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INVESTIGATION OF SOLVENT DEGRADATION PRODUCTS IN
RECYCLED URANIUM RECOVERY PLANT SOLVENT

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RECYCLED URANIUM RECOVERY PLANT SOLVENT

I. INTRODUCTION

As part of an investigation of solvent stability, a direct analysis of recycled Uranium Recovery Plant solvent* has been made to determine the type, source, and properties of the impurities which have been generated in the solvent and are present in the solvent after it has been in use for some time. This work has been directed towards the separation and identification of the impurities by compound class, and the conclusions are set forth in this report. Another purpose of this report is to present the separation scheme employed, which will likely find similar application.

The separation of solvent impurities was largely effected chromatographically. Infrared spectrophotometry was employed to follow the course of extractive or chromatographic separations and provide simultaneously an identification of components of the fractions obtained. Where possible, specific chemical tests were used to confirm conclusions drawn from the infrared spectra. To evaluate the fractions as regards their effect on the process, uranium distribution measurements were used.

II. SUMMARY AND CONCLUSIONS

(A) Impurities which originate from the diluent and which have been positively identified are:

- (1) Aliphatic** nitro compounds, resulting from nitration by nitric or nitrous acid.
- (2) Aliphatic carboxylic acids, resulting from oxidation reactions of nitric or nitrous acid.

* 20 volume per cent Tributyl phosphate in Shell E-2342 Diluent.

**As used through this report, the term aliphatic includes alicyclic compounds.

- (3) Aliphatic nitroso compounds, produced by the action of nitrous acid on secondary nitro compounds.
- (B) Impurities which originate from the diluent and whose presence are strongly indicated, but which have not been positively identified are:
- (1) Aromatic compounds, probably nitro and nitroso.
 - (2) Ketones or aldehydes which may be intermediates in oxidation reactions leading to carboxylic acid formation.
- (C) Impurities which originate from TBP (tributyl phosphate) are:
- (1) Dibutyl phosphate resulting from hydrolysis of TBP.
 - (2) Tributoxyethyl phosphate, present originally as an impurity in TBP.
 - (3) Two additional phosphorus compounds not specifically identified.
- (D) Uranium distribution measurements on the chromatographically separated fractions show that impurities arising from the diluent are the principal cause of deterioration in solvent quality. The fractions containing phosphate esters were among those having no deleterious effect.
- Separations were not sufficiently complete to evaluate the effect of impurities on an individual basis. Using butyl nitrite and nitropropane as "stand ins" for the nitrite esters and nitro compounds, however, it was shown that nitrite esters may be very deleterious while nitro compounds may be relatively innocuous.
- (E) Of the various impurities found in the recycled RCW sample, only DBP can be predicted to be removed efficiently by the present solvent treatment procedure. However, failure to find more than trivial amounts of material of an aromatic character among the impurities indicates these are removed. It seems probable that a portion of the organic acids and nitroso compounds are also removed.

(F) Products similar, if not identical, to impurities found in recycled Uranium Recovery Plant RCW, can be synthesized by combined nitric and nitrous acid attack on Shell Spray Base* at elevated temperatures.

III. DISCUSSION OF SEPARATIONS

Because of the complexity of the solvent mixture to be examined and the relatively low total concentration of the materials of interest, no single analytical technique is capable of eliciting the information desired. Each individual constituent in the diluent upon chemical reaction with components of the aqueous phase may give rise to several new substances. Since there may be as high as 20,000 separate constituents present in the diluent, the resulting mixture will include these plus several times their number of substances, all present in low concentration. Included within this mixture of impurities arising from the diluent, and the complex diluent itself, is tributylphosphate (TBP). Arising from TBP there will be certain impurities. These may be expected to be comparatively few in number, and one at least is known, dibutylphosphate, i.e., (DBP). This substance was analyzed for separately and removed by aqueous carbonate washing prior to further analysis of the solvent.

Since it is not possible to analyze a mixture of this complexity directly, and since it was desired to test the individual fractions for effects on the separation process, the technique of chromatographic separation was employed to break the mixture down into simpler fractions. Because of the widely different molecular weight range, the individuals of a particular compound class are not concentrated in a narrow band on the column but are diffused over a wide range. This results in considerable overlapping of the various compound classes and requires a high separation efficiency. Multiple chromatographic separations were indicated and were used in this work.

*Shell E-2342 differs chemically from Shell Spray Base in that it is slightly lower in unsaturates and aromatic constituents.

The separations were carried far enough to resolve the impurities arising from TBP completely and to separate these from the bulk of impurities arising from the diluent. The latter were partially resolved. No attempt was made to completely separate these fractions into individual compounds, for even if this were possible, the amount of each individual compound would be too small to permit identification.

