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HW-19739

Technology - Hanford Processes

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PROGRESS REPORT FOR NOVEMBER, 1950
CHEMICAL RESEARCH SECTION

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by

O. F. Hill and F. J. Leitz
Chemical Research Section
Technical Divisions

December 18, 1950

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Technology - Hanford Processes

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PROGRESS REPORT FOR NOVEMBER, 1950
CHEMICAL RESEARCH SECTION

I. METAL PRODUCTION PROCESS STUDIES (W. H. Reas, Group Leader)

A. ISOLATION BY THE PRECIPITATION OF PLUTONIUM(IV) ARSENATE (P. M. Brown, K. M. Harmon)

Previously (HW-19503), the results of a 5 gram (0.5 liters F-10-P solution) plutonium(IV) arsenate precipitation were reported in which incomplete precipitation was observed even after several hours of stirring, heating, etc. Since this effect was not noted in the laboratory on the ca. 2 ml scale, it was thought that the surface to volume ratio and the type and efficiency of stirring might be quite important. Thus, further laboratory work has been performed on the 25 ml scale to investigate these effects. Experiments were performed to determine the effect of using a stainless steel precipitator under the conditions and with the results given in Table I. The results of experiments performed at room temperature indicate that lower plutonium losses are obtained with more vigorous stirring and with a precipitator fabricated of stainless steel. One additional experiment at room temperature is contemplated using a stainless steel precipitator and employing vigorous stirring. At 80°C., the rates of precipitation of plutonium arsenate in stainless steel and glass vessels are comparable; however, fewer fines are formed in stainless steel.

The hydrofluorination of the cake from the second 5 gram-scale precipitation of plutonium(IV) arsenate from F-10-P solution (reported HW-19503) gave a bulky but normal appearing fluoride. Unfortunately, the solid weighed 25% more than it would have were it all PuF_4. Since continued HF treatment gave no weight reduction, it has been assumed that the fluoride is highly contaminated by a foreign element, probably lanthanum, and no attempt at reduction to the metal has been made.

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Table I

PLUTONIUM(IV) ARSENATE SOLUBILITIES

M HNO_3	M H_3AsO_4	Conditions	Stirring Time (Hrs.)	Plutonium Initial g/l	Plutonium Final g/l	Plutonium % Loss
1.815	0.413	Stainless steel cone, very slow stirring, precipitation at room temperature	3	8.45	0.353	4.18
			4 1/2		0.217	2.57
1.66	0.399	Glass cone, very slow stirring, precipitation at room temperature	5 1/2	7.90	2.32	29.4
			7		1.64	20.8
			Standing overnight		1.08	13.8
1.66	0.399	Glass cone, rapid stirring, precipitation at room temperature	5	7.90	0.598	7.57
			7		0.384	4.86
0.619	1.005	Glass cone, slow stirring, heated to ca. 80°C. for conversion to dense phase. Large amount of fine flocculent precipitate formed after ca. 3 hours	1 1/2	7.81	0.920	11.8
			2 1/2		0.308	3.95
			3 1/2		0.157	2.01
			4 1/2		0.0915	1.17
			5 1/2		0.0537	0.688
0.618	0.935	Stainless steel cone, slow stirring, heated to ca. 80°C. for conversion. Not so many fines formed as in above experiment	1 1/4	7.95	1.136	14.3
			2 1/4		0.498	6.27
			3 1/4		0.268	3.37
			4 1/4		0.154	1.94
			5 1/4		0.0942	1.187
			6 1/4		0.0572	0.724

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B. ISOLATION BY THE PRECIPITATION OF PLUTONIUM(III) FLUORIDE (K. M. Harmon)

An interesting possibility for coupling the Redox and Metal Reduction Processes lies in the precipitation of PuF_3 from a concentrated IIBP stream, followed by dehydration and reduction of the product cake. A brief preliminary investigation of the properties of PuF_3 precipitates formed at room temperature and in 1 or 2 $\underline{M}$ nitric acid, has shown such precipitates to settle quite rapidly and to exhibit solubilities of the order of 0.01-0.02 gm Pu/l. Solubilities and precipitate volumes for 22 mg samples of plutonium as the precipitated fluoride are summarized in Table II. The precipitates, when centrifuged, all occupied a volume of about 0.025 ml (bulk density = ca. 0.87 g/cm^3).

