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# DEPOSITION OF RUTHENIUM ON ORGANIC MATERIALS

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Report Number: ORNL-614

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Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

LABORATORY SECTION

# DEPOSITION OF RUTHENIUM ON ORGANIC MATERIALS

A. T. Gresky

DATE ISSUED

APR 24 1950

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## 1.0 Abstract

A process for deposition of ruthenium on organic surfaces is presented. This process is based on the simple reduction of ruthenium tetroxide to ruthenium dioxide by organic substance.

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## 2.0 Introduction

A means of removing ruthenium activity from fission product solutions was desired for use in chemical separations processes. Distillation of the volatile ruthenium tetroxide has been considered. However, many technical and engineering problems, arising from the handling of the volatile, active substance and its tendency to reduce and deposit on the equipment employed, are inherent in the method.

The literature describes the ease of reduction of osmium tetroxide by organic substances to form osmium dioxide and the use of this characteristic to create biological stains and dyes. The corresponding property of the closely related element, ruthenium, has been considered briefly as a means of fission product separation and also as a means of preparing an active source for use in various types of research. The latter use may be attractive since the 290 day $Ru^{106}$ provides a source for the most energetic beta rays (4.0 Mev) found in the fission product group.

This report describes a simple procedure which utilizes oxidation of ruthenium to the tetroxide at room temperature by para-periodic acid and deposition of ruthenium dioxide from aqueous solutions onto solid organic material.

## 3.0 Summary

The ruthenium deposition procedure, which involves the conversion of ruthenium compounds to ruthenium tetroxide by oxidation with para-periodic acid and finally the deposition of the dioxide on organic materials, has been developed. The oxidation is carried out in dilute nitric acid at room temperature, well below the boiling point of ruthenium tetroxide. The deposition is effected rapidly by agitation, or more slowly by simple contact, of the oxidized solution and the organic substance. As much as 99.7% ruthenium removal from tracer solutions has been demonstrated using this procedure.

Although tygon plastic was studied in more detail than other substances as a reducing material, brief investigations indicated that many other organic substances could be adapted to this use.

## 4.0 The Oxidation of Ruthenium to $RuO_4$

Several oxidizing agents have been investigated for the conversion of ruthenium to $RuO_4$. Para-periodic acid and sodium hypochlorite were found to be superior because of their rapid action at room temperature. Para-periodic acid allows oxidation in acid solution while sodium hypochlorite permits oxidation in basic solution.

These two reagents convert ruthenium metal, ruthenium dioxide, and most ruthenium salts to be tetroxide with ease; however there is evidence that some ruthenium species, such as nitrosyl complexes, are oxidized with extreme difficulty.

Para-periodic acid was found to be the best oxidizing agent in the deposition experiments which were carried out under acid conditions. In general, increasing the nitric acid concentration enhanced the effectiveness of ruthenium oxidation and deposition (Table 1). As high as 99.7% ruthenium removal from solutions has been demonstrated in tracer studies using this technique.

## 5.0 The Application of Ruthenium Deposition to Separation Processes

Ruthenium deposition from Redox process feeds was studied by contacting oxidized dissolver solutions, at low acid concentrations and at room temperature, with tygon stirrers. These studies indicated that quantitative ruthenium removal was limited by several factors. High salt concentration (2M uranyl nitrate) was found to decrease the rate of plating, and it was evident that dissolver solutions contained considerable quantities of ruthenium compounds which were unoxidizable under the conditions used. The amount of ruthenium which was oxidizable by $H_5IO_6$ was found to vary from 15% to 85% of the total in several different dissolver solutions.

Additional difficulties were encountered in solvent extraction following the removal of ruthenium by the above method. The undeposited ruthenium fraction was found to possess very undesirable scrubbing characteristics and high organic solvent solubility. Attempts to reduce this ruthenium to lower valence states failed to improve this condition or produced very erratic results.

Studies employing eight ORNL Pilot Plant second uranium cycle feeds indicated that the quantity of ruthenium oxidizable with periodic acid varied from 7% to 90% and the ruthenium decontamination obtained in these Pilot Plant runs was found to be a inversely proportional to the amount of oxidizable ruthenium present.

Similar studies of first cycle feeds indicated the same correlation. It was further found that the fraction of the ruthenium which was oxidizable decreased as the dissolution of an irradiated uranium slug approached

completion (Table 2).

