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CHEMISTRY OF THE INTERCYCLE EVAPORATOR INCIDENT OF NOVEMBER 20, 1959

W. Davis, Jr.
W. H. Baldwin
A. B. Meservey

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CHEMICAL TECHNOLOGY DIVISION

and

CHEMISTRY DIVISION

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W. Davis, Jr.
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ABSTRACT

On November 20, 1959, at 2255 hours, an evaporator in Cell 6 of the ORNL pilot plant exploded during equipment decontamination operations. From the schedule of operation, associated calculations of chemical inventories, and the results of subsequent laboratory studies of the reactions of the various materials known to be present in the evaporator at the time of the explosion, it was concluded that the explosion was probably the result of rapid reaction of nitric acid and alkali nitrates with phenol contained in a decontamination reagent. Although the phenol contained in the reagent was found to contribute significantly to the violence of reaction, various amines in the formulation also react very vigorously when heated with nitric acid. It is also possible that degradation products of tributyl phosphate, present as cruds, contributed to the explosion.

CONTENTS

		Page
1.0	Introduction	4
2.0	Chemical Inventories Prior to Incident	4
	2.1 Prior to Last Decontamination Run	6
	2.2 During Last Decontamination Run	6
3.0	Laboratory Tests	8
	3.1 Qualitative Tests	8
	3.2 Reaction Initiation Temperatures	9
	3.3 Flammability of Solid Residues	9
4.0	Discussion	11
	4.1 Laboratory Tests	11
	4.2 Chemical Reactions of Nitric Acid with Organic Compounds	13
5.0	Conclusions	14
6.0	Appendix	15
	6.1 P-15 Evaporator-Volume Calculations	15
	6.2 Schedule of Events Concerning Cell 6 Evaporator	16

1.0 INTRODUCTION

On November 20, 1959, an explosion occurred in an intercycle evaporator in Cell 6 of the Bldg. 3019 Pilot Plant at Oak Ridge National Laboratory,[1] thereby spreading radioactive contamination through parts of this building and the adjacent grounds and roads. This report describes the probable chemical reactions that produced the explosion in order to help minimize the future occurrence of such incidents in solvent extraction plants.

Prior to and at the time of the explosion the above-mentioned evaporator was being decontaminated to permit personnel access to Cell 6 for the purpose of performing direct maintenance on several process equipment components. The decontamination involved the use of Turco-4501, which is a proprietary decontaminating agent, nitric acid, sodium hydroxide, and water. The schedule of the use of these materials, in a system that probably contained some products of the degradation of tributyl phosphate (TBP), provides the primary basis for evaluating the general cause of the explosion, as described below. Because there are a number of different organic components in Turco-4501, some of these, separately and together, as well as TBP and some of its degradation products were tested for exothermic reactivity when heated with nitric acid.

The schedule of operations and other data pertinent to Pilot Plant operations were provided, primarily, by J. R. Parrott, J. H. Walker, and W. T. McDuffee. The authors also thank E. M. Shank for help in obtaining many of the details of the process equipment and its operation.

2.0 CHEMICAL INVENTORIES PRIOR TO INCIDENT

The organic overflow from the scrub column of the Bldg. 3019 first cycle solvent extraction system is split into two approximately equal streams, each of which flows to a stripping column, from which the uranium-plutonium bearing aqueous raffinate streams flow to two nearly identical intercycle evaporators (Fig. 1). The evaporator in which the explosion occurred is designated P-15. This evaporator system is composed of the steam stripping tank, P-5, a heat exchanger loop, P-7-M and P-15-M, and a vapor de-entrainer, P-2. The unit was last used in the processing of radioactive fuel solution on October 22, 1959 (see appendix). After the last run, the system was purged with nonradioactive feed, then with 6 M HNO_3, then water, and was finally drained. At this point the background radiation level in Cell 6, in which the P-15 evaporator was contained, was too high to permit access for the performance of several necessary maintenance jobs. For this reason, equipment decontamination was initiated. The decontamination operations are divided, for purposes of this report, into two sections: (1) operations ending at about 1500 hours on November 20, 1959; (2) operations starting at about 1500 hours on this date. This division is based on the system being drained completely at the former time.

(1) Nuclear Safety: Vpl 1. No. 3 March 1960, Page 78.