Hydroxylamine hydrochloride was used to reduce the stock plutonium solution (90% plutonium(IV) and 10% plutonium(VI)) to the plutonium(III) oxidation state. In 0.93 $\underline{M}$ HNO_3, the reduction was rapid at room temperature; in 1.9 $\underline{M}$ HNO_3, the solutions required heating to complete the reduction reaction; and in 3 $\underline{M}$ HNO_3, the reduction could not be made to go to completion.

The laboratory work so far indicates this process to be of promise, provided sufficient separation from corrosion products and aluminum can be obtained, and provided that the metal reduction can be made to work satisfactorily.

Table II

SOLUBILITIES AND VOLUMES OF PuF_3 PRECIPITATES

Total plutonium present: 21.9 mg
Final slurry volume: 0.6 ml

				Plutonium	
Expt. No.	$\underline{M}$ HNO_3	$\underline{M}$ HF	Ppt. vol., ml*	Soly., g/l	% Loss
3-8-1	0.93	0.4	0.10	1.9	5.2
3-8-2	"	1.3	0.15	0.018	0.05
3-8-3	"	2.1	0.15	0.010	0.03
3-8-4	"	3.0	0.19	0.014	0.04
3-9-1	1.9	1.3	0.10	0.019	0.05
3-9-2	"	2.1	0.10	0.011	0.03
3-9-3	"	3.0	0.11	0.014	0.04
3-9-4	"	3.8	0.14	0.023	0.06
3-9-5	"	4.7	0.15	0.015	0.04

* After settling one-half hour

C. RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE WASTES (W. W. Schulz)

Further consideration has been given to the feasibility of utilizing a solvent extraction process to recover plutonium from the nitric acid leachings of slag and crucible.

Experiments were first carried out using ten milliliters of leachings from slag and crucible and three contactings with an equal volume of hexone. At the completion of the extractions the three organic phases were combined and stripped once with an equal volume of 0.01 M HNO_3. The results obtained are listed in Table III.

Table III

HEXONE EXTRACTIONS OF PLUTONIUM FROM LEACHING SOLUTION

Aqueous: Leaching solution (0.375 M HNO_3 and made 1.44 M ANN)

Organic: Hexone (0.5 M HNO_3)

Expt. No.	E_a^o Values*			% Pu left in final aqueous	E_a^o value for stripping
	1st Extr.	2nd Extr.	3rd Extr.		
1	45	ca. 9	ca. 1	0.1	0.007
2	39	ca. 6	ca. 1	0.1	0.003

* Analytical difficulties necessitate reporting only approximate values of the extraction coefficients.

The results indicate a 99.9% recovery of plutonium for three extractions. Stripping with 0.01 M HNO_3 gave satisfactory recoveries of plutonium from the hexone phase as the E_a^o values indicate.

The favorable results obtained in the first extraction experiments suggested the possibility that leaching solutions might be recycled to the IIA column in the Redox Process. Accordingly, experiments were carried out using a 100:1 dilution of leaching solution with IIAFS solution and three contactings with an equal volume of hexone. The results of these experiments are shown in Table IV.

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Table IV

HEXONE EXTRACTIONS OF PLUTONIUM FROM LEACHING SOLUTION AFTER DILUTION WITH IIAFS SOLUTION

Aqueous: Leaching solution diluted 100:1 with IIAFS solution (0.375 M HNO_3 and 1.3 M ANN)

Organic: Hexone (0.5 M HNO_3)

Expt. No.	E_a^o Values 1st Extr.	 2nd Extr.	 3rd Extr.
3	4.5	1.5	0.21
4	4.8	1.2	0.25
5	6.5	1.5	0.19

The results obtained for distribution ratios of plutonium(IV) under the conditions given above agree well with previously reported values (HW-18353).

Experiments have also been carried out using TBP as the extractant. Extractions with TBP using CCl_4 as the diluent offer the advantage of obtaining a large volume reduction of the final plutonium solution. As in the experiments with hexone, distribution ratios were obtained for three extractions of the leaching solution and the results obtained are given in Table V.

