlorine purge.

In run C-58, carbon tetrachloride vapor only was used as the chlorinating agent and a product containing 34 per cent chlorine was obtained.

When chlorine gas only was used for the chlorination, the product contained 10.4 per cent by weight chlorides. However, 13.9 per cent of the original 32.0 per cent C_2O_4 remained in the product. These data indicate about 43 per cent utilization of the carbon in the $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{XH}_2\text{O}$ feed at 350°C.

In a sublimation run 100 grams of ThCl_4 containing 35.0 per cent chlorides was digested at 750°C for two hours using a CCl_4 and Cl_2 purge. About 75 grams of ThCl_4 containing 37.65 per cent by weight chloride remained in the reactor as a fused mass. The remaining 25 grams was distributed on the quartz reactor housing and in the off gas system. Pure ThCl_4 contains 37.93 per cent by weight chlorides and 62.07 per cent by weight of thorium.

2.2 Reduction of ThCl_4 with NaHg

Experiments were carried out in which 32.7 g ThCl_4 was reacted with 250 ml of NaHg at ~200-235°C for 1-2 hours. The reactor vessel consisted of a 1000 ml glass pot fitted with a stainless steel lid, paddle wheel agitator, and draft tube. The agitator operated at ~1150 RPM and provided sufficient heat to carry out the reactions at the desired temperature.

Results of two of the experiments, using ThCl_4 gave yields of 80 and 84%, respectively. Two other experiments using sublimed ThCl_4 gave reduction yields of 89.4 and 97%. The thorium material balance in the later runs was 78.5 and 86%.

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Table 1

Chlorination of Thorium Oxalate Using Cl_2 and CCl_4 Mixtures

Run No.	Percent by Weight				CH_3OH Insoluble	Run Time Hours	Temp °C	Moles Feed per Mole Th	
	Th	Cl	ThO_2	H_2O				Cl_2	CCl_4
C-49	59.4 $\text{C}_2\text{O}_4=38.3$	-	-	-	-	1	25-400	-	-
C-50	56.7 $\text{C}_2\text{O}_4=40.8$	-	-	-	-	2	25-300	-	-
C-51	61.6	29.5	1.1	1.0	37.8	2.6	600	6	1.4
C-52	59.4	36.0	0.7	0.8	7.0	2.5	600	6	2.2
C-53	60.9	35.8	1.2	0.5	7.0	2.5	600	7	2.6
C-54	64.2	35.9	0.8	0.5	8.0	2.5	600	7	2.4
C-55	65.6	33.9	1.2	0.5	20.4	2.0	600	6	2.1
C-56	62.6	34.8	1.2	0.2 ^a	19.1	4.0	600	12	2.8
C-57	68.6 $\text{C}_2\text{O}_4=13.9$	10.4	15.5	0.4 ^a	96.0	1.0	250-350	10	0
C-58	64.8 $\text{C}_2\text{O}_4=0.04$	34.3	1.2	0.33 ^a	20.3	1.5	600	10	5.3
Sublimation	61.4	37.65	-	-	-	-	-	-	-

a Decrease in H_2O content resulted in improvement in analytical method.

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