Photostat Price \$ 4.80

Microfilm Price \$ 2.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

THE STABILITY OF PUREX SOLVENT TO
RADIATION AND CHEMICAL ATTACK

By

J. L. Swanson

Chemical Separations Unit
Chemical Research Sub-Section

May 24, 1955

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the
General Electric Company under Contract # W-31-109-Eng-52

Declassified With Deletions: August 25, 1959

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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE STABILITY OF PUREX SOLVENT TO
RADIATION AND CHEMICAL ATTACK

I. INTRODUCTION

In a previous document⁽¹⁾ it was reported that chemical attack on hydrocarbon diluents for tributyl phosphate (TBP) results in the formation of substances deleterious to plant operation. These substances cause increases in uranium distribution coefficients under dilute "C" column conditions, increases in coalescence times, lowering of the rate of uranium extraction, decrease in dispersion time, enhanced fission product retention by the solvent, and enhanced foaming during the course of UNH calcination.

The work to be reported here was done in an effort to determine more precisely the influence of the different variables which affect the rate of solvent deterioration due to chemical action as well as to study solvent deterioration as a function of radiation dosage. The sole interest in this study has been in those products of deterioration which are not removable by carbonate washing and hence might be expected to build up in the solvent over a number of cycles.

II. SUMMARY AND CONCLUSIONS

(1) The rate of solvent deterioration due to chemical action in systems representative of those to be found in the Purex plant was studied as a function of the variables involved. The rate of deterioration was found to be directly proportional to the concentration of acid, directly proportional to the concentration of nitrate ion, and proportional to the square root of the concentration of nitrite ion. These observations can be expressed as the rate law

$$dE_a^0/dt = K (H^+) (NO_3^-) (NO_2^-)^{0.5}$$

SECRET

DECLASSIFIED

where dE_a^0/dt is the rate at which the $^{99}C^{00}$ contact extraction coefficient increases as a function of time and the concentrations of reactants are those present in the aqueous phase before equilibration.

(2) The rate of solvent deterioration due to chemical action was found to double for each 5 C temperature increase.

(3) Soltrol 170 diluent was found to resist chemical attack a factor of two better than Shell E-2342 diluent. The stability of Ultrasene was found to be about the same as that of Shell E-2342, and the stabilities of Bayol D and Amsco 125-90W were found to be about the same as that of Soltrol 170.

(4) Radiation was found to produce no appreciable solvent deterioration until the solvent had received a dose of 20 watt-hr/liter.

The deterioration

occurring between 20 and 200 watt-hr/liter was found to be due to the action of radiation on TBP rather than the diluent. Somewhere between 200 and 400 watt-hr/liter damage to the diluent begins to produce serious deleterious effects.

(5) The above conclusions, plus certain estimates and assumptions given in the discussion, allow a calculation of the equilibrium level of the solvent deterioration products in the Purex plant. With the plant operating at 60 C under HW No. 3 Flowsheet conditions with Soltrol 170 as diluent, this level should not be high enough to hinder plant operation. With the same flowsheet and diluent at 70 C, however, the level of the deterioration products would exceed that necessary to hinder plant operation.

(6) Of the tests of solvent quality employed in this work, the $^{99}C^{00}$ contact extraction coefficient test was found to be best for studying solvent quality as a function of chemical or radiation damage.

III. EXPERIMENTAL AND RESULTS

A. Chemical Damage

These experiments were performed by contacting equal volumes of carbonate washed organic (30% TBP-diluent) and aqueous phases in a constant temperature bath. The solutions were contained in taped flasks to exclude light. Samples were withdrawn at intervals and, after washing with water and sodium carbonate, were subjected to the various quality tests described in the Appendix.

The conclusions drawn from these experiments are based on the "C" contact extraction coefficient measurements. These extraction coefficients were found to increase linearly as a function of time in the time range studied (up to 150 hours) during the course of the reaction, thus giving a simple relationship for the rate of solvent deterioration, dE_a^0/dt .

When it was desired to determine the dependence of the rate of deterioration on a given variable, a series of experiments was done in which all variables but the one of interest were held constant. Under these conditions, $dE_a^0/dt = K (V)^n$; that is, the rate of deterioration is equal to a constant times the concentration of the variable raised to some power. Taking logarithms of both sides of the equation, $\log dE_a^0/dt = \log K + n \log (V)$. Thus a plot of $\log dE_a^0/dt$ as a function of $\log (V)$ gives a straight line having a slope equal to n , the dependence of the rate of solvent deterioration on the variable in question.

