CLASSIFICATION

[redacted]

DECLASSIFIED

ION NO.

BNWL-CC--1517

DE92 009037

BATTELLE-NORTHWEST

BATTELLE MEMORIAL INSTITUTE / PACIFIC NORTHWEST LABORATORY

P. O. BOX 999 / RICHLAND, WASHINGTON 99352

DATE

February 1, 1968

TITLE AND AUTHOR

CHARACTERIZATION OF THE ORGANIC MATERIAL IN THE 112 BY TANK

Wallace W. Schulz

CONTRACT

[X] - 1830

[ ] - 1831

PROJECT NO.

W/O # A-68467

RESERVED FOR TECH. INFO. USE

DISTRIBUTION

NAME	COMPANY	LOCATION	NAME	COMPANY	LOCATION
Battelle-Northwest			ARHCO		
1. J. M. Atwood			12. S. J. Beard		
2. L. A. Bray			13. M. H. Campbell		
3. R. E. Burns			14. W. L. Godfrey		
4. E. A. Coppinger			15. M. J. Kirkman		
5. D. R. de Halas			16. P. W. Smith		
6. R. L. Moore			17. R. J. Sloat		
7. W. W. Schulz			18. R. E. Tomlinson		
8. H. H. Van Tuyl					
9. E. E. Voiland					
10. 300 Area Files					
11. 300 Area Files					

MASTER

DISTRIBUTION RESTRICTED TO U.S. ONLY

ROUTE TO	PAYROLL NO.	COMPANY	LOCATION	FILES ROUTE DATE	SIGNATURE AND DATE

DECLASSIFIED

[redacted]

CLASSIFICATION

34-1100-025 (4-66) ABC-GL RICHLAND, WASH.

[redacted]

DECLASSIFIED

BNWL-CC-1517

CHARACTERIZATION OF THE ORGANIC MATERIAL IN THE 112 BY TANK

by

Wallace W. Schulz
Applied Chemistry Section
Chemistry and Chemical Engineering Department

February 1, 1968

INFORMATION CONCERNING USE OF THIS REPORT

PATENT STATUS

This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U. S. Atomic Energy Commission. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Chief, Chicago Patent Group, U. S. Atomic Energy Commission. 9800 So. Cass Ave., Argonne, Illinois.

PRELIMINARY REPORT

This report contains information of a preliminary nature prepared in the course of work under Atomic Energy Commission Contract AT(45-1)-1830. This information is subject to correction or modification upon the collection and evaluation of additional data.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

64-1100-057 (6-65)
AEC-RLGG RICHLAND, WASH.

CHARACTERIZATION OF THE ORGANIC MATERIAL IN THE 112 BY TANK

by

Wallace W. Schulz

INTRODUCTION

In-tank solidification (ITS) of large quantities of aged, alkaline radioactive waste solutions is an integral part of the overall Hanford Waste Management program. Thus, the first ITS unit is currently operational in the 102 BY tank and a second ITS unit recently became operational in the 112 BY tank.

The 112 BY tank contains neutralized Metal Recovery Plant waste of the estimated[1] gross salt composition 3.4M $NaNO_3$-0.044M NaCl-0.31M NaOH. Tank samples and photographs of the tank interior confirm that a layer of organic material covers at least part of the aqueous waste.[2] The exact volume of the organic material is not known but is presumed small. However, because of possible and unknown hazards, this organic material complicates ITS operations. The experiments summarized in this report were performed to determine the composition and some of the properties and reactions of the organic material to define such hazards, if any. Such

---

(1). M. J. Kirkman. Personal Communication. Atlantic Richfield Hanford Co., 1967.

(2). P. W. Smith, Isochem Co. Letter "Organic Phase in Underground Storage Tanks," August 3, 1967 to R. E. Burns, Pacific Northwest Laboratory.

information is timely not only to ITS of the contents of the 112 BY tank but also because similar organic phases may be present in other wastes scheduled for ITS.