The results of Experiments 6 and 7 indicate that a ten-fold volume reduction and recoveries of greater than 99% may be obtained for three contactings of leaching solution with TBP-CCl_4 phase. The composition of the white scum which formed at the interface of the aqueous and organic phases during the second contacting in Experiments 6 and 7 and the reason for its formation have not as yet been determined. However, as can be seen from the results of Experiments 8 and 9, formation of this layer does not occur when the leaching solution is 5 M in HNO_3. The low distribution ratios obtained in Experiments 8 and 9 point to the desirability of having $Al(NO_3)_3$ present to complex the fluoride ion present in the leaching solution.

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Table V

TBP EXTRACTIONS OF PLUTONIUM FROM LEACHING SOLUTION

Expt. No.	Aqueous	Organic	Ratio Feed to Extractant	E_a^o Values(1) 1st Extr.	E_a^o Values(1) 2nd Extr.	E_a^o Values(1) 3rd Extr.	% Pu in Final Aqueous	Remarks
6	1.43 M ANN 0.375 M HNO_3	5% TBP in CCl_4	1:1	143	ca. 3	ca. 0.1	0.1	Layer of white material formed at interface during second contacting.
7	1.43 M ANN 0.375 M HNO_3	30% TBP in CCl_4	14:1	339	--	--	0.6	"
8	5.08 M HNO_3 No ANN(2)	"	10:1	ca. 11	ca. 12	ca. 13	8.4	Formation of layer did not occur.
9	"	"	10:1	ca. 15	ca. 13	ca. 13	6.3	"

(1) Since difficulties have been encountered in obtaining accurate plutonium analyses of the TBP phase, the extraction coefficients were calculated using the aqueous phase analytical data and the initial plutonium content in the leach solution.

(2) Leaching solution filtered just prior to extraction.

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II. BISMUTH PHOSPHATE PROCESS STUDIES (R. E. Burns, Group Leader)

A. EXTRACTION AS A FUNCTION OF THE BISMUTH TO PLUTONIUM RATIO (H. S. Gile)

The volume of dissolver solution used per run in the canyons is determined by the grams of plutonium per ton of irradiated metal, since the batch size is based on a given amount of plutonium. Obviously, as the g/T level increases, the volume of dissolver solution used per run decreases. Although for some time the plant has been processing material of increasing g/T level, no change has been made in the amount of bismuth phosphate precipitated per run in the extraction step. With a view to a possible reduction in the amount of bismuth phosphate precipitated per run a study is being made of plutonium loss in the extraction step as a function of g/T while keeping the initial bismuth concentration constant. Present studies involve precipitating 2.5 grams of bismuth per liter of solution in the extraction step.

Experimentally, simulated dissolver solution was spiked with an appropriate amount of plutonium and carried through the reduction and bismuth phosphate precipiation steps. Plant conditions were approximated with respect to reagents and digestion times. However, in some instances times for the addition of reagents were shorter than employed in the plant. Analysis of the supernatants was by two methods, viz., the Ca-3b procedure used in the plant to determine total plutonium in metal waste solution and a recently described cerous fluoride procedure (HW-18697) for determining plutonium and americium separately in process solutions. In most cases the Ca-3b procedure gave results close to the values for plutonium plus americium as obtained by the cerous fluoride procedure. Plutonium losses obtained at 370, 565, and 740 g/T levels are given in Table VI.

Although the data are somewhat scattered, the degree of scattering is not unexpected for laboratory-scale carrying of plutonium on bismuth phosphate. There appears to be no increase in plutonium loss up to the 740 g/T level. In fact, to the extent that the average values are meaningful, there is a slight decrease in the percentage plutonium loss with increasing g/T in the range studied. Future work will include extension of the present studies to higher g/T levels and a similar series of experiments in which the initial bismuth concentration will be 1.8 grams per liter.

