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INVESTIGATION OF EXPLOSIVE CHARACTERISTICS OF PUREX SOLVENT DECOMPOSITION PRODUCTS (RED OIL)

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INVESTIGATION OF EXPLOSIVE CHARACTERISTICS OF PUREX SOLVENT DECOMPOSITION PRODUCTS (RED OIL)

I. INTRODUCTION

It has long been recognized that contacting ICU with Purex solvent over prolonged periods of time will produce a complex mixture of uranium-containing decomposition products. This mixture is known by us as "red oil" and by the British as "third phase". This mixture, while not completely characterized, is known to contain uranium salts of TBP decomposition products and/or uranium salts of nitrated fragments of the hydrocarbon diluent (1). Continued recycling and concentration of TBP contacted solutions produces this heavy third phase very readily. This third phase is believed to be the unstable nitrated mixture found in the equipment after the incident at the Savannah River Pilot Plant (2, 3).

Current design for the Hanford Purex Plant is such that the conditions obtained at Savannah River are not approximated at any point. Uranium nitrate solutions are continuously concentrated at low temperatures which favor steam distillation of solvent. Uranium solutions which are to be calcined are steam stripped of solvent prior to concentration. The waste concentration-acid recovery system is designed to remove the organics continuously with the overhead except for small quantities which are continuously removed with the acid wastes.

The studies outlined below were made to establish the nature and required conditions for reactions of violent nature to demonstrate the magnitude of the margin of safety in the Purex and Metal Recovery production plants.

II. SUMMARY AND CONCLUSIONS

A. A rapid reaction of explosive violence is obtainable from mixtures of "red oil" and uranium solutions only under conditions of incipient calcination (ca. 150°-160°C).

B. Eight experiments under reflux conditions (for 6-8 hours duration) to simulate the Purex uranium concentrators and three additional reflux experiments simulating the Purex waste concentrators (UNH = 0.1M) resulted in slow evolution of NO_2 but no uncontrolled reaction of explosive violence.

C. The residual solutions from the reflux studies, when combined and evaporated, showed rapid decomposition only as calcining conditions were approached. The violence of the decomposition appears to be a function of 1) the absolute amount of "red oil" present, and 2) a secondary function of the ratio of UNH to "red oil".

D. From the nature of the design of the Purex Plant, conditions necessary to obtain violent explosive reactions between "red oil" and uranium solutions are effectively minimized for Hanford operations.

III. EXPERIMENTAL

Since none of the 321 Building "red oil" was still available for these experiments, the initial laboratory efforts were directed to the synthesis of this mixture. One hundred ml of 30% TBP - 70% Shell Spray Base were added to 800 ml of 50% IAW-50% ICU (resultant aq. conc. = 0.1 M UNH and 1.1 M HNO_3) and refluxed for 72 hours before a

third heavy phase of 1.14 Specific Gravity was observed in the reflux mixture. The mixture was then concentrated to ca. 1/3 volume and the specific gravity of the yellow-orange third phase reached 1.36. This third phase (75 ml) was the "red oil" used in the various experiments described below.

A. Vapor Phase Reactions

1. Conditions Simulating Uranium Solution Concentrators

In the following eight experiments UNH crystals and varying amounts of solvent, red oil and 90% HNO_3, were refluxed to permit vapor phase reaction of butyl alcohol (formed from solvent decomposition) with NO_2 fumes. Decomposition occurred but in no case did the reaction approach explosive conditions. The experimental data for the eight experiments are shown in Table I and Table II below.

All reflux experiments were conducted in 500 cc round bottom flasks fitted with standard-taper 24/40 jointed bulb condensers, and heat was applied with Glas-Col mantles. The investigation was conducted with safety shield precautions.

Data in Tables I and II indicate that red oil is readily formed when TBP is vigorously attacked by concentrated nitric acid in the presence of UNH under reflux conditions. Spray Base, in a nitric acid-UNH system, is only slightly attacked, and little if any "red oil" is formed.

This confirms previous studies which indicated "red oil" is formed primarily from TBP decomposition and its decomposition products (reacting with UNH). The behavior in Experiment 8 confirms that UNH is not required for the nitration of "red oil".

2. Conditions Simulating Purex Waste Concentrators

In these experiments concentrated acid solutions containing low concentrations of UNH, $NaNO_3$, and $FeSO_4 \cdot (NH_4)_2SO_4$ were refluxed for eight hour periods with either Purex solvent or "red oil".

Composition of solutions and experimental behavior of these reactions are shown in Table III.

In the above described experiments, which approximate waste treatment conditions, it is evident that, when organic was present to two per cent by volume, the amount of decomposition was very slight. Under plant conditions of operation, where the organic will be continuously steam stripped during concentration, this two volume per cent represents a large increase over what is expected to be present (1).