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Ref. Elev., feet	VOLUMES, liters P-5	Loop, P-7-M/P-15-M	Connecting Piping	Total
16				
15				
14				
13				
12				
11	337.84	30.93	5.08	373.85
	317.65	30.20	4.70	352.55
	297.46	29.48	4.31	331.25
	277.27	28.75	3.93	309.95
	257.08	28.02	3.54	288.64
10	236.89	27.30	3.16	267.35
	216.70	26.57	2.77	246.04
	196.51	25.84	2.39	224.74
	176.71	24.75	2.00	203.46
9	156.15	22.94	1.28	180.37
	134.94	21.93	0.18	157.05
	113.58	21.09	0.18	134.85
	92.22	20.25	0.18	112.65
8	70.86	19.41	0.18	90.45
	49.50	18.57	0.18	67.75
	28.14	17.73	0.18	46.05
	7.46	16.89	0.18	24.53
7	0.00	16.05	0.18	16.23
		15.21	0.17	15.38
		14.37	0.16	14.53
		13.53	0.15	13.68
6		12.69	0.00	12.69
		11.85		11.85
		11.01		11.01
		10.17		10.17
5		9.33		9.33
		8.49		8.49
		7.65		7.65
		5.78		5.78
4		4.74		4.74
		4.01		4.01
		3.29		3.29
		2.56		2.56
3				
2				
1				
0				

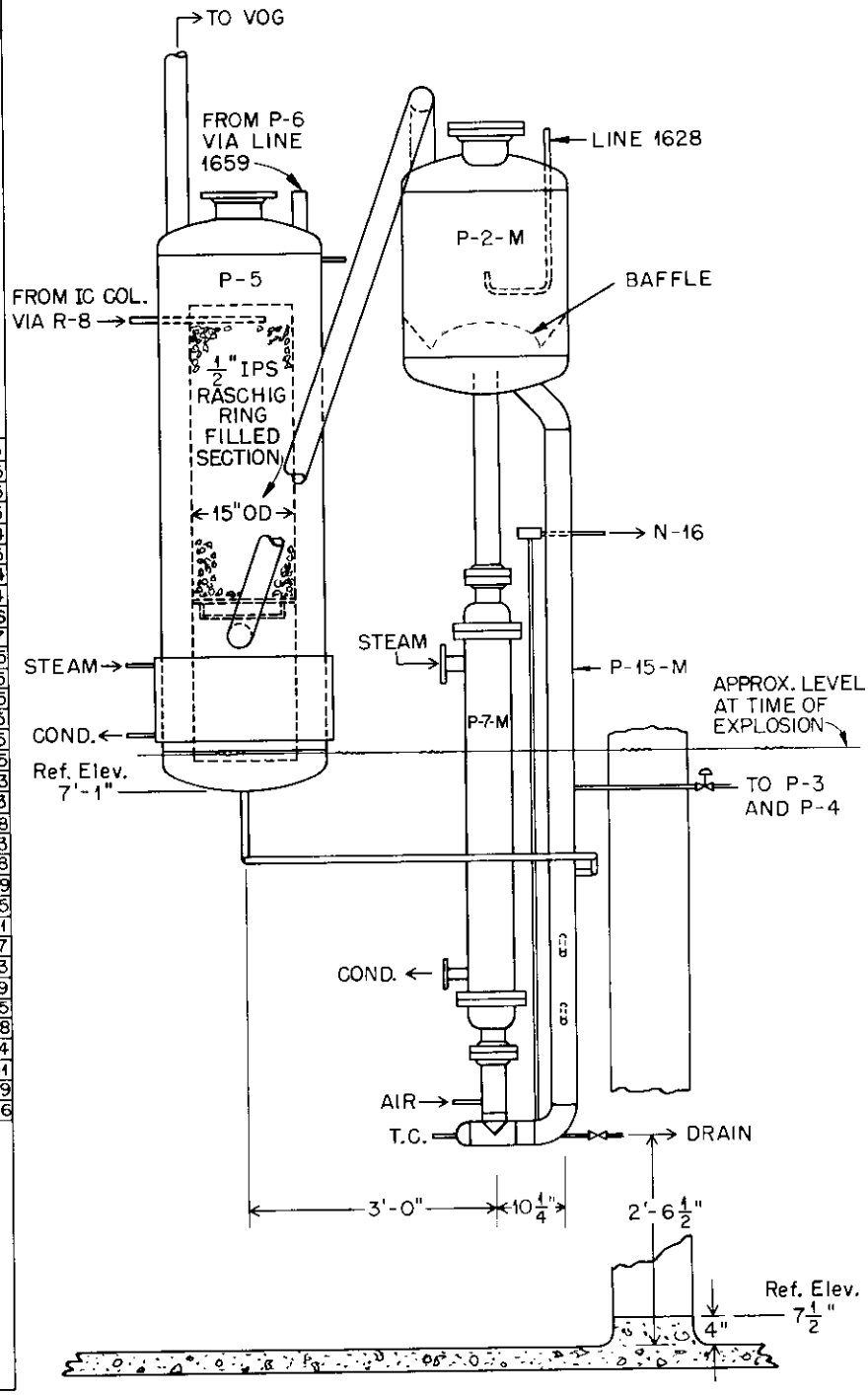

Fig. 1. Evaporator and stripper involved in explosion.