Table VI

PLUTONIUM LOSSES IN THE EXTRACTION PROCESS AS A FUNCTION OF GRAMS PLUTONIUM PER TON METAL

g/T	% Plutonium Loss	
	Ca-3b Procedure	Cerous Fluoride Procedure
370	2.8	2.6
	1.2	0.95
	1.5	1.3
	0.44	0.28
	5.9*	5.0*
	0.86	1.4
	Av. 1.36	Av. 1.31
565	1.0	0.95
	0.58	0.31
	1.2	0.81
	0.75	0.46
	2.3	1.8
	1.8	1.5
	Av. 1.27	Av. 0.97
740	0.84	0.55
	0.54	0.32
	0.47	0.25
	1.5	1.2
	1.3	1.0
	2.1	1.1
	Av. 1.13	Av. 0.74

* Not included in calculating the averages shown

B. REMOVAL OF IODINE FROM DISSOLVER SOLUTION (C. H. Holm)

Experience in the operation of the radioactive iodine production unit at Oak Ridge has shown that the presence of very small amounts of mercury in dissolver solution renders the iodine very difficult to remove by sparging. In view of the poor results obtained in recent attempts to remove iodine from simulated dissolver solution by sparging it was felt that an investigation of means of insuring that the active iodine remains unvolatilized until disposed of as waste was warranted.

Since mercury is not the only cation mentioned by Oak Ridge as interfering with the sparging of iodine, several cations known to form complexes with iodide were tried in a preliminary survey. Simulated dissolver solution (1.5 M UNH – 0.3 M HNO_3 – 10^{-5} M I^-) was made 10^{-4} M in the cation under study. The solution was then air sparged at 45°C. at a flow rate corresponding to 575 CFM on a plant scale. Table VII shows the per cent of active iodine removed when Hg^{++}, Cd^{++}, Zn^{++}, Pb^{++} or Bi^{+++} was present in the solution. The data presented show that, of these ions, only mercury has an appreciable retarding effect on the sparging of iodine.

Table VII

REMOVAL OF IODINE FROM SIMULATED DISSOLVER SOLUTION
CONTAINING VARIOUS IODIDE-COMPLEXING CATIONS

Simulated Dissolver Solution: 1.5 M UNH – 0.3 M HNO_3 – 10^{-5} M I^- traced with I^{131} as I^-

Concentration of complexing agent = 10^{-4} M

Sparging temperature = 45°C.

Complexing Ion	Time Sparged, Min.	Active Iodine Removed, %
Hg^{++}	60	0.06
Cd^{++}	60	57.0
Zn^{++}	30	61.3
Pb^{++}	30	67.6
Bi^{+++}	40	69.4
None-control	60	77.0

For any procedure involving retention of active iodine in solution to be successful in preventing contamination of the canyon air, it must insure that iodine is not volatilized in any succeeding plant operation. Although actual sparging is done only in storage cells (to insure proper mixing of successive

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dissolver cuts), all solution transfers are by steam jetting. These jetting operations may represent a certain amount of sparging. The degree to which iodine is removed from simulated dissolver solution containing 10^{-4} M $Hg(NO_3)_2$ by air sparging after each process step from dissolution to the bismuth phosphate extraction was studied. Table VIII shows the iodine removed at each step when the iodine was added to the initial dissolver solution as I^-, I_2 or IO_3^-. These results indicate that, even with sparging considerably more extreme than would be encountered under actual plant conditions, a negligible amount of iodine originally present as I^- and small amounts originally present as I_2 and IO_3^- are likely to escape from the solution between the conclusion of dissolving and the extraction step if mercuric ion is present.

Assuming that the escape of iodine from dissolver solution is small prior to the extraction step it is then desirable that the iodine not be carried on bismuth phosphate in order that it can be removed in the metal waste. To check this point, the extraction procedure was performed on each of the three solutions resulting from the studies reported in Table VIII. In the case where the iodine was added to the dissolver solution as I^-, about 10 per cent of the iodine was carried by the bismuth phosphate; for iodine added initially as I_2, two per cent and as IO_3^-, three per cent was carried. Since some iodine does follow the bismuth phosphate it will be desirable to determine the behavior of the iodine during a bismuth phosphate by-product precipitation.

These experiments will be repeated omitting the mercury to determine how much of the iodine behavior noted may be ascribed to the presence of mercury. The results so far obtained are sufficiently promising to warrant investigation of the effects which the presence of mercury in the feed may have on the TBP process. The fate of iodine when complexed by mercury in dissolver solution prepared for Redox is also being considered.