TABLE I

COMPOSITION OF REFLUX SOLUTIONS

Exp.	Wt. of UNH, (gms)	Vol. 90% HNO_3, (ml)	Vol. of 30% TBP in Spray Base, (ml)	Vol. TBP, (ml)	Vol. Spray Base, (ml)	Vol. Red Oil, (ml)	Reflux Time, (hrs)
1	200	3	5	--	--	--	8
2	200	3	--	--	--	5	6
3	200	10	--	--	--	20	6
4	200	25	30	--	--	--	8
5	100	25	--	--	30	--	8
6	100	25	--	15	--	--	8
7	100	0	--	15	30	--	8
8	---	12	--	--	--	12	8

TABLE II

BEHAVIOR OF REFLUX REACTIONS

Exp.	
1	Fumes of NO_2 after 15 minutes. None for final 4 hours. Red oil formed.
2	Copious NO_2 fumes for entire period.
3	Heavier fumes than Experiment 2 for entire period.
4	Heavy fumes after 1 hour. Gradually decreased. Red oil formed.
5	Slight fumes after 20 minutes.
6	Copious fumes after 4 minutes and for entire reflux period. Red oil formed
7	Slight fumes after 40 minutes which ceased after 5 minutes and remained negligible. Red oil formed.
8	Fumes at once and continued for entire period.

TABLE III

PUREX WASTE SYSTEM STUDIES

	Exp. 9	Exp. 10	Exp. 11
Volume of Solution charged (ml)	200	200	200
Volume of 30% TBP in Spray Base (ml)	4	4	0
Volume of red oil (ml)	0	0	4
Conc. of HNO_3(M)	8	10	10
Conc. of UNH (M)	.1 (10 gm)	.1 (10 gm)	.1
Conc. of $NaNO_3$(M)	.5	.5	.5
Conc. of $FeSO_4 \cdot (NH_4)_2SO_4$(M)	.1	.1	.1
Reflux Duration (hr)	8	8	8
Fume Evolution	(a)*	(b)*	(c)*

*
(a) No fuming for 3 hours, then very slight.
(b) No fuming for 1 hour, then very slight.
(c) Fumed after 15 minutes; fumed for 4 hours and then ceased.

B. Calcining Reaction Studies

Since none of the vapor phase reaction studies gave either an explosion or an extremely rapid nitration reaction of the type experienced at Savannah River, it was decided to combine the residual reaction mixtures from the vapor phase studies and evaporate them to dryness.

Experiment 12

The reaction mixtures from Experiments 1-3 were combined using 500 ml of flush water and concentrated in a 1L two-neck flask equipped with pot thermometer and take-off condenser. Solution was taken off overhead and collected in a receiver. Fumes occurred at 140°C. When the pot temperature reached 150°C and the overhead temperature reached 125°C, an explosion of mild intensity occurred which blew the pot thermometer from the flask.

Foaming also occurred which forced ca. 80% of the flask contents into the receiver, but with such force and rapidity that the condenser was left clear of solids. Examination of the pot after the explosion showed yellow, white and black crystalline substances on the wall of the pot. This indicates that calcination had started to occur at the time of foaming.

Experiment 13

In this experiment the residue from Experiment 4 plus 300 ml of flush water was used. The evaporation proceeded routinely and fumes of NO_2 were observed at 130°C. When 146°C was reached in the pot, foaming occurred, and the flask contents were ejected to the receiver as in Experiment 12; however, there was no explosion, and the thermometer remained securely in the flask although the temperature rose to 210°C. The ejected material contained 50% uranium, was sticky in nature and smelled strongly of organic. This experiment differed from Experiment 12 in that here a higher ratio of organic/UNH in the residual mass charged to the pot was used.

Experiment 14

This experiment utilized the mixed residues from Experiments 5-7 and 300 ml of flush water.

It differed from Experiment 12 in that, at 120°C (pot temperature), red fumes appeared and continued to be evolved until, at 152°C, an explosion occurred. The force of the explosion blew the thermometer out of the pot but ejected no pot contents. When the flask cooled, the contents, which were easily removed, were found to consist of black, dry, odorless, coke-like material. They analyzed 74.8% U and 2.7% C, which would indicate a U_3O_8-C mixture. The difference in character between Experiment 12 and Experiment 14 is thought to be due to the difference in UNH content.

Experiment 15

The residues from Experiments 8-11 were used for evaporation in this reaction. No foaming or explosion was noted in this case. The evaporation proceeded uneventfully and produced, after calcination, a mixture of iron and uranium oxides. Temperature was raised to 340°C with no explosion or foaming. The smooth calcination observed in Experiment 15 points up the validity of present Purex rework treatment, which hydrolyzes TBP decomposition products to harmless inorganic fragments.

Experiment 16

One hundred grams of UNH and 35 ml of 30% TBP-70% Spray Base and 700 ml of water were concentrated. During the concentration the organic steam distilled to the extent of 99+% by volume.

When the pot reached 140°C, red fumes of incipient calcination were observed, and at 150°C, foaming and calcination occurred, with a temperature rise to 220°C. Reaction was of sufficient vigor that ca. 20% of the pot contents were ejected to the receiver. This experiment confirms the fact that only a trace of TBP decomposition products is required to produce foaming in calcination.

Experiment 17

Two hundred grams of UNH and 10 ml of "red oil" were heated slowly, increasing the temperature at the rate of 30°C/hr. Red fumes were observed at 80°C, and these continued until 140°C when they became very heavy. At 148°C the reaction became exothermic, and external heating was stopped. Foaming became suddenly violent at 154°C, and the temperature rose to 165°C.

The results of Experiments 12-17 confirm the work of V. J. Reilly (4).

Robert W. Wagner

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ABSTRACT

Laboratory production of an explosion between UNH and "red oil" under calcination conditions has been accomplished. Attempted production of a vapor phase explosion was unsuccessful below 150-160°C. Since such severe conditions are necessary to obtain an explosive reaction, it appears that present Purex plant design is adequate to avoid explosive conditions.