2.1 Prior to Last Decontamination Run

Between the times 1740 hours on November 18 and 1500 hours on November 20, the P-15 evaporator system was washed with Turco-4501, with water, with 30% (5.6 M) aqueous nitric acid, with water, with 25% (7.9 M) aqueous sodium hydroxide, and finally with water. The sequence of 200 gal of water - 400 liters of 25% sodium hydroxide - 300 gal of water was performed with the drain valve at the bottom of the P-15-M pipe open (Fig. 1); hence, there was no solution in the evaporator at 1500 hours on November 20 except that which adhered to the equipment and packing surfaces. On this basis chemical inventories, except TBP degradation products adhering to metal surfaces, prior to about 1500 hours on November 20 had little or no effect on the subsequent explosion.

2.2 During Last Decontamination Run

The last decontamination run was started at 0400 hours, November 20, with the addition of 200 liters of Turco-4501 to tank P-6. This was diluted to 250 liters by steam jetting in P-6 for decontamination of that tank. It was further diluted to 262 liters at 1525 hours, when it was jetted from P-6 into the side of the top of P-5 through line 1659 (Fig. 1), but was subsequently concentrated to 238 liters during the 2 hours of cyclic boiling-decontamination. From Fig. 1 it may be seen that the lower ~15% of the Raschig ring container was immersed in this solution at the start of the boildown. After this solution had been drained to tank P-3, a heel of about 16.5 liters of solution was left in P-7-M and P-15-M (Fig. 1), equivalent to 13.9 liters of Turco-4501 plus 2.6 liters of water.

At 2050 hours on November 20, 270 liters of ~3.98 M HNO_3 was added to the evaporator through decontamination line 1628 into P-2 (Fig. 1). From the construction of P-2, this acid would flow into the cooler leg, P-15-M, displace a small amount (~1.6 liters*) of the Turco-water heel, and then would flow into P-5. The total volume of liquid in the system was 286 liters, of which about 29 liters was in the P-7-M/P-15-M loop. This latter solution was composed of the equivalent of ~12.6 liters of "as received" Turco-4501 and 16.4 liters of ~4 M HNO_3.

In order to describe the probable change in the structures of the components of Turco-4501, it is necessary to consider the general composition of this material. It is a strongly basic solution of the alkali salts of various organic hydroxy acids, various amines, surface active agents, and phenol. At 25°C its density is 1.416 g/ml. From potentiometric titration by strong acid the following approximate composition was deduced:

Strong base	3.9 N
Weak organic acids	1.7
Stronger acids, such as phenol	3.1
Total	8.7 N

*This represents the volume in about 13 in. of 3-in.-dia pipe between the drain line to P-3/P-4 and the 1/2-in.-dia pipe line connecting P-15-M to the bottom of P-5.

It is estimated that prior to starting the last boildown, there was in the P-7-M/P-15-M heat exchanger loop only about 5.2 moles of nitric acid per liter of Turco-4501. Thus, at the start of boiling, the nitric acid—Turco-4501 mixture in the loop was probably still alkaline. During the 85-min interval between the start of boiling at 2130 hours and the explosion at 2255 hours, 205 liters of 1.42 M acid was distilled into P-6. In addition, ~35 liters of solution leaked from P-5, through P-7-M, to P-3. Thus the average rate of flow of 4 M HNO_3 from P-5 to P-7-M was about 2.8 liters/min. At this rate about 5 min would have elapsed from the start of boiling to the neutralization of the Turco-4501. Conversion of the amines to substituted ammonium nitrates and nitration of the organic material would then have begun.

It is considered probable that, in addition to Turco-4501, there were in the intercycle evaporator some products of the degradation of tributyl phosphate (TBP). The degradation products di- and monobutyl phosphoric acids are known to form with some cations, e.g., Fe(III), Zr, and U(VI), compounds which are only slightly soluble in aqueous solutions such as those normally processed in the P-15 evaporator. In addition, an appreciable fraction of TBP dissolved or entrained in these solutions would be decomposed in P-5 and in P-15-M. The inventory of these materials at the time of the last addition of Turco-4501 is not known.

As mentioned above, about 35 liters of the nitric acid—Turco-4501 mixture leaked into P-3 during the 85 min boiling. This plus the 205 liters of 1.42 M HNO_3 constituted the total flow from P-5 to P-15-M. The leakage is therefore equivalent to 14-15% of this flow. This point is mentioned since the leaking solution may have carried 14-15% of the nitric acid—Turco-4501 reaction products, thereby decreasing the organic inventory in the intercycle evaporator.

The status of material in the heat exchanger system P-7-M/P-15-M is important because of possible solids deposition. For example, upon acidifying 13.9 liters of Turco-4501, several kilograms of alkali nitrates might be formed. Most of this would have been in the P-7-M/P-15-M/P-2 sections of the evaporator, which sections contained only about 18 liters of total solution plus solids at the time of the explosion. Therefore alkali nitrates would have precipitated unless their solubility in the nitrated solution exceeded about 550 g/liter. For comparison, the solubility of potassium nitrate in water at 100°C is 2470 g/liter.