The following sections describe the separations employed and the identifications by compound class. In general, it will be seen that the first step was to analyze for and separate DBP, which is easily accomplished with a sodium carbonate wash. Treatments such as solvent extraction and phase-splitting with hydrochloric acid were then tried in an attempt to separate TBP from the impurities. This met with only limited success. More promising, and used in much of this work as a preliminary step to chromatography, was a vacuum distillation which separates the diluent and much of the TBP from the impurities of interest.

The infrared spectra were of utmost value in the chromatography, since they revealed the extent of separation. Since many fractions were shown to require rechromatographing, the infrared technique showed which ones had the same composition and, hence could be combined to provide adequate sample size.

A. Preliminary Examination of RCW

A five gallon sample of used plant solvent (RCW) was taken from TK-17-1 during June 1954, and reserved for this study.

(1) Determination of DBP

Analysis of the RCW sample by Brite's⁽¹⁾ method yielded a value of 136 ppm. Extraction of two liters of this sample with five per cent Na_2CO_3 yielded, after some manipulation, 0.2 ml of an oil which proved to be impure DBP.

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(2) Examination of the Aromatic Hydrocarbons in RCW

One gallon of RCW was split into three phases by treatment with two liters of 12.N HCl. The diluent portion was separated and washed with methanol and water until nearly free of TBP (<0.5 per cent by volume). In this procedure the impurities follow TBP, and the diluent fraction is virtually colorless.

The aromatic portion of this diluent fraction was isolated by chromatography on silica gel and compared with a similar fraction isolated in the same way from a like quantity of "as received" Shell Spray Base. This comparison shows marked differences in the aromatic hydrocarbon content of the diluent before and after use in the process. This suggests that the aromatic hydrocarbons are involved in the reactions which lead to the development of colored impurities in plant RCW.

B. Chromatography on Alumina

J. L. Swanson demonstrated that the impurities in the carbonate washed RCW sample could be concentrated without loss or detectable decomposition by distillation at a pressure of one millimeter of mercury at 90-110 C. This procedure was, therefore, employed as a preliminary step to permit use of a large quantity of starting material which is at once reduced to a satisfactory volume for use on laboratory columns. The procedure also points to the possibility of distilling used solvent on a plant scale to effect its purification. Alumina was selected as the most useful chromatographic adsorbant. Unlike calcium oxide, most though not all, of the impurities are recoverable, and unlike silica gel, its tendency to adsorb TBP is not great.

A vacuum concentrated sample dissolved in carbon tetrachloride was placed on an alumina column which was then washed successively with carbon tetrachloride, chloroform, methanol, and acetic acid. Each of these agents removed a portion of the material adsorbed on the column.

Residual material left on the column could be removed with hot 6.0 N HCl, leaving the column clean, but all efforts to recover and identify the substances in this fraction met with failure.

Infrared examination of these four fractions after removal of the solvents showed the fractions to be incompletely resolved into compound classes. Hence, each fraction was redissolved in carbon tetrachloride and rechromatographed on separate columns.

The general scheme of separation and analysis which finally evolved is shown in the flow diagram, Figure 1. This scheme does not effect as complete a separation as desired and might well have been extended one more stage, i.e., fractions having very similar composition as indicated by infrared could have been rechromatographed on separate columns. The labor of doing so, however, would be at least equal to that already invested.

The phosphate ester impurities, being few in number, were distributed at separate points along the column. Their presence introduced complications, since they themselves are good elutants for the oxygenated impurities arising from the diluent. The latter tended to concentrate with the phosphate esters. This did have the advantage that concentration of colored impurities in the otherwise colorless phosphorus compounds marked the latter's position on the column and facilitated their collection in separate fractions.

The composition of the various fractions isolated by this procedure is shown in Table I. Fraction B was the most weakly adsorbed, fraction M the most strongly adsorbed, and in general the radioactivity of the fractions increased with increasing tendency for adsorption.

Also included in Table I are dilute UNH equilibrium values, as a measure of the effect of the impurities on solvent quality. Presented are the distribution values obtained between 1 g/l uranium solutions and 30

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per cent TBP-Shell Spray Base solutions containing two per cent by volume of the impurity fraction. It should be noted that an $E_a^0 \sim 0.02$ represents solvent which empirically results in borderline plant operations with respect to column stability, losses, and decontamination.

The characteristic infrared absorption data and specific test procedures used in the identification of fractions are tabulated in Table II. The chemical formulas, names, and a few equations depicting reactions of interest are presented in Table III.

The aromatic reaction products appeared only in fraction B and were present only to ca 0.1 per cent. The phenyl ring frequencies are observed in the infrared spectrum together with nitro group and an unidentified carbonyl type absorption. A strongly positive nitroso test is also given by this fraction, using the sensitive Lieberman reaction.⁽²⁾ It seems reasonable to associate the various functional groups with the aromatic ring and assume that this fraction is comprised of a mixture of aromatic nitro and nitroso compounds plus an aromatic acid or ketone rather than to assume a mixture of aromatic and aliphatic compounds. The aliphatic fractions are found exclusively in the more strongly adsorbing fractions. The order of absorption on the column was aliphatic, TBP, then aromatic fractions.