This procedure for removing ruthenium by organic plating from $RuO_4$ solutions was abandoned as a practical process method in favor of new approaches to the problem.

## 6.0 The Application of Ruthenium Deposition to Source Preparation

Considering the possibility that this principle of ruthenium deposition on organics might find practical use in source preparations for physical or biological research, brief investigations were made in this direction.

Readily available organic materials such as cork, rubber, and plastics were contacted with solutions containing macro amounts of $RuO_4$ to determine their deposition characteristics. Cork and rubber reduced the tetroxide rapidly but did not form adherent deposits. Such substances as lucite, fluorothene, and polythene failed to reduce ruthenium tetroxide. Transflex and tygon reduced tetroxide rapidly and formed adherent deposits, with the black dioxide penetrating the body of the samples. Teflon reduced the tetroxide slowly but formed a smooth adherent deposit on its surface. This deposit showed little penetration. In all cases where deposition occurred, it was observed that large excesses of the $RuO_2$ could be rubbed or flaked off. After the removal of the loosely held material, an adherent coating resulted.

Teflon, of the plastics observed, was probably superior as a source backing because the coating did not penetrate the material. Hence, the absorption of the beta radiation by the backing was minimized.

Relatively simple contacting equipment of glass may be designed to accomplish the plating of ruthenium and allow a minimum of radiation exposure. Primary considerations involve provisions for: shielding,

localizing the source on the organic surface, mild agitation, transfer of solutions, and a sealed system to reduce hazards associated with $RuO_4$ volatility.

A procedure for the deposition of $RuO_2$ on organic surfaces is outlined below:

(1) Install the desired organic material in properly designed contacting equipment.

(2) Add ruthenium tracer in quantities desired.

(3) Adjust the solution to 0.1 M $HNO_3$.

(4) Make the solution 0.1 M $H_5IO_6$ (excess) and seal the equipment.

(5) Agitate for at least two hours.

Table I

Effect of Acid Concentration and Time of Contact

on Ruthenium Dioxide Plating on Tygon

Conditions of Experiment: Solutions containing equal quantities of ruthenium tracer and excess $H_5IO_6$ (0.01M) were contacted by agitation with tygon tubing stirrers for varying periods of time. β counting of residual solutions indicated percentage ruthenium removed.

| $HNO_3$ N | % Ru Plated at Time Intervals | | | |
|---|---|---|---|---|
| | 15 Min. | 30 Min. | 1 Hr. | 2 Hr. |
| 0.1 | 62 | 86 | 92 | 95 |
| 0.3 | 58 | 88 | 94 | 97 |
| 1.0 | 66 | 82 | 96 | 97 |
| 2.0 | 64 | 90 | 96 | 98 |

Table II

Relation of "Oxidizable" Ruthenium in Dissolver Solutions

to Ruthenium Distribution Coefficients in the Redox Solvent Extraction Process

Conditions: Samples were obtained at intervals during the $HNO_3$ dissolution of a single irradiated uranium slug, so that "% U dissolved" refers to the relative completion of dissolving. % oxidizable ruthenium (by $H_5IO_6$ at R.T.) was determined by tygon plating experiments.

| % U Dissolved | % Oxidized Ru | Ru D. C. (O/A) |
|---|---|---|
| 24 | 50 | 0.06 |
| 84 | 29 | 0.04 |
| 95 | 23 | 0.03 |
| 100 | 19 | 0.01 |

Table III

Properties of Ruthenium Tetroxide (Treatise, J. W. Mellor, Vol XV, Handbook 1945)

| Property | |
|---|---|
| Mol. Wt | 165.7 |
| Density | 3.29 (21°/4°) |
| Mol. vol. | 51.4 |
| Crystal form | Yellow rhombic |
| Melting point | 25.5°C |
| Boiling point | 106°C (Volatile, and will distill at lower temp.) |
| Vapor density | 5.77 (100°C and 106 mm) |
| Vapor pressure | 183 mm (108.8°C); 20 mm (42°C); 0 mm (0°C) |
| Solubility | $H_2O$ (2.033 $gm^{20°}$ - 2.25 $gm^{74°}$); sol. a., alk., |
| Odor | Like ozone (inactive vapor non-poisonous, as is $O_sO_4$ |
| Peroxidation | Unlikely, i.e. inconsistent with volatility |
| Reaction | Weakly Acidic |
| Stability | Stable and volatile at 100°C; decomposes at 107°C |

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