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Table VIII

EVOLUTION OF IODINE ON SPARGING PRE-EXTRACTION SOLUTIONS

Sparging rate = 8.5 cc/m/ml = 575 CFM plant scale
Hg $\underline{M} = 10^{-4}$
I $\underline{M} = 10^{-5}$ inert. Traced with I^{131}

Tank	Composition of Solution	Sparging Time, Min.			% I^{131} Removed		
		I^-	I_2	IO_3^-	I^-	I_2	IO_3^-
Dissolver	1.52 $\underline{M}$ UNH 0.31 $\underline{M}$ HNO_3	90	60	180		2.3	0.7
Dissolver	Wash water	30	30	30		0.0	0.1
4-8	1.05 $\underline{M}$ UNH 0.215 $\underline{M}$ HNO_3	30	30	60		0.2	0.3
4-8	1.02 $\underline{M}$ UNH 0.209 $\underline{M}$ HNO_3 0.99 $\underline{M}$ H_2SO_4	30	40	40		1.9	0.1
6-3	0.6 $\underline{M}$ UNH 0.13 $\underline{M}$ HNO_3 0.88 $\underline{M}$ H_2SO_4	30	30	30		0.9	0.04
6-3	0.58 $\underline{M}$ UNH 0.126 $\underline{M}$ HNO_3 0.56 $\underline{M}$ H_2SO_4 0.115 $\underline{M}$ $NaNO_2$	30	30	30		1.7	0.5
				Total:	0.5	7.0	1.7

C. VARIATIONS IN THE CONCENTRATION CYCLE (H. L. Brandt)

Efforts to combine the bismuth phosphate and lanthanum fluoride by-product precipitation steps of the concentration process have not been successful. In the three runs shown in Table IX, the current flowsheet was followed except that the lanthanum fluoride by-product precipitation was made without removing the bismuth phosphate by-product precipitate.

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Table IX

PLUTONIUM LOSSES IN THE CONCENTRATION PROCESS

	% Plutonium Loss		
	Run I	Run II	Run III
Combined $BiPO_4$ and LaF_3 cake after rework	2.92	1.53	0.09*
Rework solution	0.12	0.16	
LaF_3 product cake	97.65	96.2	103.13
Supernatant from LaF_3 product precipitation	7.32	4.39	11.51

* Cake not reworked

As the data show, plutonium losses to the combined by-product precipitates have been of the same magnitude as those to the lanthanum fluoride by-product cake in the plant, but efforts to recover this plutonium by the rework procedure currently in plant use have failed. The high and erratic losses in the subsequent lanthanum fluoride product precipitation are difficult to explain since the combining of the two by-product precipitations makes very little change in the composition of the solution which proceeds to the product precipitation.

For the immediate future, efforts will be centered on altering the rework procedure to make it effective in recovering plutonium from the combined by-product cakes.

III. TRIBUTYL PHOSPHATE EXTRACTION STUDIES

A. EFFECT OF ALUMINUM NITRATE ON PLUTONIUM(IV) EXTRACTION (R. L. Moore)

Extraction studies previously reported (HW-18646) showed that very high uranium distribution ratios are obtained when $Al(NO_3)_3$ is substituted for HNO_3 as salting agent in TBP extractions. A distribution coefficient, E_a^o, of nearly

10,000 was obtained for uranyl nitrate from 1.8 M $Al(NO_3)_3$ into 12 1/2 volume per cent TBP-CCl_4 compared to an E_a^o of only eight from HNO_3 of the same total nitrate concentration. In view of these results it seemed worth while to determine whether or not plutonium(IV) behaves similarly. It was anticipated that such data may prove valuable in connection with the recovery of plutonium from slag and crucible material as well as in designing a plutonium second cycle in a Purex-type process, particularly if fluoride complexing agents are employed in the partition column.

The data so far obtained are presented in Table X. It will be noted that the distribution coefficients approach or exceed values of 1,000 for $Al(NO_3)_3$ concentrations of 1.5 M in the case of 30% TBP or 2.0 M for 10% TBP. In actuality, the numbers may be substantially larger since part of the activity remaining in the aqueous phase may be due to americium. Analyses for americium in the aqueous phase are as yet incomplete.