1. Comparison of Diluents

Various 30% TBP-diluent mixtures were contacted at 50 C with an aqueous phase containing 0.09 M UNH, 5.2 M HNO₃, and 0.02 M NaNO₂.

SECRET

- 5 - 003

DECLASSIFIED

The diluents tested were Shell Spray Base, Ultrasene, Shell E-2342, Bayol D, Soltrol 170, and Amsco 125-90W.

Besides the experiments in which the same two phases were shaken together during the entire experiment, some experiments were done in which the entire organic phase was periodically (twice a day) stripped with water and sodium carbonate and then returned to the experiment with a fresh aqueous phase of the same composition. This latter procedure more closely approximates that which would be found in plant operation, where the solvent is carbonate washed after each pass through the plant.

The results of the experiments in which the organic phase was not periodically stripped are shown in Figures 1A and 1B. The slopes of these lines are presented in Table I along with the slopes obtained in the experiments where the organic phase was stripped periodically between samplings.

It is seen that Soltrol 170, Bayol D, and Amsco 125-90W are equally resistant to chemical attack and are more resistant than Ultrasene and Shell E-2342 by a factor of about two. Shell Spray Base is unique in that it is the worst of the lot when shaken continuously with the same aqueous phase but is as good as any when it is stripped periodically. This observation implies that secondary reactions result in the bad solvent obtained with Spray Base, the products of the primary reactions being removable by carbonate washing.

2. Effect of Nitrite Ion Concentration on Rate of Solvent Deterioration

It has been shown⁽¹⁾ that the presence of nitrite ion accelerates the rate of solvent deterioration. In order to define this effect of nitrite ion a series of six experiments was performed in which 30% TBP-Soltrol 170 was contacted at 50 C with aqueous phases containing concentrations of nitrite ion ranging from zero to 0.10 M. The aqueous phase also contained 0.09 M UNH and 5.2 M HNO₃ in all cases.

The results of these experiments are presented in Table II. The large uncertainty in some of the slopes was due to the difficulty in measuring such low rates of deterioration. In Figure 2 the logarithm of dE_a^0/dt is plotted as a function of the logarithm of the concentration of nitrite ion present in the aqueous phase initially. It is seen that the experimental values are fit by a line having a slope of one-half, indicating that the rate of solvent deterioration is dependent on the square root of the concentration of nitrite ion.

3. Effects of Acid, Nitrate, and Uranium Concentrations on Rate of Solvent Deterioration

Although the concentrations of acid and of nitrate ion are variables which are quite firmly fixed for the Purex plant, a knowledge of their effects on the rate of solvent deterioration was felt to be desirable to enable a prediction of the rate of deterioration under varying conditions.

A series of experiments was performed in which 30% TBP-Spray Base was contacted at 50 C with aqueous phases containing 0.02 M NaNO_2 as well as uranium, nitric acid, and, in one case, sodium nitrate. The concentrations used and results obtained in these experiments are presented in Table III. In Figure 3 the results are presented graphically, the logarithm of dE_a^0/dt being plotted as a function of the logarithm of the product of acid and nitrate concentrations present in the aqueous phase initially. It is seen that the experimental points are fit by a line having a slope of one, indicating that the rate of solvent deterioration is dependent on the first power of the product of acid and nitrate concentrations in the aqueous phase initially. The same dependence was observed whether the concentrations used were those in the aqueous phase initially or at equilibrium. From this correlation, it is apparent that, for a given nitrate salting strength, the solvent deteriorates slower when the cation is some ion other than hydrogen.

The fact that the above correlation was made with experiments having uranium concentrations of from zero to 0.6 M in the aqueous phase initially shows that uranium has no appreciable effect on the rate of solvent deterioration.

4. Rate Law for Solvent Deterioration

From the measured dependencies of the rate of solvent deterioration, the rate law for the deterioration of 30% TBP-diluent in nitrate systems can be expressed as:

$$dE_a^0/dt = K (H^+) (NO_3^-) (NO_2^-)^{0.5}$$

where dE_a^0/dt is the rate of increase in $^{100}C^{100}$ contact extraction coefficient as a function of time and the concentrations used are those present in the aqueous phase before equilibration. The concentration ranges over which this law was found to hold were 2.2 to 6.5 M acid, 2.8 to 6.5 M nitrate, and 0.005 to 0.1 M nitrite.