SUMMARY AND CONCLUSIONS

The organic material in the 112 BY tank has been identified as containing about 67 vol% TBP diluted with degraded kerosene. All, or, at least most, of the organic solution will likely steam distill during ITS operations in the 112 BY tank. Experimental data indicate, however, that even if none of the TBP-diluent solution distils, the aqueous-organic mixture in the tank can be safely solidified; further, the resulting solid can be heated to high ($\geq$270 °C) temperature without ignition or explosion. It is concluded, therefore, that the organic material in the 112 BY tank will not interfere with safe ITS operation in the tank.

Efforts to prevent distillation of the organic material by dispersing and/or emulsifying it were uniformly unsuccessful. Such experiments were prompted by the current desire to limit drastically the amount of organic material sent to underground cribs. To achieve this objective for 112 BY tank operations, it is suggested further consideration be given to either physical or chemical removal of the organic phase from the large volume of aqueous condensate which will be produced.

EXPERIMENTAL PROCEDURES AND RESULTS

A. Composition, Source, and Physical Properties of Organic Material

Tests were performed with a 500 ml sample of the yellow-colored organic material. Gas-liquid chromatography shows the material contains

about 67 vol% TBP diluted with degraded kerosene, probably either Soltrol-170 or Shell Spray Base. The following amounts of radioisotopes are present (gamma energy pulse height analysis): 80 uCi/l ^{106}RuRh, 47 uCi/l ^{144}CePr, 14 uCi/l ^{137}Cs, 0.9 uCi/l ^{103}Ru, 0.82 uCi/l ^{95}ZrNb, and 0.8 uCi/l ^{134}Cs.

The density of the material is 0.901 g/ml, and its flash point is 119 °C. The latter datum was obtained with an apparatus of the Pensky-Martens type using a recommended(3) ASTM procedure. The experimental flash point is in reasonable agreement with that calculated for a 67 vol% TBP-Soltrol-170 solution using the empirical relation given in the Purex Process Technical Manual.(4) According to Burger(5), "Although the flash point of an oil has very little relation to its chemical reactivity or even to the way it burns, it is a rough measure of the safety of storage and use under circumstances when sparks, flames, or other localized high temperature sites are a possibility."

Most likely, the organic material was originally introduced, inadvertently, into the 112 BY tank as the 30% TBP-diluent extractant composition traditionally used in Hanford separations plants. Because of the age of the aqueous waste (derived originally from $BiPO_4$ Process

---

(3). "Tentative Method of Test for Flash Point by Pensky-Martens Closed Tester," ASTM Designation D93-58T, 1958 Book of ASTM Standards, Part 7. American Society for Testing Materials, p. 35. Philadelphia, Pa., 1958.

(4). Purex Technical Manual, HW-3100, p. 439, March, 1955. General Electric Co., Richland, Wash. (Secret)

(5). L. L.Burger. The Relation of Flash Point to Vapor Pressure, HW-35579, Feb., 1955. General Electric Co., Richland, Wash.

operations) in the tank, temperature and radiation conditions were insufficient to affect hydrolysis of the TBP to phosphoric acid as might have been anticipated. The conditions were sufficient apparently to cause some volatilization of the kerosene fraction.

B. Thermal Behavior of Organic Material

Although well outside the normal operating range, mechanisms can be postulated whereby liquid temperatures as high as 320 °F and sludge temperatures as high as 500 °F could be attained during or subsequent to ITS #2 operation.[1] The thermal behavior of the organic material either by itself or in combination with the aqueous phase in the 112 BY tank was studied to determine what, if any, thermal hazards might exist at these temperatures. Such studies relate to the case where essentially all the organic phase remains in the tank during all the entire ITS operations. Actually, as discussed later, a substantial fraction of the organic phase will likely steam distil during the initial phases of ITS and hence will not be present to undergo any hazardous thermal reactions.