The small volume of aromatic reaction products was unexpected in view of preliminary experiments indicative of substantial reaction involving the original aromatic hydrocarbons in the diluent. This indicates that solvent treatment has effectually removed most of these compounds. Additional data supporting this contention will be presented in a report covering chemical stability of solvents.

Fraction D yields an infrared spectrum containing a moderately strong band at 1642 cm^{-1} characteristic of nitrite esters, and a strongly positive test for nitrite is obtained by the Griess reaction.⁽³⁾ Fraction I likewise reveals this evidence for the presence of nitrite esters.

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Fractions E through G contain tributoxyethyl phosphate. Comparison of the infrared spectra of the purest of these fractions with the spectrum of pure tributoxyethyl phosphate, results in exact superposition, so the identification is unequivocal. The unexpected presence of this substance was accounted for when a comparable analysis revealed its presence in "as received" TBP.

Fraction H and also fraction J contain phosphorus compounds, probably phosphate esters, which have not been further identified. These fractions were very small in volume and contaminated by appreciable amounts of impurities.

The aliphatic carboxylic acids found in fractions H through L were identified from their infrared spectra and their presence substantiated by tests with indicator paper.

The aliphatic nitro compounds found in fractions E through L were likewise identified by infrared examination. Confirmation was sought in one instance by refluxing the sample dissolved in alcohol over zinc plus dilute hydrochloric acid. This procedure reduces the nitro compounds to amines. Recovery of the fraction and infrared examination confirmed the fact that the previously assigned nitro group absorption had nearly disappeared and a new absorption attributable to the amine $-NH_2$ structure was now present.

The presence of nitroso compounds in all but a few of the fractions was determined by use of the Lieberman reaction⁽²⁾ which depends upon the condensation of a phenol and nitroso compound to yield a characteristically colored indophenol. The nitroso compounds form as a result of the action of nitrous acid upon secondary nitro compounds⁽⁴⁾ which, in turn, are formed by nitration of iso-paraffins. Shell Spray Base contains low concentrations of iso-paraffins; so only small amounts of nitroso compounds are to be expected. On the other hand, Soltrol 170 diluent is

essentially 100 per cent iso-paraffin and yields proportionately larger quantities of secondary nitro compounds upon nitration. These, in turn, yield nitroso compounds in quantities sufficient that it was actually possible to isolate these corrosive, intensely blue compounds, in comparatively pure form. Their properties indicate that alkaline reagents should remove them from the solvent, and this is a second reason for the low concentration of this type of impurity in recycled RCW.

In addition to the compounds and compound classes specifically identified, there is some evidence (spectrophotometric) for the presence of polymeric substances in colloidal aggregation. The absorption increased steadily towards the ultraviolet region, indicating this type of material.

IV. EFFECT OF IMPURITIES ON SOLVENT QUALITY

The uranium distribution values (E_a^O) shown in Table I indicate that the impurities derived from the diluent are primarily responsible for chemical deterioration in the solvent. Fractions I and K contain no phosphorus compounds and yield the highest E_a^O values. These fractions are mixtures, and it is unfortunate that they could not be further resolved so the effect of individual components could be estimated separately. These fractions do differ, however, in that fraction I contains nitrite esters and may account for the higher E_a^O value observed. A comparison of fractions C and D lends credence to this hypothesis in that nitrite esters are a major impurity in fraction D. Further indication that nitrite esters may be deleterious was obtained when addition of 1.0 volume per cent butyl nitrite raised the E_a^O value of a 30 per cent TBP (vacuum distilled) - Shell Spray Base solution from 0.004 to 0.33.

Aliphatic nitro compounds constitute a major portion of impurities identified in these fractions. Their separation from other impurities is not complete enough to estimate their effect, taken singly. The addition 1.0 and 2.0 volume per cent nitro propane to 30 per cent TBP (vacuum

distilled) - Shell Base, however, produced little change in the E_a^O value, so it is not believed that their effect is serious. Nitropropane, admittedly, is not necessarily representative of these compounds because of its comparatively low molecular weight.

The nitro compounds may be offensive only in that being chemically very reactive, their presence results in formation of secondary reaction products having much worse characteristics. In alkaline media, the nitro compounds enolize and are very reactive in this form. It may be significant, in this connection, that 2.0 M NaOH washing raises, rather than lowers, the E_a^O values of impure solvent. Continued recycling of these reactive substances may lead to formation of secondary reaction products which would otherwise never appear, e.g., reaction with nitrous acid to yield nitroso compounds or nitrolic acids.*

High molecular weight carboxylic acids are known to behave as surface active agents. Some are known to form comparatively insoluble salts with heavy metals and this may be a factor in crud formation and in fission product retention.