In summary, just prior to the explosion, the evaporator system probably had the following chemical inventory: (1) in the steam stripper P-5, approximately 30 liters of 30-35% nitric acid* (5.6-6.7 M); (2) in the P-2/P-7-M/P-15-M combination, approximately 18 liters of the products from

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* This is based on an assumption that the 1.42 M H^+ found as condensate in P-6 from evaporation of nitric acid from P-15 corresponded to 1.42 M HNO_3 as a vapor in equilibrium with the aqueous phase in P-5 just before the explosion. However, at the start of evaporation the nitric acid content of the vapor was probably less than 1.42 M while at the time of the explosion the concentration in the vapor phase was probably greater than 1.42 M. Thus the concentration of nitric acid in P-5 at the time of the explosion was probably at the higher end, or above, the range given above.

extensive nitration of Turco-4501 and some unknown quantity of phosphoric acid and butyl nitrate obtained from the nitration of TBP degradation products. The P-2/P-7-M/P-15-M section may have contained solid alkali nitrate and possibly 2 to 3 kg of picric acid.

3.0 LABORATORY TESTS

The initial purpose of tests on the explosiveness of Turco-4501 when heated with nitric acid was to evaluate the possibility that this combination of chemicals could have caused the explosion in the intercycle evaporator since they were known to have been in the unit prior to the explosion. This question was answered in the affirmative by the first test, in which a mixture of 1 ml of Turco-4501 and 10 ml of 6 M nitric acid exploded, when heated to dryness with a heat lamp, with a loud report but without shattering the open-mouthed pyrex reaction vessel.

The objectives of laboratory tests were then broadened to include identifying the potentially explosive ingredients of Turco-4501 and to define conditions under which an explosion would or would not occur. The tests were not exhaustive but did give a broader picture of the behavior of Turco-4501, Turco-4501A, tributyl phosphate (TBP), dibutyl phosphoric acid (HDBP), monobutyl phosphoric acid (H_2MBP), and the diluent, Amsco 125-82, when heated with aqueous nitric acid solutions under conditions that might have been encountered in the pilot plant. Turco-4501A was tested since it is reported to be identical to Turco-4501 except that the former contains no phenol, which could be converted to the high explosive picric acid during reaction with nitric acid. Thus the results of tests with the two Turco formulations provide a possible answer to the role of phenol in the explosion. TBP and its degradation products HDBP and H_2MBP, as well as Amsco 125-82, were tested for comparison. Some of these materials, especially the TBP degradation products, were probably contained in the evaporator as salts of various cations, e.g. iron, plutonium, and fission product di- or monobutyl phosphates.

Experiments were performed by mixing various quantities, 1-60 ml, of one of the organic materials listed above with nitric acid. Quantities of the latter were varied from 1 to 125 ml at concentrations varying from 4-18 M. In most tests the ratio of organic and nitric acid volumes was between 5:1 and 1:10. Several tests were performed with metal nitrates present, including ferric nitrate, nickelous nitrate, uranyl nitrate (added as uranic oxide), and aluminum nitrate. The mixtures were heated by a heat lamp, an oil bath, or a hot plate. The oil bath was used when the temperature of the reactants was being recorded, and the hot plate in tests on the flammability of the solid or gaseous reaction products.

3.1 Qualitative Tests

The first tests of the reactions of Turco-4501, Turco-4501A, TBP, and Amsco 125-82 with nitric acid were qualitative. They showed that both Turco reagents react with nitric acid with vigorous evolution of the brown nitrogen

dioxide; they also showed that Turco-4501 reacts more vigorously than Turco-4501A or TBP. Turco-4501 exploded harmlessly on being taken to dryness with nitric acid, but a similar experiment with phenol and alkali hydroxide, each in the quantities present in 1 ml of Turco-4501, in 5 ml of concentrated nitric acid resulted in a shattering detonation. Amsco 125-82 reacted only slightly with nitric acid while being taken to dryness.

3.2 Reaction Initiation Temperatures

Quantitative tests were performed to determine the temperatures at which 1 to 3 ml of Turco-4501 started to react vigorously with nitric acid (Table 1). The mixtures were heated in test tubes immersed in an oil bath. Except in one test (Test D), boiling started at 106-108°C; dryness occurred at 110 to 138°C; the maximum temperatures during the terminal exothermic reaction (Fig. 2) varied from 149 to 292°C; the temperature rose very rapidly as dryness was approached. No explosions occurred during these tests, but when Turco-4501 and nitric acid were mixed and aged overnight, the subsequent reaction on heating in the oil bath was more vigorous than that involving unaged materials. No exothermic reaction occurred when the ingredients of Turco-4501 complete except for a complex amine and phenol were mixed with nitric acid and similarly heated in the oil bath.