1. Differential Thermal Analyses

Differential thermal analyses (DTA) were made with a Du Pont 900 DTA instrument; in all cases, samples were heated in air from 25 to 500 °C.

(a). 112 BY Organic Alone. Endotherms (only) were noted at about 260 to 270 °C and at about 290 °C. The latter corresponds, probably, to the boiling point of TBP (literature value[4] is 289 °C).

(b). 112 BY Aqueous Alone. A single endotherm at 106 °C, corresponding to the boiling point, was noted.

(c). Equal Volumes of 112 BY Aqueous and Organic. Endotherms (only) were noted at 106 °C, 245 to 250 °C, and 335-340 °C. The latter two were very broad.

2. Crucible Ignition Experiment

A mixture of 15 ml of the aqueous and one ml of the organic phases in the 112 BY tank was taken to dryness at 85 to 90 °C over a four hour period. The resulting mixture of white inorganic and yellow organic solids was first heated 20 hours at 120 to 140 °C and then about 96 hours at 245 to 260 °C. There were no explosions or any indication whatsoever of formation of any hazardous combinations.

3. "Hot Wire Experiment"

A stainless steel wire was heated white hot in a Meker burner flame and dropped onto a thin layer of 112 BY organic material in a porcelain disk. The organic material did not ignite or explode. The experiment simulates, albeit in a crude fashion, contact of the organic with hot welding slag such as might occur during ITS operations.

C. Steam Distillation Behavior

Based upon the results of two laboratory distillations, it is anticipated that over half of the organic material in the 112 BY tank will steam distil during ITS operations.

Laboratory distillations were made with 50 ml quantities of the 112 BY organic solution. In one experiment (Table I) steam distillation was performed at 103 to 108 °C for 29 hours at an average boilup rate of 50 ml/hr. A wider temperature range (110 to 160 °C), corresponding to that

expected in ITS operation in the 112 BY tank, was traversed in the second distillation experiment (Table II).

TABLE I. STEAM DISTILLATION OF 112 BY ORGANIC AT 103-108 °C

Distillation Conditions			Organic Distillate	
Time hrs	Temp. °C	Boilup Rate ml/hr	Volume ml	TBP M
6	1-5	48	17	0.0
6	105-108	49	8	2.14
3	103-105	43	1.5	2.35
7	103-105	36	2.0	(a)
7	103-105	68	(b,c)	-

(a) Not determined.
(b) No organic material detected in condensate.
(c) Organic in distillation pot at end of 29 hrs was 2.98M in TBP.

TABLE II. STEAM DISTILLATION OF 112 BY ORGANIC AT 110-160 °C

Distillation Conditions			Organic Distillate	
Time hrs	Temp. °C	Boilup Rate ml/hr	Volume ml	TBP M
3	110-115	88	16.3	0.0
7	125	105	20.0	2.75
3	150-160	154	5.0	(a)

(a) Not determined.

The first material to distil over in each experiment was kerosene free of TBP. This distillation behavior is expected, of course, from the difference in boiling points of TBP and kerosene. The volume of the TBP-free kerosene distillate was in reasonable agreement with that expected from 50 ml of 67% TBP-33% diluent solution.

After removal of most of the kerosene, succeeding portions of distillate contained increasing amounts of TBP. As anticipated, the total volume of organic material removed by steam distillation varied with

distillation temperature. At 103 to 108 °C only about 60% of the organic material distilled while at higher temperatures (Table II) over 80% of the TBP-kerosene solution distilled.

D. Survey of Dispersion and Emulsification Agents

There is a strong desire on the part of both the AEC and ARHCO to limit severely the volume and amount of low level radioactive waste discharged to the Hanford environs. In particular, it is desirable to restrict the amount of organic materials discharged to underground cribs because such materials foul the cribs and reduce their capacity to retain radionuclides. These incentives motivated a survey (Table III) of several commercial dispersion and emulsification agents in the hope of finding some reagent which would combine with either all, or most, of the organic phase in the 112 BY tank and thereby prevent its distillation. These efforts were uniformly unsuccessful.