V. BEHAVIOR OF IMPURITIES IN THE SOLVENT RECOVERY SYSTEM

Of the various impurities identified in the RCW sample, only DBP can be expected to be efficiently removed by the present solvent treatment procedure employing 0.25 M Na_2CO_3 . It is probable that the aliphatic carboxylic acids are partially removed as are nitroso compounds and nitrolic acids (if present). The present solvent treatment process will not remove the nitro compounds or nitrite esters. The various phosphate ester impurities will also be unaffected by the solvent treatment process.

*These substances were not identified in fractions isolated from RCW, but are hard to characterize and may have been missed.

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VI. ACKNOWLEDGMENTS

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TABLE I

COMPOSITION OF FRACTIONS SEPARATED FROM RCW*

<u>Fraction No.</u>	<u>E_a^{o**}</u>	<u>Description of Fraction Composition</u>
B	0.002	Contains the aromatic nitro and nitroso compounds, an unidentified carbonyl compound and small amounts of TBP.
C	0.0013	Nearly pure TBP, trace of nitroso compound indicated by Lieberman test.
D	0.06	Impure TBP. Strong evidence for nitrite ester presence. Unidentified carbonyl compound (ketone or aldehyde) also present.
E	0.018	Impure tributoxy ethyl phosphate. Unidentified carbonyl compound (above) as well as nitro and nitroso compounds detected.
F - G	--	Impure tributoxy ethyl phosphate.
H	0.059	Contains unidentified phosphorus compound. Sample is strongly acid to indicator paper and shows acid C=O and OH bands in infrared. Aliphatic nitro compounds are also present.
I	1.08	No phosphate esters. Strongly acid, contains acid C=O and OH in infrared. Strong evidence for presence of nitrite ester. Positive nitroso test by Lieberman reaction. Strong aliphatic nitro compound absorption in infrared.
J	0.035	Contains unidentified phosphorus compound different from fraction H. Contaminated by small amounts of impurities listed for fraction I.
K	0.205	No phosphate esters. Moderately acid to indicator paper, contains acid C=O and OH bands in infrared. Positive nitroso test by Lieberman reaction. Aliphatic nitro compounds present.
L	--	Same as fraction I.
M	--	Eluted with 6.0 M HCl. Yellow in color, sweet odor. Not separable from aqueous phase and, therefore, not further identified.

* Samples June 1954 from TK 17-1, E_g = 0.011 after carbonate washing.

**Result of an equal volume contact of the organic with 1 g/l U (as UNH) followed by analysis of the clear organic layer for uranium. The samples are 30 per cent TBP containing two per cent by volume of the impurity. These samples are normally washed with carbonate prior to test. For these samples, the carbonate wash was omitted.

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TABLE II
IDENTIFICATION TECHNIQUES

<u>Compound</u>	<u>Specific Test</u>	<u>Characteristic Infrared Absorption, μ</u>
TBP	--	8.64) 7.81 (p = O), 9.65 (P-O-C) 8.86) pair
DBP	Brite's Method ⁽¹⁾	3.8-4.0 (OH), 8.15 (P = O), 9.70 (P-O-C)
TBEP (Tributoxyethyl phosphate)	--	7.80 (P = O), 9.58 (P-O-C), 8.75 (C-O-C), 12.12
Unidentified Phosphorus comp'd.	--	7.97 (P = O), 9.58 (P-O-C), 8.80
Unidentified Phosphorus comp'd. in fraction J.	--	7.95 (P = O), 9.65 (P-O-C)
Aromatic ring compounds	--	6.33 (sharp), 6.83 (sharp), 11.63 (broad), 12.62
Nitroso compounds	Lieberman Test ⁽²⁾	Not identified
Nitrite Esters	Griess Test ⁽³⁾	6.07
Nitro compounds	Reduction to amine	6.45, 7.37
Carboxylic acids	Indicator paper	5.80 - 5.90 (C = O), 2.9 - 4.0 (OH) (broad and diffuse)
Carbonyl compounds	--	5.7 - 5.75 (C = O) (sharp)

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TABLE IIIFORMULAE AND TYPICAL REACTIONS

(1) Enolization of Nitro Compounds:

(primary, aliphatic
nitro compound,
aci-form)

(enol form)

(2) Formation of Nitroso Compounds (Pseudonitriles):

(secondary, aliphatic
nitro compound,
enol form)

(Pseudonitrile)

(3) Formation of Nitrolic Acids:

(primary aliphatic
nitro compound,
enol form)

(nitrolic acid)

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FIGURE 1
ANALYTICAL SEPARATION FLOW DIAGRAM

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