Values of K for different diluents and temperatures are given in Table IV. In those cases where several experiments were done with a certain diluent at a given temperature, the average value recorded in the table was within twenty per cent of the most probable value calculated from any one experiment done under those conditions.

5. Effect of Temperature on Rate of Solvent Deterioration

Since it is not known at what temperature the Purex process will be run, it was desirable to determine the effect of temperature on the rate of solvent deterioration. The K values for different temperatures presented in Table IV allow a calculation of this effect. In each comparison it was found that K, and therefore the rate of solvent deterioration for a given diluent at specified concentrations, doubles for each five degree centigrade temperature increase.

B. Radiation Damage

These experiments were performed by exposing the samples to gamma radiation in the 100-F Area pile basin. The radiation intensity measurements and dosage calculations were made by members of the Special Irradiations Unit. The radiation dosages calculated from these ion chamber measurements were within twenty per cent of those measured by dosimeter solutions.⁽³⁾

The irradiations of the 30% TBP-hydrocarbon diluent mixtures were performed in four different ways to test the effects of different variables on the gross damage to the solvent in the radiation field. These ways were 1) carbonate-washed solvent at ambient temperature (10 - 20 C); 2) solvent containing uranium and nitric acid at ambient temperature, but not in contact with an aqueous phase during irradiation; 3) solvent in contact with an aqueous phase containing uranium and nitric acid at ambient temperature; and 4) solvent in contact with an aqueous phase containing uranium and nitric acid at 50 C. The diluents whose stabilities were tested in the radiation field were Shell Spray Base, Shell E-2342, Ultrasene, Bayol D, Soltrol 170, and Amsco 125-90W.

The vast majority of the ^{235}U contact extraction coefficient values obtained when irradiating 30% TBP-diluent fell within experimental error of one of two straight lines when the extraction coefficient values were plotted as a function of the logarithm of the dose in the range 5×10^6 to 5×10^7 R. These extraction coefficient values were corrected to measure radiation effects by subtracting the value which would have resulted under the same conditions in the absence of radiation from the experimentally determined value. These numbers are plotted in Figure 4.

The lower line was fit by all the experiments done at ambient temperature and also by the experiments done at 50 C when the diluent was Soltrol 170, Bayol D, or Amsco 125-90W. That the solvent deterioration represented by this line is due to damage to TBP rather than to the

diluent was shown by two additional observations. When Soltrol 170 was irradiated to 3×10^7 R and then made to 30% TBP with pure TBP, the resulting $^{100}\text{C}^{100}$ contact extraction coefficient was the same as that obtained with pure TBP and unirradiated diluent. When TBP was irradiated to 1×10^8 R and then made to 30% TBP with pure diluent, the resulting $^{100}\text{C}^{100}$ contact extraction coefficient ⁽³⁾ fell on an extrapolation of the line obtained by irradiating 30% TBP-diluent up to 5×10^7 R. However, 30% TBP-diluent mixtures irradiated to 1×10^8 R gave exceedingly high extraction coefficients, indicating that somewhere between 5×10^7 and 1×10^8 R damage to the diluent becomes important. Diluents in which this effect was observed were Spray Base, Soltrol 170, and iso-octane.

The upper line was fit only by the experiments done at 50 C when the diluent was Shell Spray Base. Experiments in which the irradiation and contact with aqueous phase were done separately showed the greater slope of this line to be due to chemical attack on substances formed by the radiation. Carbonate-washed 30% TBP-Spray Base was irradiated to 5×10^7 R and then divided into two portions, one of which was carbonate-washed again. These two portions were then contacted at 50 C with an aqueous phase containing nitric and nitrous acids. In the experiment employing the solvent which had not been washed after irradiation, the solvent deteriorated about thirty times as fast as unirradiated solvent. The solvent which had been washed after irradiation deteriorated at the normal rate, showing that the highly reactive substances formed by the radiation had been removed by the carbonate wash. Similar experiments employing Soltrol 170 as diluent gave normal rates of deterioration whether the solvent was carbonate-washed after irradiation or not.