When 30-60 ml of Turco-4501 was slowly acidified with nitric acid, with constant cooling to maintain the temperature below 40°C, and subsequently heated, an exothermic reaction began at 77°C. The temperature then rose spontaneously to ~103°C and nitrogen dioxide was evolved copiously. With Turco-4501A, evolution of nitrogen dioxide started at 83°C, the heat of reaction raising the solution temperature to ~104°C. When evolution of nitrogen dioxide had ceased and the solution temperature was raised to 121°C, solids precipitated.

3.3 Flammability of Solid Residues

As a result of the possibility of fire as well as explosion on heating nitric acid with the various organic materials described above, a series of tests was performed to determine the flammability of the solid residues from these reactions. The materials were taken to dryness over a hot plate. As dryness was reached, or very shortly thereafter, i.e., at 250-300°C, a number of the residues burst into flame. Residues from Turco-4501—nitric acid and Turco-4501A—nitric acid reactions burned most violently when the ratio of organic volume to volume of concentrated nitric acid was in the range 1/1 to 1/3. With smaller ratios the burning was less violent with Turco-4501 and did not occur with Turco-4501A.

Similar tests were made with TBP, HDBP, and an HDBP-H_2MBP mixture, with and without the addition of sodium nitrate or uranic oxide. All materials evolved nitrogen dioxide, but a flame was achieved only with the gaseous reaction products from the HDBP-H_2MBP mixture containing sodium nitrate in addition to the nitric acid. No flame was produced from the residues of Amsco 125-82—nitric acid—salt reactions. Solid residues from a complex amine—nitric acid—sodium nitrate reaction were very flammable, but similar residues obtained without the salt or with uranic oxide did not burn.

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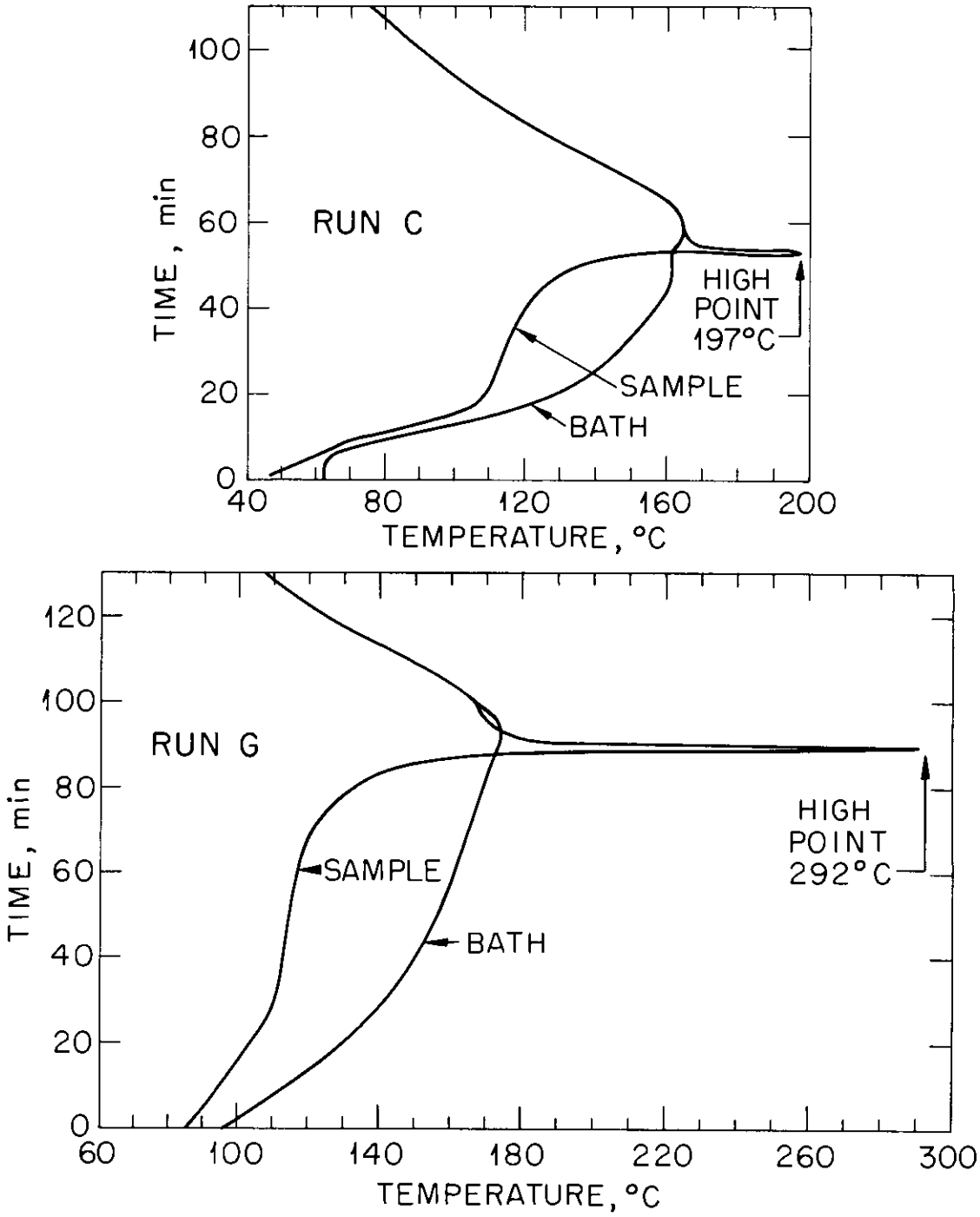