When the distribution coefficients of Table X are plotted versus the total aqueous nitrate concentration (on a log-log scale), the 10 and 30% data are found to lie on very nearly parallel curves which have an average slope of about four for total nitrate concentrations ranging from one to six molar. The displacement between the curves corresponds to a ratio of about ten (or approximately three squared) for the distribution coefficients into 10 and 30% TBP from solutions of the same nitrate concentration. These properties of the curves might be interpreted as indicating a fourth power nitrate and second power TBP dependence for the extraction of plutonium(IV). However, it should be pointed out that failure to maintain a constant ionic strength renders such an analysis questionable.

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Table X

DISTRIBUTION BEHAVIOR OF PLUTONIUM(IV) AS A FUNCTION OF ALUMINUM NITRATE CONCENTRATION

Aqueous: 0.3 M HNO_3
Indicated $Al(NO_3)_3$
ca. 17 µg/ml Pu(IV) tracer

Organic: Indicated TBP-CCl_4

Temperature = 25.0°C.

$Al(NO_3)_3$ M	Total Nitrate M	E_a^o for Pu(IV)	
		10 Vol.% TBP	30 Vol.% TBP
0	0.3	0.0078	0.1
0.25	1.05	0.10	1.69
0.5	1.8	0.72	8.8
1.0	3.3	7.7	138
1.5	4.8	127	1192
2.0	6.3	976	7075

IV. TRIBUTYL PHOSPHATE METAL RECOVERY PROCESS STUDIES (C. M. Slansky, Group Leader)

A. BUTYL ACID PHOSPHATE CHEMISTRY (R. M. Wagner)

The hydrolysis of tributyl phosphate is pertinent in the metal recovery process since certain of the products of hydrolysis can cause poor fission product decontamination and also high uranium losses. The hydrolysis is expected to go through the series: TBP $\longrightarrow$ DBP $\longrightarrow$ MBP $\longrightarrow$ H_3PO_4. Because of the analytical difficulties involved, the hydrolysis has been studied by starting at the end of the chain of reactions. The rate of hydrolysis of DBP and MBP in 3 M HNO_3 has been described (HW-18880 and HW-19503) with half lives at 76°C. of 7.9 and 18 days, respectively. The temperature dependence of MBP hydrolysis leads to a calculated ΔH of hydrolysis of 11,500 cal/mole which is comparable to the ΔH of hydrolysis of methyl acetate. The hydrolysis of MBP in 3 M HNO_3 can be summarized as follows:

Temp., °C.	K, day^{-1}	$T_{1/2}$, days
25	0.0022	315
76	0.0385	18

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The reaction in a two phase system of equal volumes of TBP and 3 M HNO_3 was followed for 25 days by measurement of the free $PO_4^{\equiv}$ in the aqueous phase and the titratable acid to the second break of H_3PO_4. The titratable acid was found equivalent to the free $PO_4^{\equiv}$ which indicates that any MBP found decomposed at a rate rapid in comparison to its rate of formation.

A temperature of 76°C. was used in these experiments in order to get measureable decomposition although plant-wise the temperature is not expected to exceed 35-40°C. The results are given in the following table:

Table XI

Time, days	% TBP Decomposed
8	0.00
9	0.07
16	0.28
19	0.49
25	0.74

From these data a linear plot of time versus per cent decomposed was obtained which had a slope of 4.35×10^{-2} %/day, following an induction period of eight days. This rate is a factor of 100 slower than the hydrolysis rate of DBP or MBP, indicating that the first step in the hydrolysis of TBP, i.e., TBP $\longrightarrow$ DBP, is rate-determining.

Experimental conditions in this study involved a daily stirring. In a column with better mixing the rate of decomposition would perhaps be slightly higher than observed here and in storage tanks it would be lower.

Further purification of butyl acid phosphates has led to revised values for some of the physical properties. In the accompanying table are listed the density and viscosity at 25°C. of TBP, DBP, and MBP. A plot of apparent molar volume versus number of butyl groups is linear and gives a value of 74 ml/mole of C_4H_9.

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Table XII

DENSITY AND VISCOSITY AT 25°C. OF BUTYL ACID PHOSPHATES

	ρ^{25}_{4}	η^{25}_{4} (millipoises)
TBP	0.9760	33
DBP	1.0650	520
MBP	1.2190	4260
H_3PO_4	1.8700	--

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