When 30% TBP-Ultrasene was irradiated while in contact with nitric acid at 50 C, the resulting extraction coefficient fell about half way between the two lines shown in Figure 4, suggesting that a line having an intermediate slope would have been obtained if more experiments had been done

using this diluent under these conditions. Two experiments under the same conditions were attempted with Shell E-2342 as diluent but were unsuccessful due to mechanical failure.

Since the "C" contact extraction coefficient values were so low at 5×10^6 R, it is apparent from the relationship $1 R = 5.1 \times 10^{-6} d \text{ watt-hr/liter}$, where d is the density of the liquid being irradiated, that solvent deterioration due to radiation does not become important until the solvent has absorbed about 20 watt-hr/liter of energy.

IV. DISCUSSION

Before any conclusions can be drawn concerning how much solvent deterioration will occur in the Purex plant or to how high a level the products of deterioration will build up, it is necessary to make certain estimates. These include average solvent lifetime, radiation dose received by the solvent in one pass, and in what manner the solvent is lost.

the average solvent molecule was estimated to make 200 passes through the HA column and an equal number through the IA column. At a solvent hold-up time in the uranium extraction columns of 7.5 minutes (2.5 minutes in the extraction section and five minutes in the scrub section), this corresponds to 50 hours in contact with two to five molar nitric acid for the average solvent molecule in the HA-IA solvent system.

SECRET

DECLASSIFIED

The radiation dose received by the solvent in one pass was estimated by assuming: (1) HW No. 3 Flowsheet flows and conditions; (2) a 2.5 minute solvent hold-up time in the extraction section of the HA column; (3) all the energy from fission product radiation is absorbed by the liquid in the column; and, (4) the fraction of energy absorbed by the solvent is equal to the fraction of the volume occupied by the solvent (18 per cent). It should be emphasized that these assumptions are slanted to give a high, rather than low, value for the dose received in one pass.

The manner in which the solvent is lost is of importance in that it determines whether or not the products of deterioration build up in the plant to an amount greater than that formed during the solvent lifetime. Solvent losses due to entrainment lead to no build up as the deterioration products are lost along with the solvent. Solvent losses due to solubility in the aqueous phase would lead to the build up of the deterioration products if the products have higher distribution coefficients than do TBP and the diluent. Assuming the aqueous streams contain one tenth of one per cent organic phase due to entrainment, the solvent loss due to entrainment would be at least four times as great as that due to solubility.

Assuming that there is no build up of deterioration products beyond the amount formed in the average solvent lifetime and using the estimates of solvent lifetime and radiation dosage to the solvent per pass it is apparent that there will be no appreciable solvent deterioration caused by radiation.

Using the estimate of solvent lifetime, the rate law for solvent deterioration due to chemical action, the average concentrations of uranium and nitric acid throughout the column⁽²⁾, and an estimate of how nitrite ion is distributed in the column, it is possible to calculate values of the K_{C^0} contact extraction coefficient of the solvent for various conditions. In Table V are presented the results of such calculations for the Purex plant operating under HW No. 3 Flowsheet conditions at different temperatures with Soltrol 170 as diluent. These calculations were carried out assuming that nitrous acid does not extract and hence is only in the extraction section of the column. If nitrous acid does extract and thus enter the scrub section, the numbers given in Table V are too low by as much as fifty per cent.

On the basis that a K_{C^0} contact extraction coefficient value of 0.02 results in operating difficulties in the plant (see Appendix), it is seen that such difficulties would arise within one solvent lifetime in the Purex plant operating at 70 C.

It should be emphasized that these estimates of how high a level the deterioration products will reach in the plant are conservative on the basis of the estimated solvent lifetime. These estimates tacitly assume that the solvent will not come in contact with extraneous materials which could yield harmful impurities to the solvent and that the solvent stays where it belongs and does not get into such places as feed tanks and intercycle concentrators where it can be severely damaged and then returned to the process. In addition, if the deterioration products are not lost due to solubility in the aqueous phase, the level of these products will build up beyond that formed in one solvent lifetime.

Another point worthy of emphasis is that in the absence of nitrite ion the rate of solvent deterioration is greatly lowered, thus allowing safe operation at the higher temperature.