Fig. 2. Temperature-time profile during evaporation to dryness of mixture of 1 ml of Turco-4501 + 18 ml of 4 *M* HNO_3 (Run C) and same reagents + 2.0 g of UO_3 (Run G).

4.0 DISCUSSION

4.1 Laboratory Tests

Laboratory tests should be considered as characterizing the relative reactivities of nitric acid with the various organic chemicals. Thus, although nitric acid—TBP did not explode in these tests, Savannah River experience * shows that this combination can be exploded or caused to react very violently when heated.

Turco-4501 undergoes several reactions with nitric acid, each of which is exothermic. First, there is the neutralization reaction between the acid and alkali hydroxide in the Turco. If this heat of neutralization is not removed by some heat transfer process, it is capable of heating the reactants to a temperature, ~77°C, where an oxidation-nitration reaction occurs as indicated by vigorous evolution of the brown nitrogen dioxide and a further rise in reaction temperature. With both Turco-4501 and 4501A, the temperature rose from ~80 to 104°C as a result of the heat of this reaction. Since this temperature is just below the boiling point of many of the mixtures tested, a further temperature rise as a result of the heat of reaction was prevented by boiloff heat removal.

The presence of the phenolic bodies (listed by the manufacturer) in Turco-4501 and the possible nitration of this component to the highly explosive picric acid suggested that this might have been the primary cause of explosion of the intercycle evaporator. Laboratory tests showed that phenol detonates readily when heated with nitric acid. Further, Turco-4501, which contains phenol, reacted considerably more vigorously with nitric acid than did Turco-4501A, which does not contain phenol. Thus the phenol component of Turco-4501 was shown to contribute very significantly to the explosiveness of this decontaminating agent when it is heated with nitric acid. However, both the known chemistry (Sect. 4.2) and the laboratory tests involving heating nitric acid with Turco-4501A or complex amines support the conclusion that the amine components of Turco-4501 will undergo deflagration when heated with nitric acid. In a closed system the resulting rapid rise in pressure could cause an explosion if the container strength was exceeded.

TBP and its decomposition products, HDBP and H_2MBP, reacted with nitric acid, as evidenced by the evolution of brown nitrogen dioxide. However, these reactions were not nearly so vigorous under the experimental conditions as were the corresponding Turco-4501, 4501A, or amine reactions.

Tests were performed to determine the possibility of a fire hazard from solid residues from reactions of nitric acid with the several organic compound—inorganic salt systems. Both the Turco formulations left residues which burst into flame on further heating. Under some conditions, residues from the nitration of the complex amine were also flammable.

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*T. J. Colven, Jr., G. M. Nichols, and T. H. Siddall, "Interim Technical Report, TNX Evaporator Incident January 12, 1953," DP-25 (May 15, 1953).

Table 1. Temperature Increases Due to Exothermic Reaction of Turco 4501 with Nitric Acid

Test	Vol of Turco-4501, ml	HNO_3 ml	HNO_3 M	Additive	Bath Heating Rate, °C/min	Approx. Temperature, °C: Initial Boiling	At Dryness	Bath	Max. of Samples
A	1	18	4		0.5	108	128	138	149
B	residue from A				4			166	166
C	1	18	4		4	108	130	160	197
D	1	10	16		3.5	122	137	168	170
E	3	54	4		3	106	117-110	158	170
F	1	18	4	72 mg U	3.5	107	133	167	170
G	1	18	4	1.6 g U	3.5	108	138-136	168	292
H	1	10	8	2.0 g UO_3; 1.0 g $Fe(NO_3)_3 \cdot 9H_2O$, 0.1 g $Ni(NO_3)_2 \cdot 6H_2O$	4	106	126-122	160	168

The temperature range, 110-138°C (Table 1), at which the test solutions dried to solids is very pertinent in understanding the evaporator explosion since the temperature in the P-7-M/P-15-M was in this range. For comparison, the set-point of the control thermocouple (T.C. at the bottom of this loop, Fig. 1) was about 115°C. The temperature in the heat exchanger was higher than 115°C but below about 150°C, an upper limit set by the pressure of the steam used to heat P-7-M. It seems very probable that solid alkali nitrate and other nitrates were deposited before the explosion was initiated.