Only one of the reagents, Mistron 25 (magnesium silicate) appeared to show any promise in the initial tests. As indicated in Table III this material appeared to adsorb the organic phase. However, subsequent distillation tests showed that the adsorptive force was not sufficient to prevent volatilization of the organic material.

DISCUSSION

The results obtained in this investigation indicate a large fraction of the TBP-diluent solution in the 112 BY tank will steam distil during ITS operations. Such distillation will occur naturally, without hazard, and provides a positive way of removing most of the organic material.

TABLE III. SURVEY OF DISPERSANTS

Conditions: 15 ml synthetic 112 BY Tank aqueous, 1.0 ml of actual 112 BY organic, and indicated amount of dispersant stirred 30 min at 25 or 80 °C.

Dispersant				
Name	Source	Amount	°C	Remark
Polycomplex A-11	Guardian Chem. Co.	0.2 ml	25	(1)
Dash	Proctor & Gamble Co.	0.1 g	25	(1)
Amway	Amway Co.	0.1 g	25	(1)
Petro AG Fines	Petro Chem. Co.	0.1 g	25	(1)
Marasperse N	American Can Co.	0.1 g	25	(1)
Marasperse C	American Can Co.	0.1 g	25	(1)
Marasperse CB	American Can Co.	0.1 g	25	(1)
Tide	Proctor & Gamble Co.	0.1 g	25	(1)
Duponal (Sodium lauryl sulfonate)		0.1 g	25 & 80	(1)
Duponal	Scientific Supplies Co.	0.5 g	25 & 80	(1)
Attapulgus "A"	Attapulgus Mineral & Chem. Co.	0.1 g	25	(1)
Attapulgus "AA"	Attapulgus Mineral & Chem. Co.	0.1 g	25	(1)
Tetrasodium pyrophosphate	Monsanto Chem. Co.	0.1 g	25 & 80	(1)
Sodium acid pyrophosphate	Monsanto Chem. Co.	0.1 g	25	(1)
Cascade	Proctor & Gamble Co.	0.1 g	80	(1)
Benax 2A1 Powder	Dow Chem. Co.	0.1 g	25	(2)
Benax 2A1 Solution	Dow Chem. Co.	0.1 g	25	(2)
Mistron 25	Sierea Talc & Clay Co.	0.1 g	25 & 80	(3)
Mistron 25	Sierea Talc & Clay Co.	0.05 g	25 & 80	(3)
Mistron 25	Sierea Talc & Clay Co.	0.05 g	25 & 80	(3)

(1) No apparent dispersion or emulsification.
(2) Emulsification during stirring but organic phase gradually rose to top when mixture stood.
(3) Mistron-25 solids collected on top of aqueous when stirring stopped. Organic layer not visible as such but appeared to be absorbed on solids.

However, even if none of the organic material is removed by distillation, the aqueous-organic combination in the tank can be safely and readily solidified and the resulting solid can be heated to high temperatures without ignition or explosion. It is concluded that the organic material in the 112 BY tank will not interfere with routine and safe ITS operations

in the tank.

However, the desire to prevent disposal of the 112 BY organic material to ground with the aqueous condensate is also appreciated. Initial efforts to realize this objective by dispersing and/or emulsifying the organic phase to prevent its volatilization were uniformly unsuccessful. While further efforts in this latter direction might be more fruitful, it is suggested that a more direct way to prevent disposal of the organic material to ground is to remove it from the aqueous condensate. This might be accomplished either by some mechanical device or possibly chemically (eg. adsorption on a bed of activated carbon). Economic and other factors involved in removing the organic material from large volumes of aqueous condensate on the one hand and of simply dispersing the organic material from the 112 BY tank to ground on the other require assessment.

END

DATE
FILMED
4/10/92