V. APPENDIXA. Tests of Solvent Quality

The products of solvent deterioration are so varied and are present in such low concentrations that even a determination of their compound classes and a rough estimate of their concentration in the solvent is a very tedious process.⁽⁵⁾

For this reason the only practical method of following solvent deterioration is to measure the magnitude of the effect, rather than the amount and type, of the deterioration products. The tests employed in this work were those which could be performed in the laboratory with relative ease and speed and yet measure effects which might be expected to have importance from the standpoint of plant operation. As has been stated in the text, the organic samples were carbonate washed before being subjected to these tests.

I. "C" Contact Extraction Coefficient

The organic phase (30% TBP-diluent) was contacted with an equal volume aqueous phase containing 1.0 g/1 U (as UNH) in water. The organic phase was then analyzed for uranium and the extraction coefficient calculated. Duplicate determinations usually agreed to within thirty per cent. When using pure TBP and unused diluent the extraction coefficient was found to be about 0.005. Experience in the Uranium Recovery Plant has shown that operating difficulties arise when this extraction coefficient is in the region of 0.02.

Of the tests employed in this work, the "C" contact extraction coefficient measurement was found to be the most useful. It is quite sensitive, thus showing measurable changes before other tests, and varies over a wide range, thus allowing more meaningful comparisons of samples.

SECRET

15 012

DECLASSIFIED

The tables and figures referred to throughout the text of this report contain examples of the comparisons of solvent quality and the conclusions which can be made on the basis of this test.

II. Rate of Uranium Extraction

This test was done in an apparatus which automatically performed a series of contactings and analyses on each sample. Each contacting was for a time of 0.0265 minutes and the analyses were made photometrically, light transmission through the aqueous phase being a measure of the uranium concentration in that phase. From the known contact times and concentration after each contact, a rate constant for the extraction of uranium was calculated. Since the rate constant for pure carbonate washed solvent was sometimes found to change from day to day, the result for an unknown sample was recorded as R, the ratio of the constant obtained with the unknown sample to the constant obtained with pure solvent on that day.

Preliminary experiments showed this test to be more sensitive at twenty per cent TBP than at thirty per cent and that the sensitivity increased with increasing uranium concentration up to 0.8 to 1.0 M. Thus, equal volumes of 1.00 M UNH in 2.0 M HNO₃ and 20% TBP-diluent were decided upon as the conditions to be used for this test.

In Figure 5 the R values for various samples are shown as a function of their ²³⁵C contact extraction coefficient values. The points shown in this figure are the reported values and do not indicate the experimental uncertainty, which is about ten per cent in the R values and thirty per cent in the extraction coefficient values. It is seen that the R values appear to approach a minimum value of around 0.6, seriously limiting the usefulness of this test in comparing the quality of solvent samples produced during the course of this work.

It should be pointed out that it probably is possible to have impurities in the solvent which would lower the rate of uranium extraction relatively more than they would raise the ^{235}C contact extraction coefficient. In such case the extraction rate test would be a better indication of solvent quality than the extraction coefficient test. The work reported here indicates that such substances are not produced by chemical or radiation damage to the solvent.

III. Dispersion - Coalescence Time Test

Twelve point five (12.5) ml of the organic sample was added to an equal volume aqueous phase 0.75 M in UNH and 2.0 M in HNO_3 contained in a 25 ml graduated cylinder. The phases were mixed with a reciprocating perforated plate stirrer operated at 60 strokes per minute with a nine cm stroke length. The time required for a packed dispersion to build up to the 21 ml mark was taken as the dispersion time. The phases were then agitated for an additional 30 seconds, the stirrer stopped, and the time required for the appearance of any part of a clear interface taken as the coalescence time.

These tests were run on only a few samples as it soon became apparent that they were not sufficiently sensitive to be useful in this work. In Table VI are listed the results which were obtained on different samples along with the ^{235}C contact extraction coefficient values. The results, expressed as the ratio of the result of the test using the unknown sample to the result using pure solvent, show very plainly that the ^{235}C contact extraction coefficient test is a much more sensitive test of solvent quality than is the dispersion-coalescence times test. It is recognized that satisfactory disengaging and coalescence times are a requisite for good column operation, even though the tests were relatively insensitive to changes produced by chemical and radiation attack as reported here.

IV. Decontamination and Fission Product Retention Measurements

One volume of solvent (30% TBP-diluent) was contacted with 0.45 volume of HAFS solution (230 g/l U, 4.0 M HNO_3), scrubbed twice with one-sixth volume of 3.0 M HNO_3 , stripped twice with two volumes of 0.03 M HNO_3 , and washed with an equal volume of 0.5 M Na_2CO_3 . These concentrations and volume ratios were chosen to give operating concentrations after equilibration.