4.2 Chemical Reactions of Nitric Acid with Organic Compounds

A number of different chemical reactions can occur between nitric acid and the materials that were in the evaporator during its last 85 min of operation. The first of these is the neutralization of the basic components of Turco-4501 by nitric acid to give alkali nitrate and nitrate salts of the amines, $R_3N \cdot HNO_3$. These neutralization reactions are exothermic, and these nitrate salts can and do act as oxidizing agents in mixtures. Potassium nitrate is one of the components of black gunpowder.

After neutralization of all the bases in the Turco-4501 and with continued evaporation, the concentration of the nitric acid in the evaporator increased. The following reactions will take place at elevated temperature, around 100°C, and in the presence of an increasing nitric acid concentration.

Reaction of Hydroxyalkyl Groups of Amines

1. Oxidation of hydroxyalkyl groups to carboxylic acid:

$$-CH_2OH + HNO_3 \longrightarrow -COOH + NO_2 + NO$$

This reaction is exothermic.

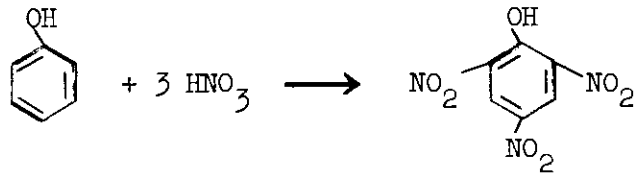
2. Nitration of hydroxyalkyl groups to nitrate esters:

$$-CH_2OH + HNO_3 \longrightarrow -CH_2ONO_2 + H_2O$$

This reaction is endothermic and the products are thermodynamically unstable.

Reactions of Phenolic Component of Turco-4501

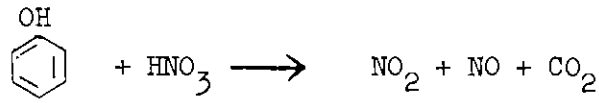
3. Nitration of phenol:



picric acid

This reaction may introduce one, two, or three nitro groups into the benzene nucleus. These nitro compounds are also unstable. Picric acid is a commercial explosive.

4. Oxidation of phenol:



Nitration of Phosphate Esters

5. $$TBP + 3HNO_3 \longrightarrow H_3PO_4 + 3\ C_4H_9ONO_2$$

Butyl nitrate formed from the nitration of TBP is an explosive.

Of the five reactions listed above, Nos. 3 and 4 take place first. In fact, nitric acid at concentrations of 2 M or less causes both oxidation and nitration of phenol. The oxidation reaction is exothermic. The nitro compounds, especially picric acid, are thermodynamically unstable and are awaiting ignition.

At the higher temperature and in the solution of increasing nitric acid concentration, reactions 1, 2, and 5 will occur. Reaction 1, the oxidation of hydroxyalkyl compounds to carboxylic acids, is an exothermic reaction. These acids are quite stable toward further oxidation. The nitration reactions, 2 and 5, are endothermic but the products, nitrate esters, react quite energetically.

5.0 CONCLUSIONS

Known inventories of Turco-4501 prior to the explosion, laboratory tests, and the known chemistry of reactions of several of the organic components of this decontaminating agent when heated with nitric acid all support the conclusion that the intercycle evaporator explosion could have been caused solely by the Turco-4501—nitric acid reaction. There is some uncertainty concerning the role of the phenolic bodies of Turco-4501 and of the probable, small quantities of TBP degradation products in the evaporator unit, particularly the heat exchanger section which is the most likely area of initiation of deflagration. Laboratory tests showed that the phenol component of Turco-4501 was largely responsible for the violence of its reaction when heated with nitric acid. However, the amine components of the Turco also reacted rapidly. Thus, although phenol contributed significantly in the explosion, there is reason to believe that the explosion could have occurred even if the phenol had been absent.

The Savannah River Plant tests (loc. cit.) have shown that TBP and its degradation products will explode when heated with nitric acid under certain conditions. Such reaction may have been contributory in the ORNL

evaporator explosion. However, there has been no evidence to suggest the presence of large quantities of TBP or its degradation products in the evaporator at the time of explosion. On the contrary, the fact that the system had previously been cleaned with Turco-4501, nitric acid, water, and sodium hydroxide solutions and the fact that no evaporator line, including, for example, the 1/2-in.-dia pipe connection from the bottom of P-5 to P-15-M (Fig. 1) was plugged, imply that there were only small quantities of cruds in the system at the time of the last addition of nitric acid.

6.0 APPENDIX

6.1 P-15 Evaporator-Volume Calculations

The elevations of the various sections of the P-15 evaporator were obtained from a sketch made by J. H. Walker, of the Pilot Plant Section, and from the original data of E. M. Shank and W. R. Winsbro on the location of P-5. The volume of the evaporator-stripper assembly at various elevations was determined prior to installation of the P-7-M heat exchanger shown in Fig. 1 and prior to other changes in P-15-M. However, volume-elevation data for the system as it existed just prior to the explosion had not been determined. Volumes listed in Fig. 1 were calculated as described below.