It was realized from the outset that this test was too tedious to be applied to more than a selected few samples - the main point of interest being to see if any decreased decontamination or increased fission product retention in the solvent resulted from solvent samples which had been exposed to chemical or radiation attack in excess of that to be expected in the Purex plant.

In Table VII the results of these tests are tabulated. It is seen that decontamination did not decrease to unacceptable values; although the amount of activity retained in the solvent increased as a function of solvent damage. However, this increased retention was appreciable only after the solvent had been damaged more severely than is anticipated in the Purex plant.

It should be emphasized that these were equilibrium type experiments and hence would not show any differences in rate of extraction or scrubbing. In addition, since the phases were separated by centrifugation after each contacting, these experiments would not show effects caused by increased entrainment in the organic phase.

JLS:jw

J. L. Swanson

SECRET

15
DECLASSIFIED

REFERENCES

- (1) Moore, R. H., "Chemical Stability of Purex and Uranium Recovery Process Solvent," HW-34501, (Secret), February 1955.
- (2) Reas, W. H., "Quarterly Report - Chemistry Unit - April, May, June 1954," HW-32781, p. 11.
- (3) McClanahan, E. D., Jr., private communication.
- (4) Hopkins, H. H., Jr., private communication.
- (5) Moore, R. H., "Investigation of Solvent Degradation Products in Recycled Uranium Recovery Plant Solvent," HW-34502, (Secret), February 1955.

SECRET115 016
DECLASSIFIED

TABLE I
RATE OF SOLVENT DETERIORATION AS A FUNCTION OF THE DILUENT

30% TBP-diluent contacted at 50 C with aqueous phase
containing 0.09 M UNH, 5.2 M HNO₃, 0.02 M NaNO₂

<u>Diluent</u>	<u>$dE_a^o/dt \times 10^4$ (1)</u>	<u>$dE_a^o/dt \times 10^4$ (2)</u>
Shell Spray Base	7.4 hr ⁻¹	1.8 hr ⁻¹
Ultrasene	3.5	3.6
Shell E-2342	3.5	3.7
Bayol D	2.0	---
Soltrol 170	1.5	1.9
Amsco 125-90W	1.4	---

- (1) Same two phases contacted throughout the experiment.
- (2) Organic phase carbonate washed periodically and returned with a fresh aqueous phase.

TABLE II

DEPENDENCE OF RATE
CONCENTRATION

30% TBP-Spray Base c
containing 0.02 M NaNO₂

Concentrations are those
before equilibration

<u>(H⁺)</u>	<u>(UNH)</u>
2.6 M	0.09 M
2.6 ⁽¹⁾	--
3.9	--
3.5	0.57
5.2	0.09
5.2	0.57
6.5	--

(1) Also contained 2.6 M NaNO₂

DEPENDENCE OF RATE OF SOLVENT DETERIORATION ON
NITRITE CONCENTRATION

30% TBP-Soltrol contacted at 50 C with 0.09 M UNH + 5.2 M
HNO₃ + various concentrations of sodium nitrite

<u>(NaNO₂)</u>	<u>dE_a⁰/dt x 10⁴</u>
zero ⁽¹⁾	0.0 → 0.5 hr ⁻¹
0.005 M	0.3 → 0.8
0.010	0.4 → 1.5
0.020	1.1 → 1.8
0.050	1.9 → 3.0
0.10	1.5 → 3.4

(1) Assured by presence of urea.

TABLE IV

VALUES OF K FOR DIFFERENT DILUENTS AND TEMPERATURES

$$K = \frac{dE_a^0/dt}{(H^+) (NO_3^-) (NO_2^-)^{0.5}}$$

dE_a^0/dt = rate of increase of "C" contact extraction coefficient as a function of time (hours)

Concentrations are those in aqueous phase before equilibration (in moles/liter)

<u>Diluent</u>	K at 10^4 at		
	<u>35 C</u>	<u>50 C</u>	<u>70 C</u>
Shell Spray Base	0.22	1.9*	--
Ultrasene	--	0.91	--
Shell E-2342	--	0.86	--
Bayol D	--	0.49	--
Soltrol 170	--	0.33*	5.2*
Amsco 125-90W	--	0.34	--

*Average of several experiments.