P-7-M/P-15-M Volumes. Volumes of the 3-in.-dia schedule 40 pipe were based on standard manufacturing data which correspond to 0.121 liter/in. Volumes of a 90° weld elbow, a weld tee, and a weld cap, all schedule 40, 3-in.-dia IPS, were measured with water. Respective values were 0.850, 1.090, and 0.178 liter. Volumes of the heat exchanger, P-7-M, and of the two 7-in.-dia IP flange—3 in.-dia IP flange assemblies were calculated from dimensions listed on the Manning and Lewis Engineering Company, Newark, N. J., Dwg. B-4086, date 8/15/55. This drawing and the Union Carbide Nuclear Company Purchase Order W29X-15761 list the specifications for the 6145 stainless steel exchanger. Volumes in the tubes of the heat exchanger are 0.159 liter/in.

P-5 Volumes. The volume of P-5 as a function of elevation was calculated primarily by use of ORNL Dwg. D-11764. Corrections were made for the volumes occupied by the 15-in.-o.d. cylinder used to contain Raschig rings, the ring holder, Raschig rings, etc. Raschig rings were assumed to pack to a void volume of 86%, i.e., 70 lb of rings per cubic foot of geometrical volume.

Volume Uncertainties. The uncertainties of the volumes listed at various elevations in Fig. 1 arise primarily from two sources: (1) how closely the P-5 vessel complies with the dimension listed in ORNL Dwg. D-11764; and (2) how many, if any, Raschig rings fell through the ring container into the bottom of P-5. It is doubtful that these, or other, uncertainties could introduce an error of more than about 1 in. in the calculation of where the liquid level in the P-15 loop would have been in the absence of boiling just prior to the explosion.

6.2 Schedule of Events Concerning Cell 6 Evaporator

11-18-59

1740 hours: 520 liters of water was added to P-5 through the R-1 stripping column. The evaporator previously contained a water heel of 16.5 liters.

2025 hours: The P-15 evaporator loop was drained through the valve to the P-3/P-4 storage tanks (Fig. 1) to the system heel of about 16.5 liters.

2100 hours: Turco-4501 was added to the loop via decontamination line 1628 into P-2 until the liquid volume was 104 liters. This solution was boiled from 2145 to 2345 hours.

11-19-59

0010 hours: The evaporator solution would not drain when the valve to P-3/P-4 was opened. When 15 liters of water was added to the evaporator, drainage started and was continued until the system contained only the 16.5-liter heel.

0200 hours: The evaporator was washed with 50 gal of water added through P-2 and drained to the system heel of 16.5 liters. The valve to P-3/P-4 was then closed.

0500 hours: Nitric acid, 30%, was added to the loop through P-2 until the volume was ~230 liters. This solution was heated from 0545 to 0630 hours.

0630 hours: Drainage to P-3/P-4 was started at this time and completed, to the 16.5-liter heel level, at 0745 hours when the valve to P-3/P-4 was closed.

0945 hours: Water was added via P-2 to the 398 liter level.

1005 hours: Drainage of solution to P-3 was started.

1230 hours: Drainage of the loop to the 16.5 liter heel was completed and the valve to P-3/P-4 closed.

1445 hours: The drain valve at the bottom of the loop was opened after which the system was flushed with 200 gal of water, added through P-2, which was drained to the sump.

11-20-59

0005 hours: The system was flushed with about 400 liters of hot, 25% NaOH solution, added through P-2, which was drained to the sump. The valve to the sump was open during this flushing operation.

0400 hours: 200 liters of Turco-4501 was added to tank P-6.

0500 hours: Flushing of the evaporator loop with sodium hydroxide solution was completed and flushing with 300 gal of water, added through P-2, was started.

1500 hours: The drain valve was closed. At this time the only liquid in the evaporator loop was that adhering to the system walls and perhaps a few hundred milliliters below the drain valve.

1525 hours: Turco-4501 was jetted from tank P-6 to the evaporator loop through line 1659 (Fig. 1). During internal jetting within P-6 and during jetting to the evaporator loop, the 200 liters of Turco-4501 was diluted to 262 liters.

1545 hours: Heating of the Turco-4501 for the last decontamination operation was started. During the subsequent 2 hr of boiling about 24 liters of liquid was evaporated from the loop.

1940 hours: Draining of Turco-4501 solution to tank P-3 was started.

2045 hours: Drainage of the system to the heel of 16.5 liters was completed. The valve to P-3/P-4 was then closed.

2050 hours: 270 liters of 3.98 M HNO_3 was added to the evaporator through decontamination line 1628 into P-2 (Fig. 1).

2130 hours: Heating of the solution was initiated. During the next 85 min of boiling, 205 liters of 1.42 M acid was distilled into tank P-6 and 35 liters of solution leaked into tank P-3 through the valve to P-3/P-4.

2255 hours: The evaporator exploded.

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