TABLE VESTIMATE OF DEGREE OF SOLVENT DETERIORATION AFTER
ONE SOLVENT LIFETIME IN THE HA-IA PUREX SOLVENT SYSTEM

HW No. 3 Flowsheet conditions, Soltrol 170 as diluent,
nitrous acid in the extraction section only

<u>Temperature of Operation</u>	<u>"C" Contact E_a</u>
50 C	0.006
60	0.009
70	0.021

TABLE VICOMPARISON OF SENSITIVITY OF DISPERSION-COALESCENCE TIME
TEST AND "C" CONTACT EXTRACTION COEFFICIENT TEST

Expressed as ratio of result obtained with unknown sample to
result using pure solvent

For pure solvent, $dt = 58 \text{ sec}$, $ct = 58 \text{ sec}$, $E_a^0 = 0.005$

<u>Dispersion Time</u>	<u>Coalescence Time</u>	<u>E_a^0</u>
0.6	1.2	18
0.4	2.7	16
0.8	3.3	7
0.9	1.2	10
0.2	2.5	12
0.6	1.0	20
0.9	1.2	17
0.9	0.8	7
0.8	1.6	4
1.0	1.3	4
1.0	0.9	9

TABLE VII

DECONTAMINATION AND FISSION PRODUCT RETENTION
MEASUREMENTS AS A FUNCTION OF SOLVENT DAMAGE

30% TBP-Soltrol 170

A. Contacted at 50 C with aqueous phase containing
 0.09 M UNH + 5.2 M HNO₃ + 0.02 M NaNO₂

B. Exposed to radiation

	<u>Chemical Attack</u> hours	<u>log dF</u>		<u>c/m/ml x 10⁻³ carbonate- washed sample</u>	
		Beta	Gamma	Beta	Gamma
A	0	4.84	4.06	0.6	0.6
	28	4.50	3.90	1.6	1.0
	70	3.83	3.89	2.6	1.8
	114	4.69	3.81	3.9	5.8
<u>Radiation Dose</u>					
	<u>R</u>				
B	1.3 x 10 ⁷	4.78	4.21	2.9	4.4
	3.5 x 10 ⁷	5.00	4.59	4.4	11.2

SECRET

105 323

REF ID: A79177

FIGURE 1A

RATE OF SOLVENT DETERIORATION
AS A FUNCTION OF THE DILUENT

30% TBP - diluent contacted at 50C with
0.09M UNH + 5.2M HNO₃ + 0.02M NaNO₂

FIGURE 1B

RATE OF SOLVENT DETERIORATION
AS A FUNCTION OF THE DILUENT

30% TBP - diluent contacted
at 50C with 0.09M UNH + 5.2 M HNO₃ + 0.02M NaNO₂

FIGURE 2

DEPENDENCE OF RATE OF SOLVENT DETERIORATION
ON NITRATE CONCENTRATION

30% TBP - Soltrol contacted at 50C with 0.09M UNH + 5.2M HNO₃

dE_a^0/dt = rate of increase in "C" contact extraction coefficient
 as a function of time (hours)

Concentration = molarity in aqueous phase before equilibration

FIGURE 3

DEPENDENCE OF RATE OF DETERIORATION ON (H^+) AND (NO_3^-)

30% TBP - Spray Base contacted at 50C with aqueous phase containing 0.02M $NaNO_2$ and varying amounts of acid, uranium, and nitrate

dE_a^0/dt = rate of increase in "C" contact extraction coefficient as a function of time (hours)

Concentration = molarities in aqueous phase before equilibration

FIGURE 4

SOLVENT DETERIORATION AS A FUNCTION OF RADIATION DOSE

30% TBP - diluent exposed to gamma radiation

Δ 30% TBP - Soltrol 170, Bayol D, Amsco 125 - 90W, Shell E-2342, Ultrasene, or Shell Spray Base at ambient temperature, whether in contact with nitric acid or not. 30%TBP-Soltrol 170, Bayol D, or Amsco 125-90W at 50C while in contact with nitric acid.

$\circ$ 30% TBP - Spray Base at 50C while in contact with nitric acid.

FIGURE 5

RATE OF URANIUM EXTRACTION AS A FUNCTION
OF "C" CONTACT EXTRACTION COEFFICIENT

○ = Chemical Damage Experiments

▽ = Radiation Damage Experiments